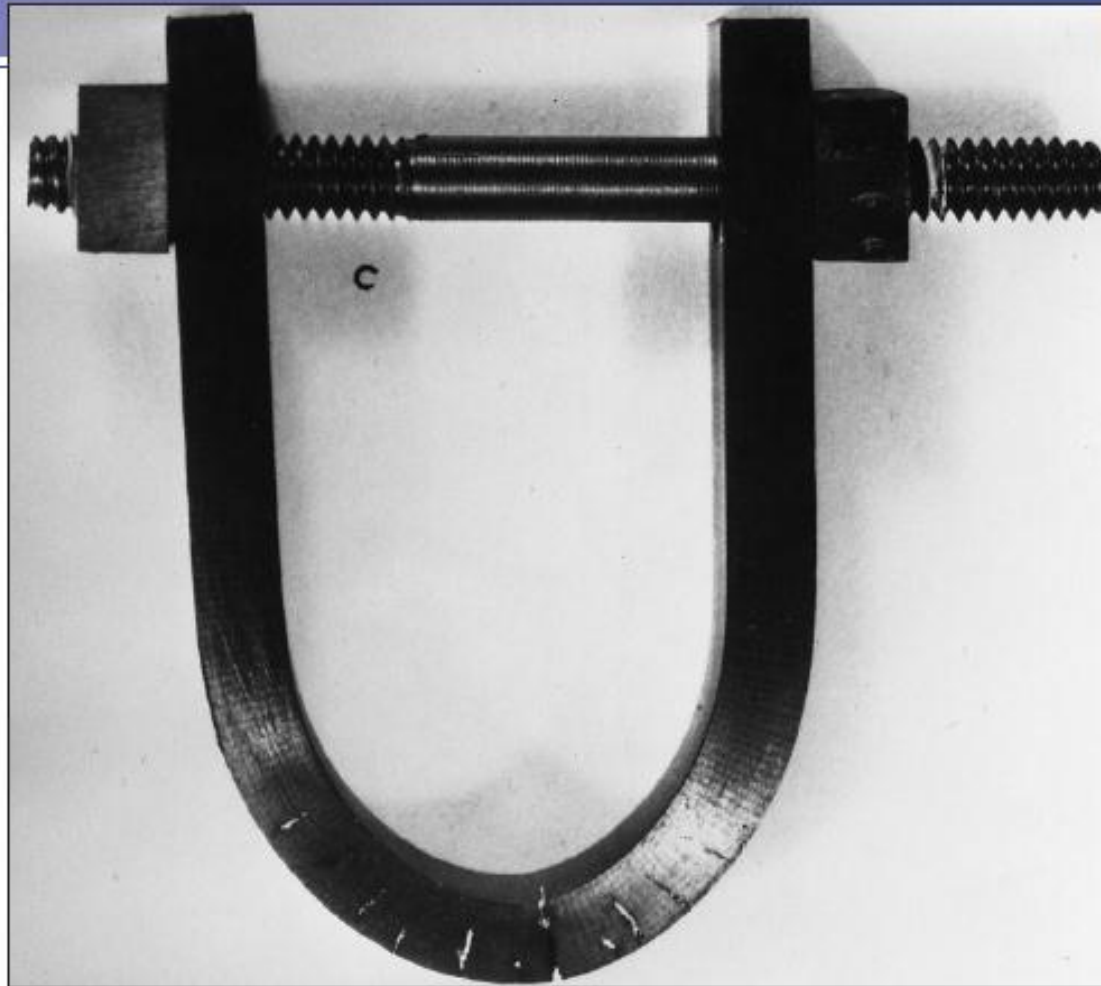Chapter **17** Corrosion and Degradation of Materials

WHY STUDY *Corrosion and Degradation of Materials?*

With a knowledge of the types of and an understanding of the mechanisms and causes of corrosion and degradation, it is possible to take measures to prevent them from occurring. For example, we may change the nature of the environment, select a material that is relatively nonreactive, and/or protect the material from appreciable deterioration.

- *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.*

Learning Objectives

After careful study of this chapter you should be able to do the following:

1. Distinguish between oxidation and reduction electrochemical reactions.
2. Describe the following: galvanic couple, standard half-cell, and standard hydrogen electrode.
3. Compute the cell potential and write the spontaneous electrochemical reaction direction for two pure metals that are electrically connected and also submerged in solutions of their respective ions.
4. Determine metal oxidation rate given the reaction current density.
5. Name and briefly describe the two different types of polarization, and specify the conditions under which each is rate controlling.
6. For each of the eight forms of corrosion and hydrogen embrittlement, describe the nature of the deteriorative process, and then note the proposed mechanism.
7. List five measures that are commonly used to prevent corrosion.
8. Explain why ceramic materials are, in general, very resistant to corrosion.
9. For polymeric materials discuss (a) two degradation processes that occur when they are exposed to liquid solvents, and (b) the causes and consequences of molecular chain bond rupture.

17.1 INTRODUCTION

- 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.

- 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, 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 structures.

Corrosion of Metals

17.2 ELECTROCHEMICAL CONSIDERATIONS

- *For metallic materials, the corrosion process is normally electrochemical, that is, a chemical reaction in which there is transfer of electrons from one chemical species to another.*

- *Metal atoms characteristically lose or give up electrons in what is called an oxidation reaction. The site at which oxidation takes place is called the anode; oxidation is sometimes called an anodic reaction.*

- *The electrons generated from each metal atom that is oxidized must be transferred to and become a part of another chemical species in what is termed a reduction reaction. The location at which reduction occurs is called the cathode.*

$$M \longrightarrow M^{n+} + ne^-$$

Oxidation reaction
for metal M

*An overall electrochemical reaction must consist of **at least one oxidation and one reduction reaction**, and will be the sum of them; often the individual oxidation and reduction reactions are termed **half-reactions**. There can be **no net electrical charge accumulation** from the electrons and ions; that is, the total rate of oxidation must equal the total rate of reduction, or all electrons generated through oxidation must be consumed by reduction.*
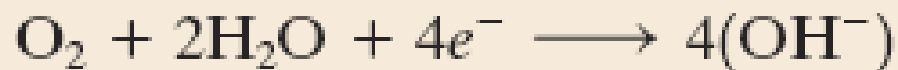
Reduction reaction

- Reduction of hydrogen ions in an acid solution.

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

- Reduction reaction in an acid solution containing dissolved oxygen

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

- Reduction reaction in a neutral or basic solution containing dissolved oxygen

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

- Reduction of a multivalent metal ion to a lower valence state

$$M^{n+} + e^- \longrightarrow M^{(n-1)+}$$

- Reduction of a metal ion to its electrically neutral atom

$$M^{n+} + ne^- \longrightarrow M$$

It is possible for two or more of the reduction reactions above to occur simultaneously.

Example 1: *Zinc metal immersed in an acid solution containing H$^+$*
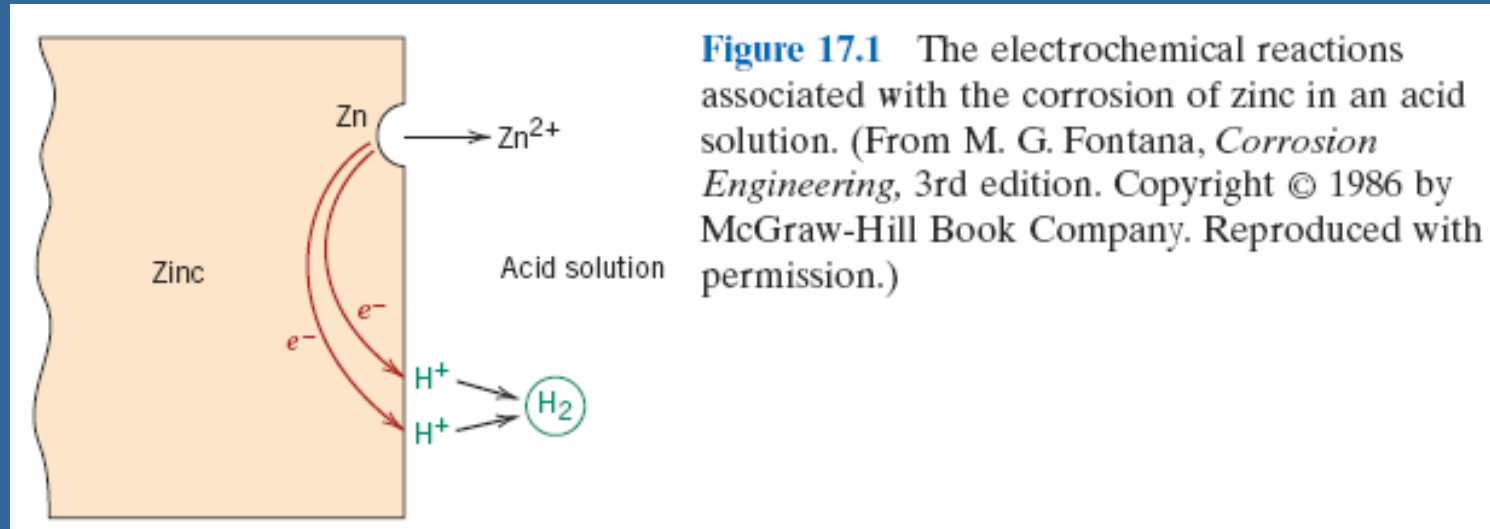
Figure 17.1 The electrochemical reactions associated with the corrosion of zinc in an acid solution. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

- *zinc will experience oxidation or corrosion according to*

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

- *H$^+$ ions are reduced according to*

$$2H^+ + 2e^- \longrightarrow H_2 \, (gas)$$

- *The total electrochemical reaction*

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2 \, (gas)$$

Example 2: Oxidation or rusting of iron in water, which contains dissolved oxygen

This process occurs in two steps:

- **Fe is oxidized to Fe^{2+} [as $Fe(OH)_2$]**

$$Fe + \tfrac{1}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

- **Fe^{2+} to Fe^{3+} [as $Fe(OH)_3$]**

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow 2Fe(OH)_3$$

Concept Check 17.1

Would you expect iron to corrode in water of high purity? Why or why not?

Galvanic couple
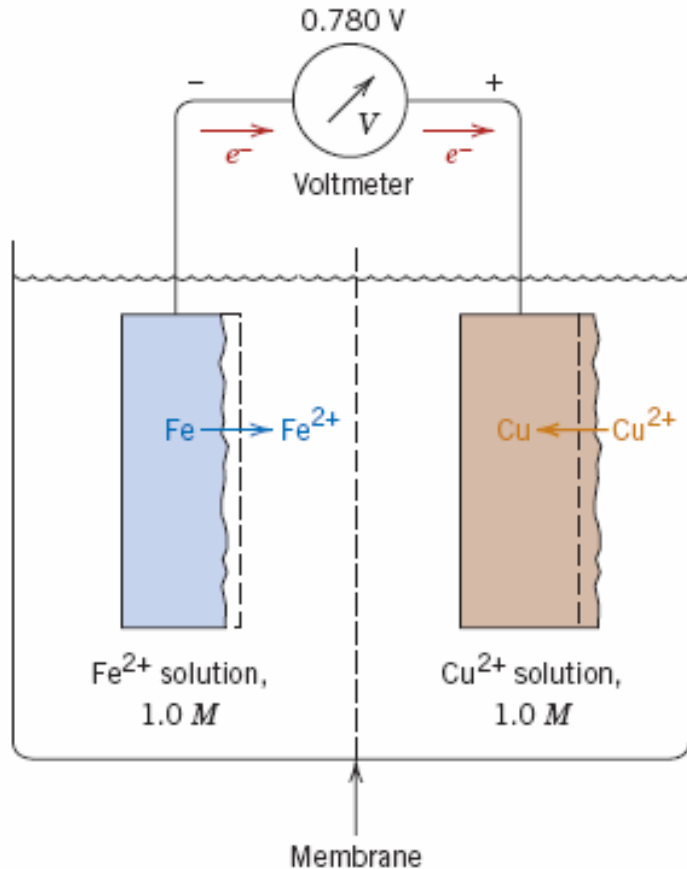
Figure 17.2 An electrochemical cell consisting of iron and copper electrodes, each of which is immersed in a $1M$ solution of its ion. Iron corrodes while copper electrodeposits.
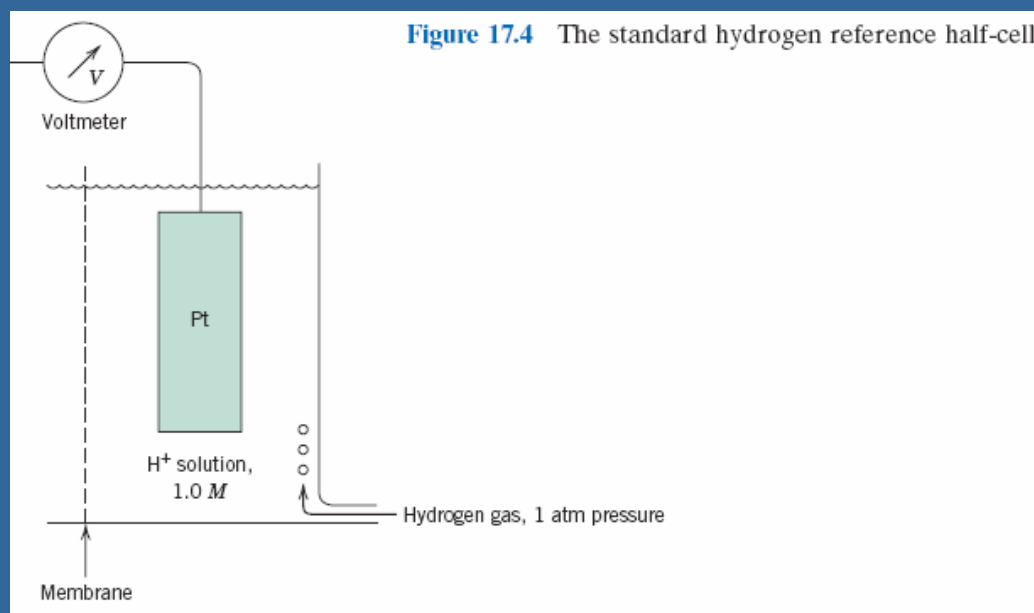
$$Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+}$$

A potential of 0.78 V results for a Cu-Fe galvanic cell at 25 ℃

A *galvanic couple* —two metals electrically connected in a liquid electrolyte wherein one metal becomes an anode and corrodes, while the other acts as a cathode.

- *Various electrode pairs have different voltages (Electrode Potentials); the magnitude of such a voltage may be thought of as representing the driving force for the electrochemical oxidation–reduction reaction.*

- *A pure metal electrode immersed in a 1M solution of its ions and at 25°C is termed a standard half-cell.*

- *Standard hydrogen electrode:* *It consists of an inert Pt electrode in a 1M solution of H^+, saturated with H_2 that is bubbled through the solution at a pressure of 1 atm and a temperature of 25℃ .*

Figure 17.4 The standard hydrogen reference half-cell.

Voltmeter

Pt

H^+ solution, 1.0 M

Hydrogen gas, 1 atm pressure

Membrane

- *The electromotive force (emf) series is generated by coupling to the standard hydrogen electrode, standard half-cells for various metals and ranking them according to measured voltage.*

Table 17.1 represents the corrosion tendencies for the several metals
- **Those at the top (i.e., gold and platinum) are noble, or chemically inert.**
- **Moving down the table, the metals become more susceptible to oxidation.**

Table 17.1 The Standard emf Series

	reduction reactions Electrode Reaction	Standard Electrode Potential, V^0(V)
Increasingly inert (cathodic) ↑	$Au^{3+} + 3e^- \longrightarrow Au$	+1.420
	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \longrightarrow Pt$	~+1.2
	$Ag^+ + e^- \longrightarrow Ag$	+0.800
	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.340
	$2H^+ + 2e^- \longrightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.126
	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.136
	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.250
	$Co^{2+} + 2e^- \longrightarrow Co$	−0.277
	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.403
	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.440
Increasingly active (anodic) ↓	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.744
	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.763
	$Al^{3+} + 3e^- \longrightarrow Al$	−1.662
	$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.363
	$Na^+ + e^- \longrightarrow Na$	−2.714
	$K^+ + e^- \longrightarrow K$	−2.924

Consider the generalized reactions involving the oxidation of metal M_1 and the reduction of metal M_2 as

$$M_1 \longrightarrow M_1^{n+} + ne^- \qquad -V_1^0 \qquad (17.16a)$$

$$M_2^{n+} + ne^- \longrightarrow M_2 \qquad +V_2^0 \qquad (17.16b)$$

where the V^0's are the standard potentials as taken from the standard emf series. Since metal M_1 is oxidized, the sign of V_1^0 is opposite to that as it appears in Table 17.1. Addition of Equations 17.16a and 17.16b yields

$$M_1 + M_2^{n+} \longrightarrow M_1^{n+} + M_2 \qquad (17.17)$$

and the overall cell potential ΔV^0 is

$$\Delta V^0 = V_2^0 - V_1^0 \qquad (17.18)$$

For this reaction to occur spontaneously, ΔV^0 must be positive; if it is negative, the spontaneous cell direction is just the reverse of Equation 17.17. When standard half-cells are coupled together, the metal that lies lower in Table 17.1 will experience oxidation (i.e., corrosion), whereas the higher one will be reduced.

Influence of Concentration and Temperature on Cell Potential

Nernst equation—electrochemical cell potential for two half-cells that are electrically coupled and for which solution ion concentrations are other than $1M$

$$\Delta V = (V_2^0 - V_1^0) - \frac{RT}{n\mathscr{F}} \ln \frac{[M_1^{n+}]}{[M_2^{n+}]}$$

Simplified form of Equation 17.19 for $T = 25°C$ (room temperature)

$$\Delta V = (V_2^0 - V_1^0) - \frac{0.0592}{n} \log \frac{[M_1^{n+}]}{[M_2^{n+}]}$$

The Galvanic Series

Table 17.2   The Galvanic Series

	Platinum
	Gold
	Graphite
	Titanium
	Silver
	⎡316 Stainless steel (passive)
	⎣304 Stainless steel (passive)
	⎡Inconel (80Ni–13Cr–7Fe) (passive)
Increasingly inert (cathodic) ↑	⎣Nickel (passive)
	⎡Monel (70Ni–30Cu)
	⎢Copper–nickel alloys
	⎢Bronzes (Cu–Sn alloys)
	⎢Copper
	⎣Brasses (Cu–Zn alloys)
	⎡Inconel (active)
	⎣Nickel (active)
	Tin
	Lead
Increasingly active (anodic) ↓	⎡316 Stainless steel (active)
	⎣304 Stainless steel (active)
	⎡Cast iron
	⎣Iron and steel
	Aluminum alloys
	Cadmium
	Commercially pure aluminum
	Zinc
	Magnesium and magnesium alloys

This represents the relative reactivities of a number of metals and commercial alloys in seawater.

17.3 CORROSION RATES

- **Corrosion penetration rate (CPR)** *or the thickness loss of material per unit of time, is a function of specimen weight loss, density, area, and time of exposure*

$$CPR = \frac{KW}{\rho At}$$

W is the weight loss after exposure time t;

A represent the density and exposed specimen area, respectively,

K is a constant, its magnitude depending on the system of units used.

The CPR is conveniently expressed in terms of either mils per year (mpy) or millimeters per year (mm/yr).

Expression relating corrosion rate and current density, *the current per unit surface area of material corroding—which is designated i. The rate r, in units of mol/m^2-s, is determined using the expression*
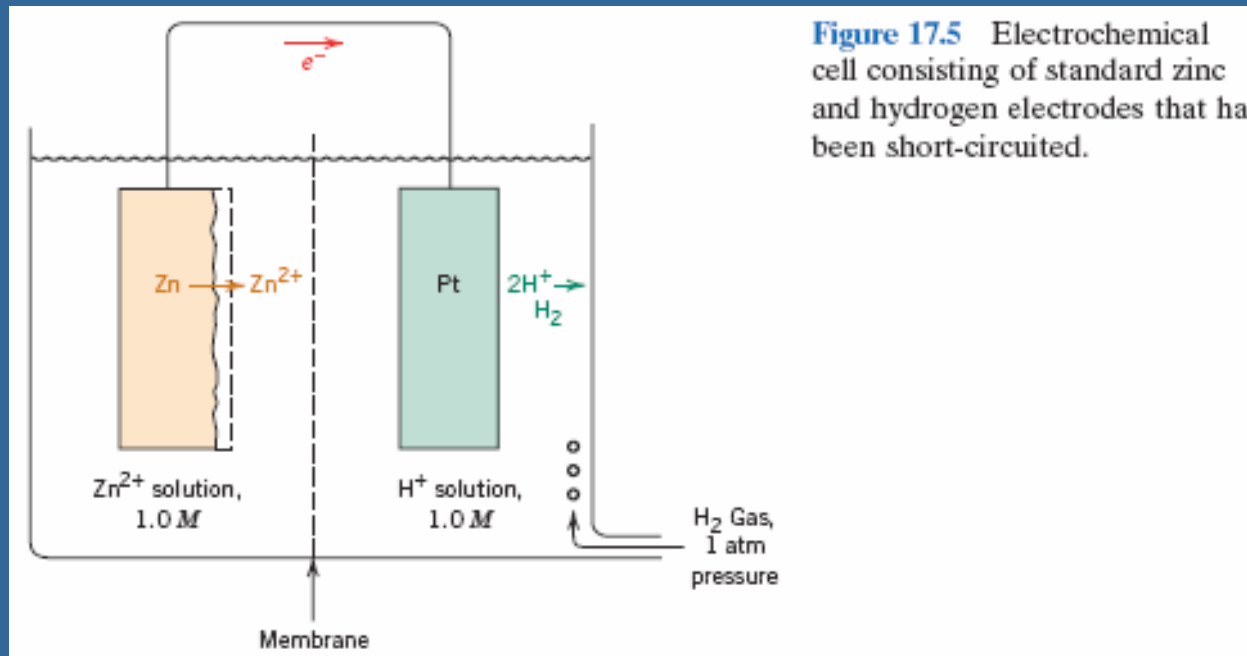
$$r = \frac{i}{n\mathscr{F}}$$

where, n is the number of electrons associated with the ionization of each metal atom, and F is 96,500 C/mol.

17.4 PREDICTION OF CORROSION RATES

- **Polarization**

The displacement of each electrode potential from its equilibrium value is termed **polarization,** and the magnitude of this displacement is the *overvoltage,* normally represented by the symbol η.


Figure 17.5 Electrochemical cell consisting of standard zinc and hydrogen electrodes that has been short-circuited.

- There are two types of polarization—activation and concentration.

Activation Polarization

Activation polarization refers to the condition wherein the reaction rate is controlled by the one step in the series that occurs at the slowest rate. The term "activation" is applied to this type of polarization because an activation energy barrier is associated with this slowest, rate-limiting step.

Considering the reduction of hydrogen ions to form bubbles of hydrogen gas on the surface of a zinc electrode
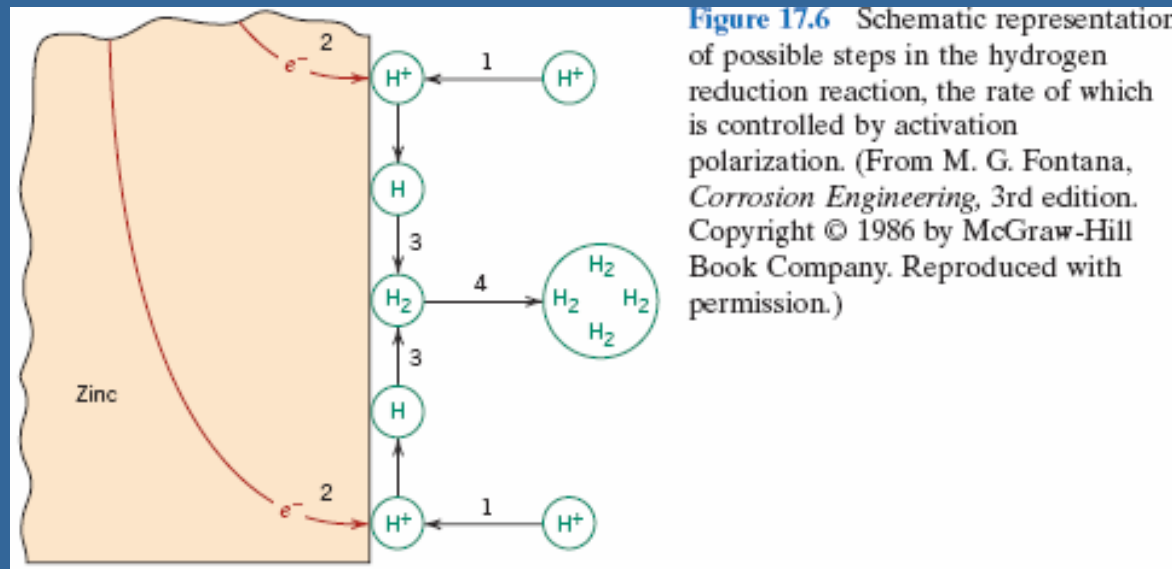
Figure 17.6 Schematic representation of possible steps in the hydrogen reduction reaction, the rate of which is controlled by activation polarization. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

1. Adsorption of H^+ ions from the solution onto the zinc surface
2. Electron transfer from the zinc to form a hydrogen atom,

$$H^+ + e^- \longrightarrow H$$

3. Combining of two hydrogen atoms to form a molecule of hydrogen,

$$2H \longrightarrow H_2$$

4. The coalescence of many hydrogen molecules to form a bubble

*The **slowest** of these steps determines the rate of the overall reaction.*

For activation polarization, the relationship between overvoltage η_a and current density i is

$$\eta_a = \pm\beta \log \frac{i}{i_0} \qquad (17.25)$$

where β and i_0 are constants for the particular half-cell. The parameter i_0 is termed the *exchange current density*, which deserves a brief explanation. Equilibrium for some particular half-cell reaction is really a dynamic state on the atomic level. That is, oxidation and reduction processes are occurring, but both at the same rate, so that there is no net reaction. For example, for the standard hydrogen cell (Figure 17.4) reduction of hydrogen ions in solution will take place at the surface of the platinum electrode according to

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

with a corresponding rate r_{red}. Similarly, hydrogen gas in the solution will experience oxidation as

$$H_2 \longrightarrow 2H^+ + 2e^-$$
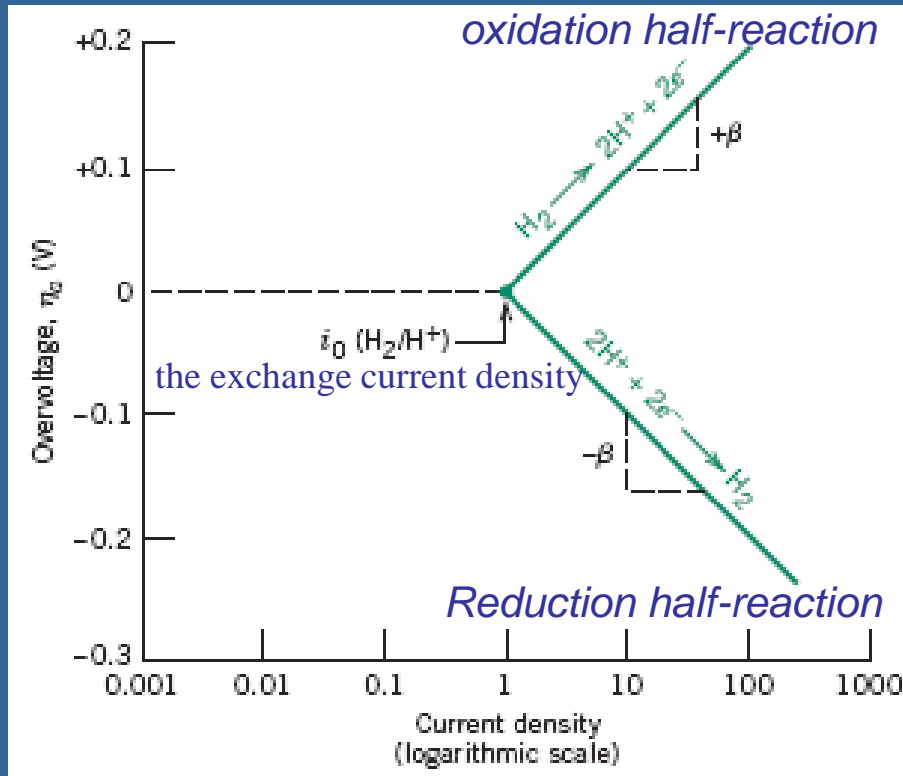
at rate r_{oxid}. Equilibrium exists when

$$r_{red} = r_{oxid}$$

This exchange current density is just the current density from Equation 17.24 at equilibrium, or

$$r_{red} = r_{oxid} = \frac{i_0}{n\mathscr{F}} \qquad (17.26)$$

Figure 17.7 For a hydrogen electrode, plot of activation polarization overvoltage versus logarithm of current density for both oxidation and reduction reactions. (Adapted from M. G. Fontana, *Corrosion Engineering,* 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

Both line segments originate at the exchange current density, and at zero overvoltage, since at this point the system is at equilibrium and there is no net reaction.
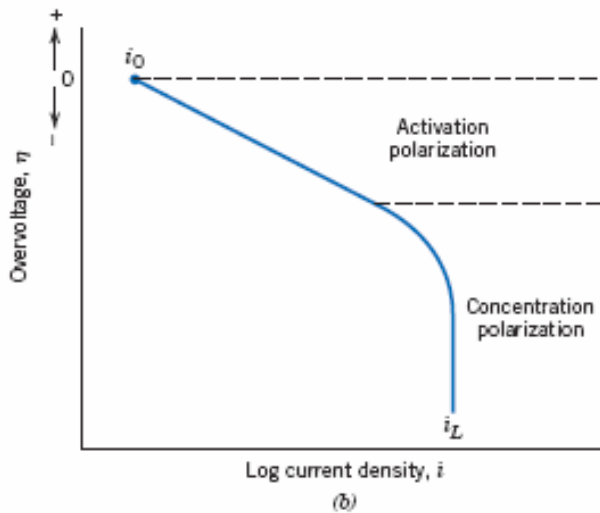
Concentration Polarization

• *Concentration polarization exists when the reaction rate is limited by diffusion in the solution.*
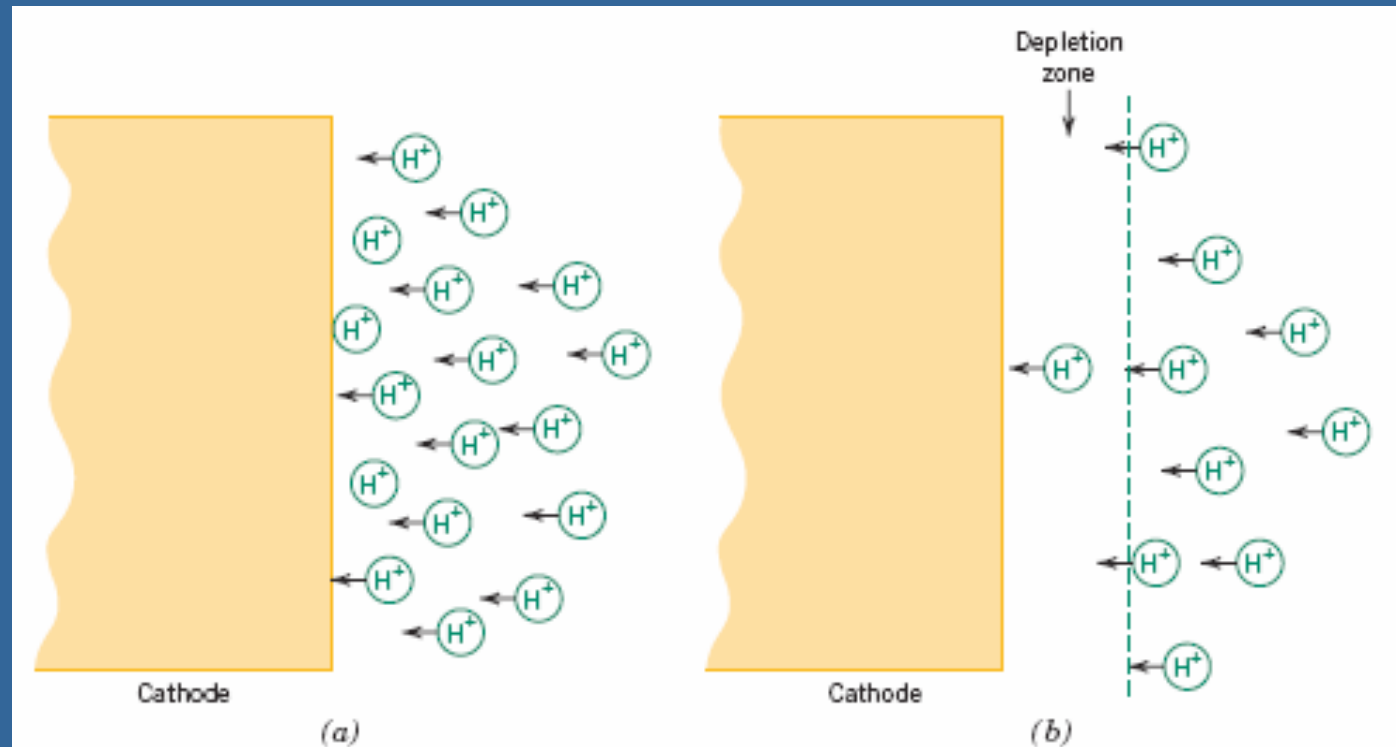
Figure 17.8 For hydrogen reduction, schematic representations of the H$^+$ distribution in the vicinity of the cathode for (a) low reaction rates and/or high concentrations, and (b) high reaction rates and/or low concentrations wherein a depletion zone is formed that gives rise to concentration polarization. (Adapted from M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)
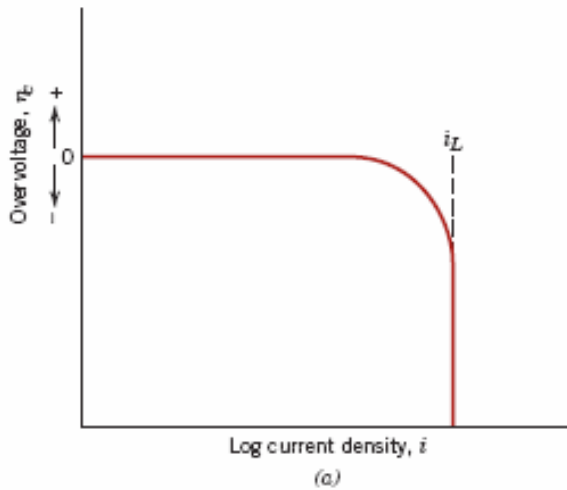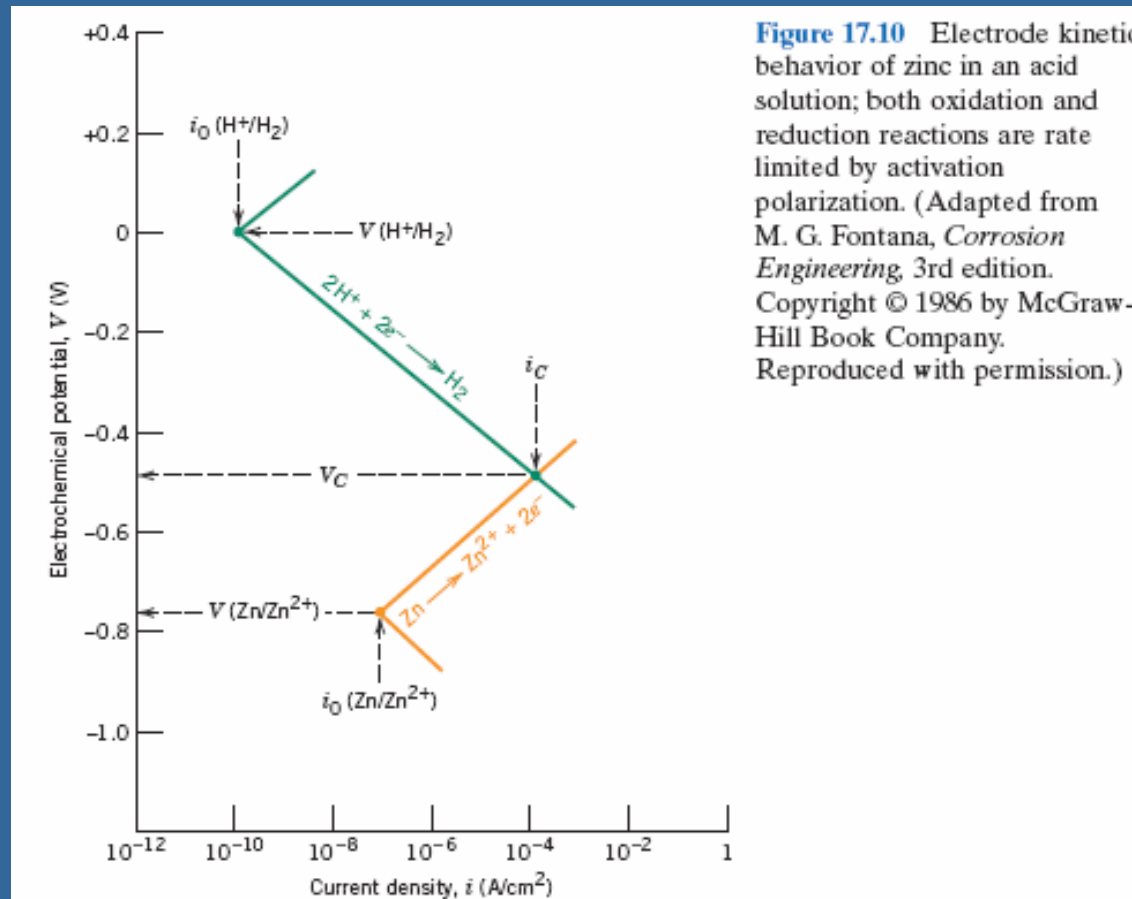
Figure 17.9 For reduction reactions, schematic plots of overvoltage versus logarithm of current density for (a) concentration polarization, and (b) combined activation–concentration polarization.
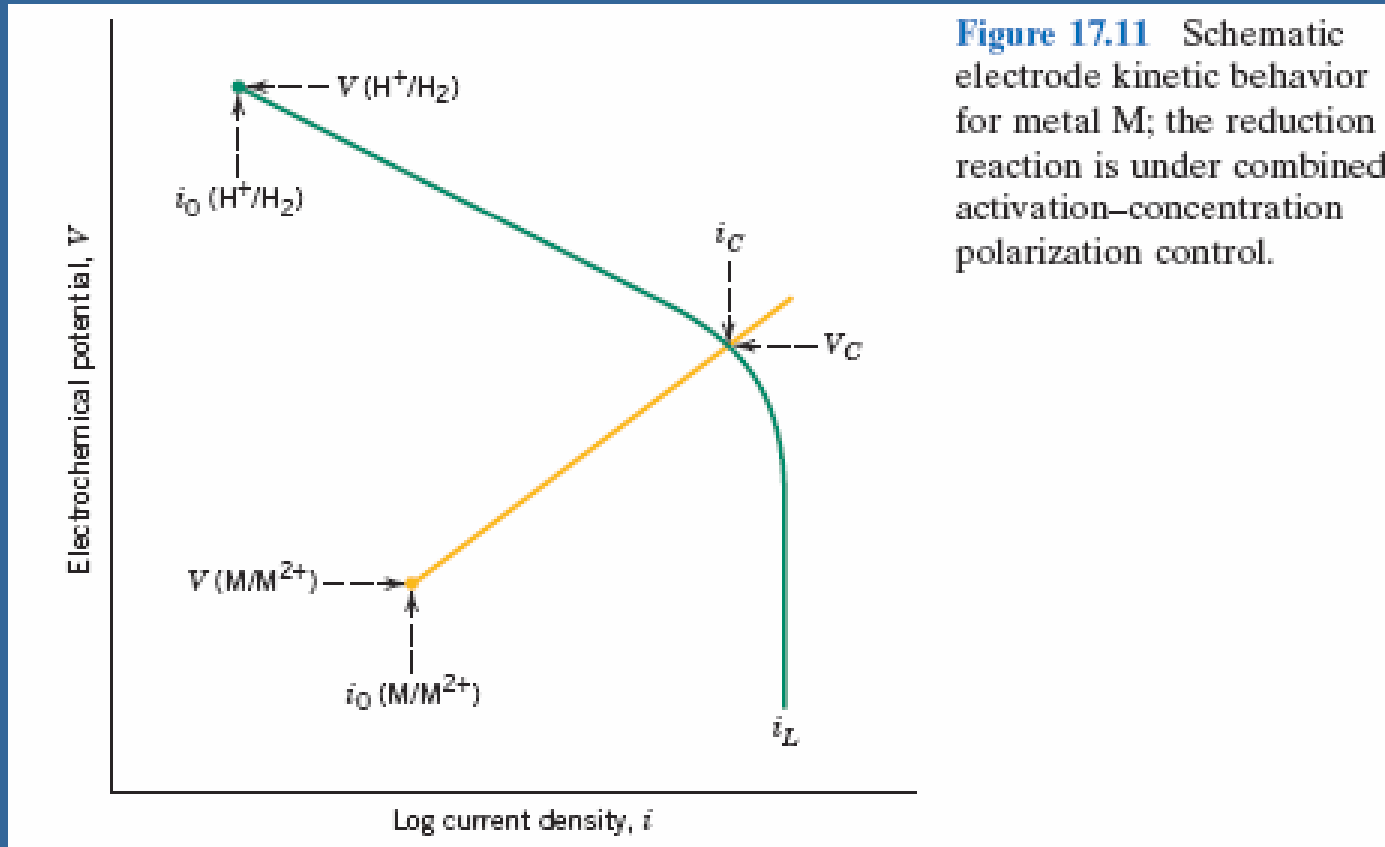
Both concentration and activation polarization are possible for reduction reactions. Under these circumstances, the total overvoltage is just the sum of both overvoltage contributions

Corrosion Rates from Polarization Data

Figure 17.10 Electrode kinetic behavior of zinc in an acid solution; both oxidation and reduction reactions are rate limited by activation polarization. (Adapted from M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

Case1: Both oxidation and reduction reactions are rate limited by activation polarization.

Corrosion Rates from Polarization Data

Figure 17.11 Schematic electrode kinetic behavior for metal M; the reduction reaction is under combined activation–concentration polarization control.

Case2: both concentration and activation polarization control the reduction reaction, whereas only activation polarization is important for oxidation.

Rate of Oxidation Computation

Zinc experiences corrosion in an acid solution according to the reaction

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

The rates of both oxidation and reduction half-reactions are controlled by activation polarization.

(a) Compute the rate of oxidation of Zn (in mol/cm²-s) given the following activation polarization data:

For Zn	For Hydrogen
$V_{(Zn/Zn^{2+})} = -0.763$ V	$V_{(H^+/H_2)} = 0$ V
$i_0 = 10^{-7}$ A/cm²	$i_0 = 10^{-10}$ A/cm²
$\beta = +0.09$	$\beta = -0.08$

(b) Compute the value of the corrosion potential.

Solution

(a) To compute the rate of oxidation for Zn, it is first necessary to establish relationships in the form of Equation 17.25 for the potential of both oxidation and reduction reactions. Next, these two expressions are set equal to one another, and then we solve for the value of i that is the corrosion current density, i_C. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows: For hydrogen reduction,

$$V_H = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{0_H}}\right)$$

and for Zn oxidation,

$$V_{Zn} = V_{(Zn/Zn^{2+})} + \beta_{Zn} \log\left(\frac{i}{i_{0_{Zn}}}\right)$$

Now, setting $V_H = V_{Zn}$ leads to

$$V_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{0_H}}\right) = V_{(Zn/Zn^{2+})} + \beta_{Zn} \log\left(\frac{i}{i_{0_{Zn}}}\right)$$

And solving for $\log i$ (i.e., $\log i_C$) leads to

$$\log i_C = \left(\frac{1}{\beta_{Zn} - \beta_H}\right)\left[V_{(H^+/H_2)} - V_{(Zn/Zn^{2+})} - \beta_H \log i_{0_H} + \beta_{Zn} \log i_{0_{Zn}}\right]$$

$$= \left[\frac{1}{0.09 - (-0.08)}\right][0 - (-0.763) - (-0.08)(\log 10^{-10})$$

$$+ (0.09)(\log 10^{-7})]$$

$$= -3.924$$

or

$$i_C = 10^{-3.924} = 1.19 \times 10^{-4}\,\text{A/cm}^2$$

And, from Equation 17.24,

$$r = \frac{i_C}{n\mathcal{F}}$$

$$= \frac{1.19 \times 10^{-4}\,\text{C/s-cm}^2}{(2)(96{,}500\,\text{C/mol})} = 6.17 \times 10^{-10}\,\text{mol/cm}^2\text{-s}$$
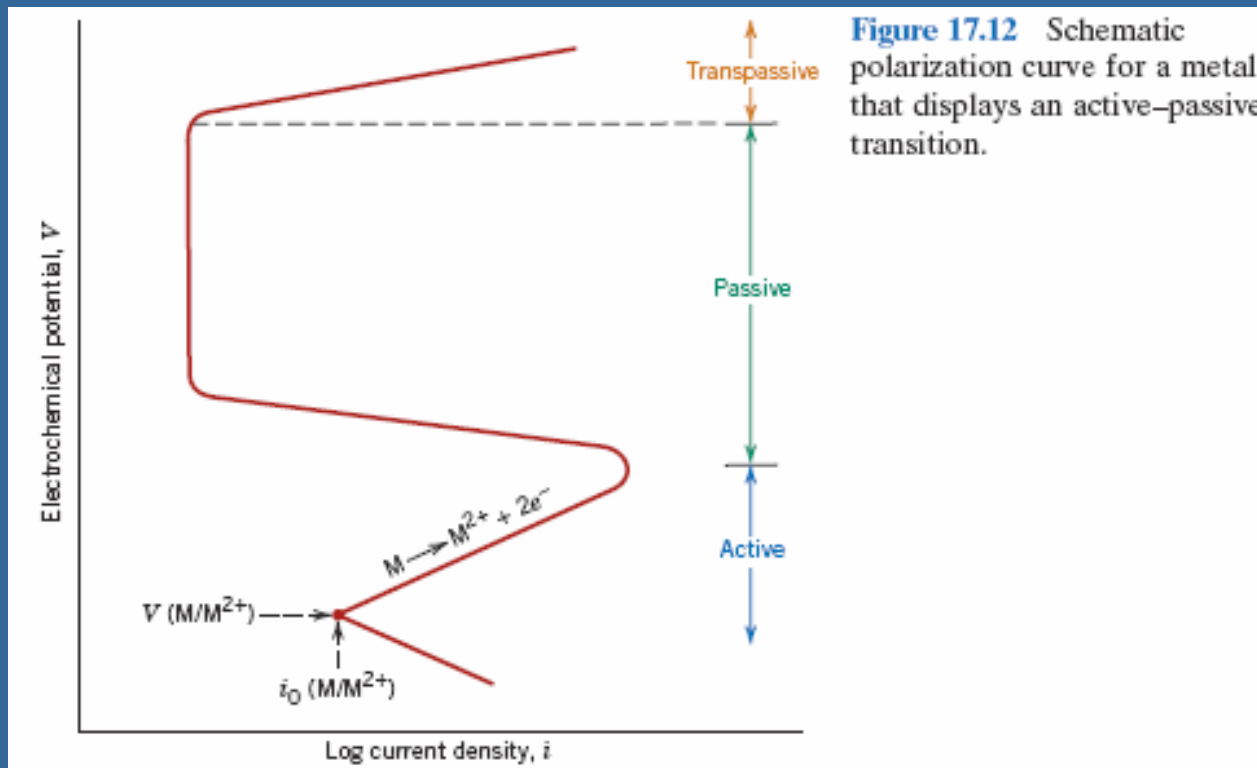
(b) Now it becomes necessary to compute the value of the corrosion potential V_C. This is possible by using either of the above equations for V_H or V_{Zn} and substituting for i the value determined above for i_C. Thus, using the V_H expression yields

$$V_C = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i_C}{i_{0_H}}\right)$$

$$= 0 + (-0.08\,\text{V}) \log\left(\frac{1.19 \times 10^{-4}\,\text{A/cm}^2}{10^{-10}\,\text{A/cm}^2}\right) = -0.486\,\text{V}$$

This is the same problem that is represented and solved graphically in the voltage-versus-logarithm current density plot of Figure 17.10. It is worth noting that the i_C and V_C we have obtained by this analytical treatment are in agreement with those values occurring at the intersection of the two line segments on the plot.

17.5 PASSIVITY

- *Some normally active metals and alloys, under particular environmental conditions, lose their chemical reactivity and become extremely inert. This phenomenon, termed* **passivity**

- *Passivity is displayed by chromium, iron, nickel, titanium, and many of their alloys.*

- *This passive behavior results from the formation of a highly adherent and very thin oxide film on the metal surface, which serves as a protective barrier to further corrosion.*

Figure 17.12 Schematic polarization curve for a metal that displays an active–passive transition.

- *At relatively low potential values, within the "active" region the behavior is linear as it is for normal metals.*

- *With increasing potential, the current density suddenly decreases to a very low value that remains independent of potential; this is termed the "passive" region.*

- *Finally, at even higher potential values, the current density again increases with potential in the "transpassive" region.*
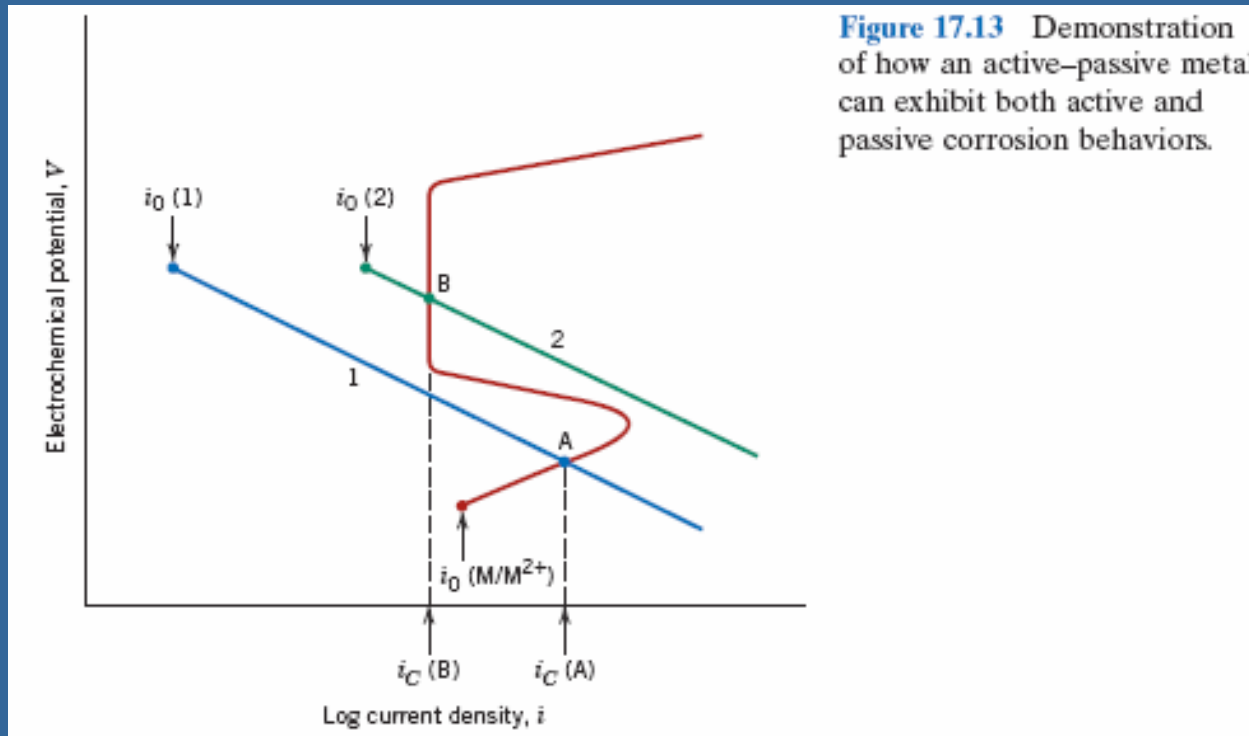
Figure 17.13 Demonstration of how an active–passive metal can exhibit both active and passive corrosion behaviors.

Figure 17.13 illustrates *how a metal can experience both active and passive behavior depending on the corrosion environment*. Included in this figure is the S-shaped oxidation polarization curve for an active–passive metal M and, in addition, reduction polarization curves for two different solutions, which are labeled 1 and 2. This difference in corrosion rate between the two solutions may be significant—several orders of magnitude.
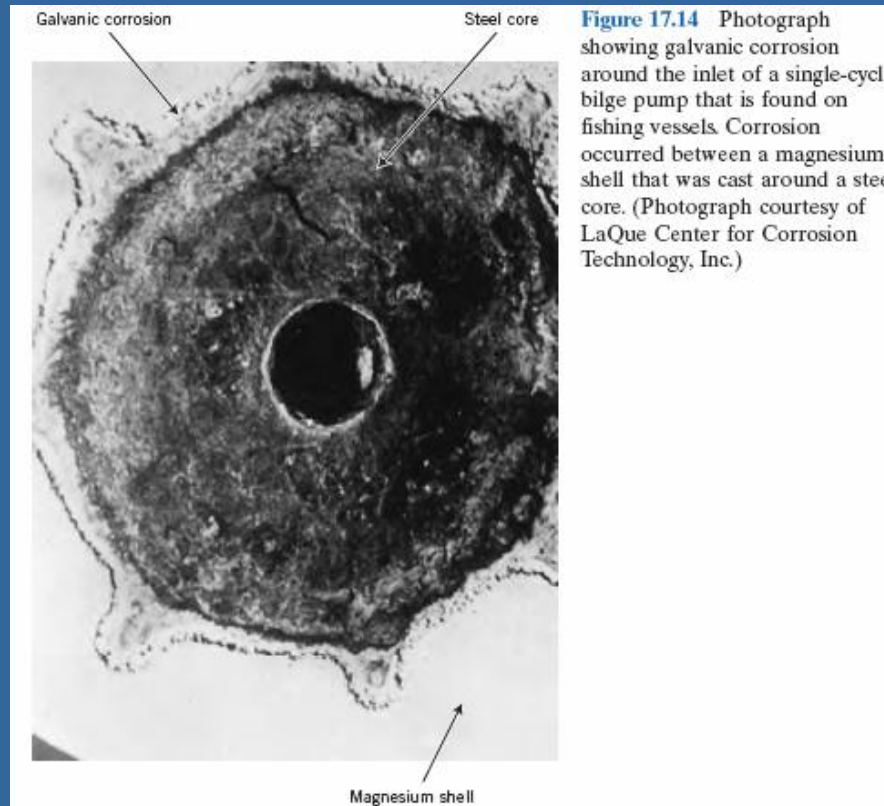
17.6 ENVIRONMENTAL EFFECTS

- **The variables in the corrosion environment,**
  - *fluid velocity*
  - *temperature*
  - *composition.*

- **The concentration of the corrosive species (e.g., H^+ in acids)**

- **Ability to passivation**

- **Cold working or plastically deforming**

17.7 FORMS OF CORROSION

- *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.

    - *Examples* include general rusting of steel and iron and the tarnishing of silverware.

- *Galvanic corrosion* *occurs when two metals or alloys are electrically coupled while exposed to an electrolyte. The more reactive metal in the particular environment will experience corrosion; the more inert metal, will be protected from corrosion.*

  – *For example, steel screws corrode when in contact with brass in a marine environment; or if copper and steel tubing are joined in a domestic water heater, the steel will corrode in the vicinity of the junction.*

Galvanic corrosion

Galvanic corrosion / Steel core / Magnesium shell

Figure 17.14 Photograph showing galvanic corrosion around the inlet of a single-cycle bilge pump that is found on fishing vessels. Corrosion occurred between a magnesium shell that was cast around a steel core. (Photograph courtesy of LaQue Center for Corrosion Technology, Inc.)

The rate of galvanic attack depends on the relative anode-to-cathode surface areas that are exposed to the electrolyte. For a given cathode area, a smaller anode will corrode more rapidly than a larger one.

Measures taken to reduce galvanic corrosion

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**.*

- *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.*

  - *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.*

  - *Crevice corrosion may be prevented by using welded instead of riveted or bolted joints, using nonabsorbing gaskets when possible, removing accumulated deposits frequently, and designing containment vessels to avoid stagnant areas and ensure complete drainage.*

Figure 17.15 On this plate, which was immersed in seawater, crevice corrosion has occurred at the regions that were covered by washers. (Photograph courtesy of LaQue Center for Corrosion Technology, Inc.)
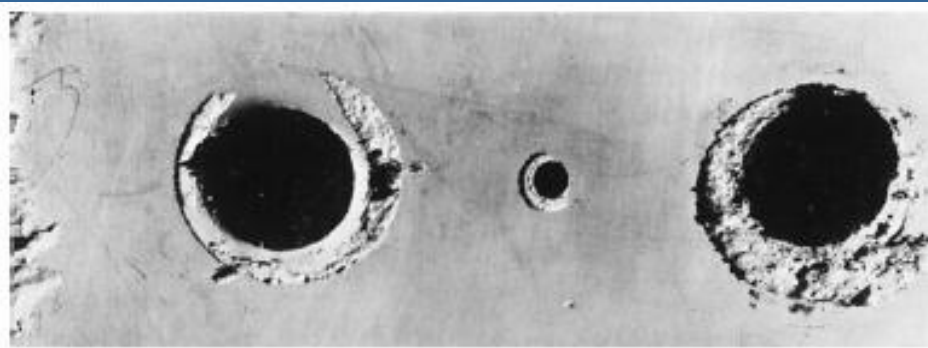
Mechanism of crevice corrosion

Figure 17.16 Schematic illustration of the mechanism of crevice corrosion between two riveted sheets. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)
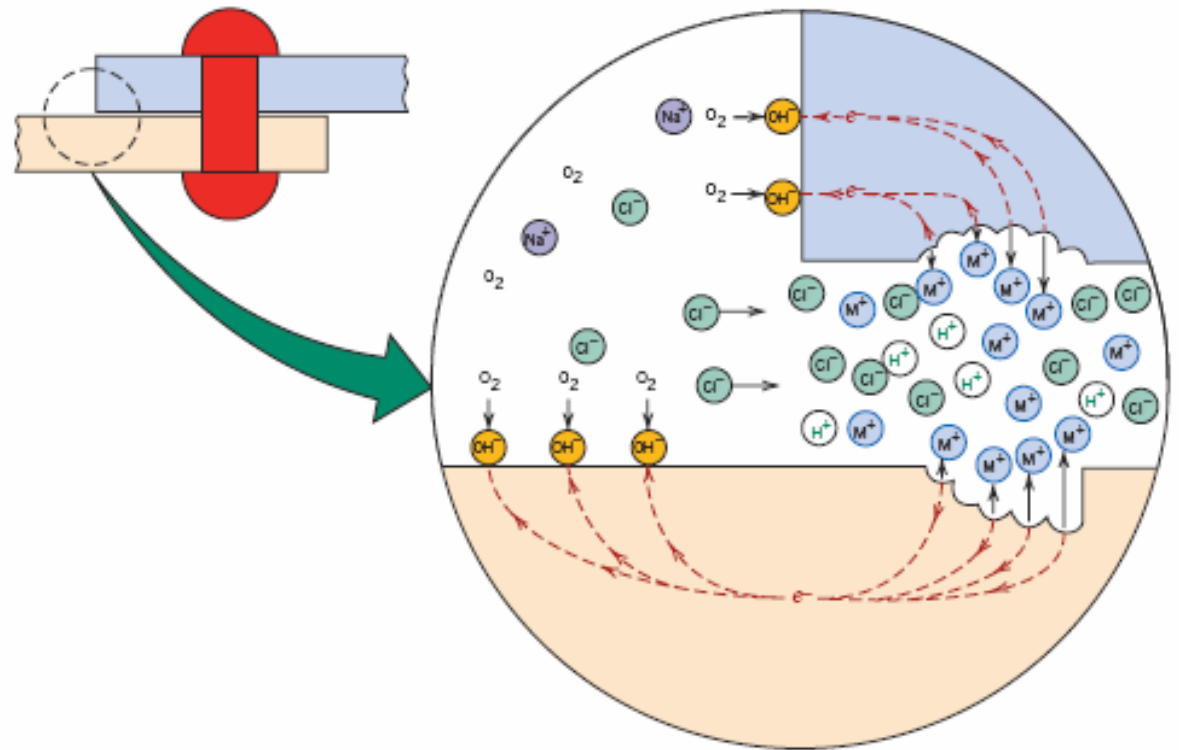
- *Pitting is another form of very localized corrosion attack in which small pits or holes form. It is an extremely insidious type of corrosion, often going undetected and with very little material loss until failure occurs.*
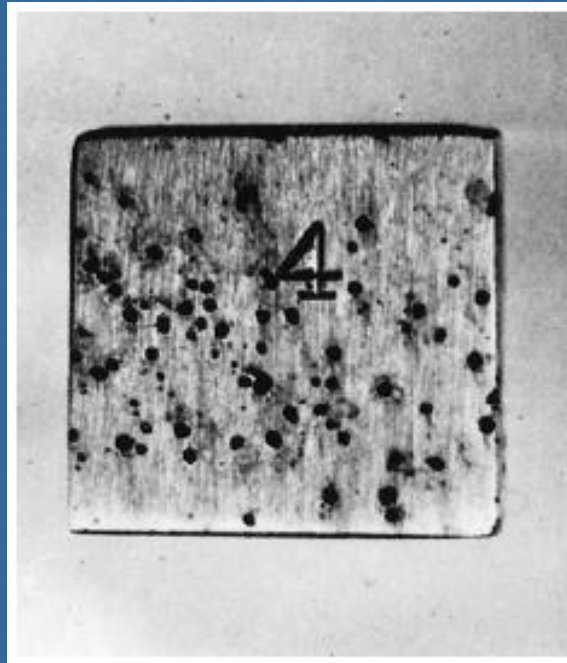

Figure 17.17 The pitting of a 304 stainless steel plate by an acid-chloride solution. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

- *The mechanism for pitting is probably the same as for crevice corrosion*
  - *Oxidation occurs within the pit itself, with complementary reduction at the surface.*

  - *Gravity causes the pits to grow downward, the solution at the pit tip becoming more concentrated and dense as pit growth progresses.*

  - *A pit may be initiated by a localized surface defect such as a scratch or a slight variation in composition.*

- ***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.*

  - *This type of corrosion is especially prevalent in some stainless steels.*

  - *Intergranular corrosion is an especially severe problem in the welding of stainless steels, when it is often termed **weld decay**.*

Figure 17.18 Schematic illustration of chromium carbide particles that have precipitated along grain boundaries in stainless steel, and the attendant zones of chromium depletion.

Grain boundary

$Cr_{23}C_6$ precipitate particle

Zone depleted of chromium
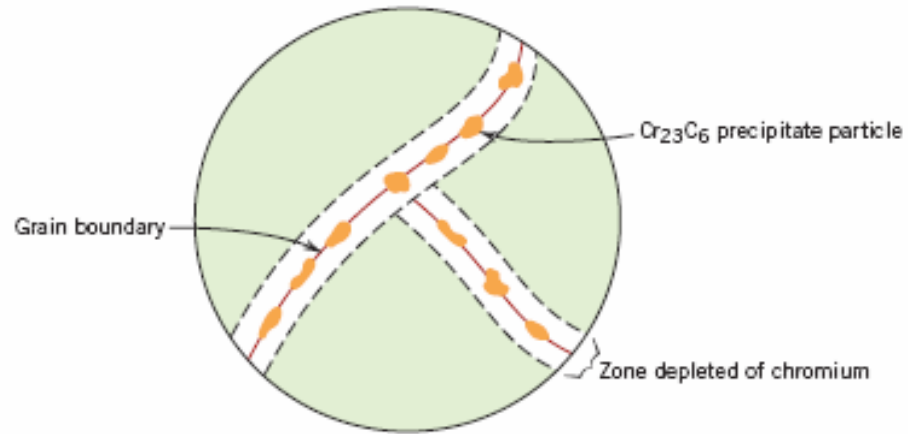
Figure 17.19 Weld decay in a stainless steel. The regions along which the grooves have formed were sensitized as the weld cooled. (From H. H. Uhlig and R. W. Revie, *Corrosion and Corrosion Control*, 3rd edition, Fig. 2, p. 307. Copyright © 1985 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

Intergranular corrosion

Weld
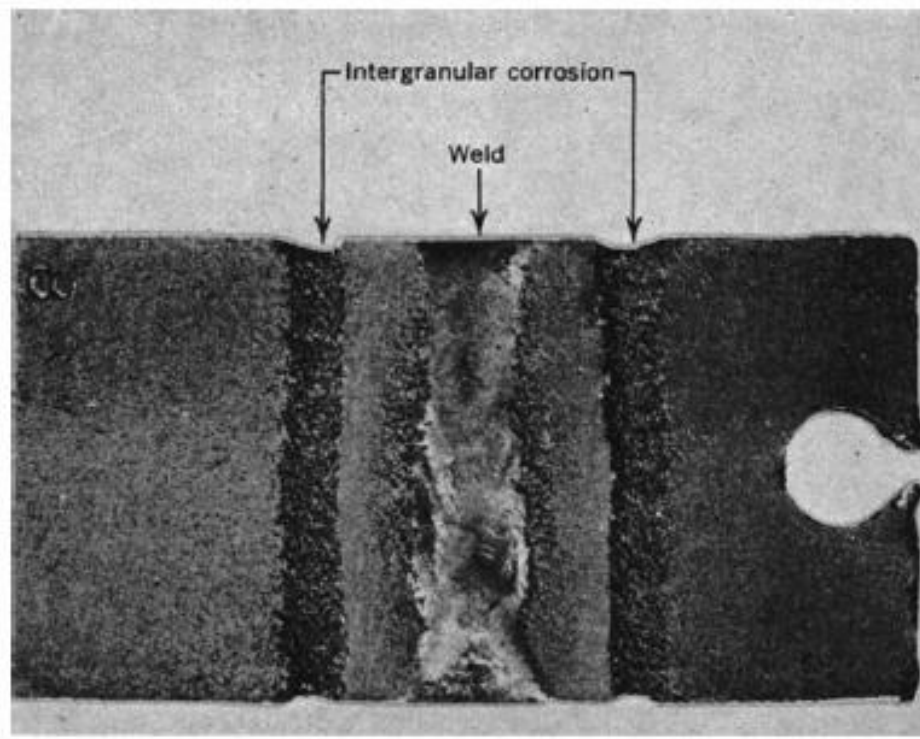
Stainless steels may be protected from intergranular corrosion by the following **measures:**

1. *Subjecting the sensitized material to a* **high-temperature heat treatment** *in which all the chromium carbide particles are redissolved*

2. **Lowering the carbon content** *below 0.03 wt% C so that carbide formation is minimal*

3. **Alloying the stainless steel** *with another metal such as niobium or titanium, which has a greater tendency to form carbides than does chromium so that the Cr remains in solid solution.*

- **Erosion–corrosion** *arises from the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion.*

  - *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.*

  - *Increasing fluid velocity normally enhances the rate of corrosion. Also, a solution is more erosive when bubbles and suspended particulate solids are present.*

Figure 17.20 Impingement failure of an elbow that was part of a steam condensate line. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

- *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.*

- *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,** *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.*

  - *The stress that produces stress corrosion cracking need not be externally applied.*

Figure 17.21
Photomicrograph showing intergranular stress corrosion cracking in brass. (From H. H. Uhlig and R. W. Revie, *Corrosion and Corrosion Control*, 3rd edition, Fig. 5, p. 335. Copyright 1985 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)
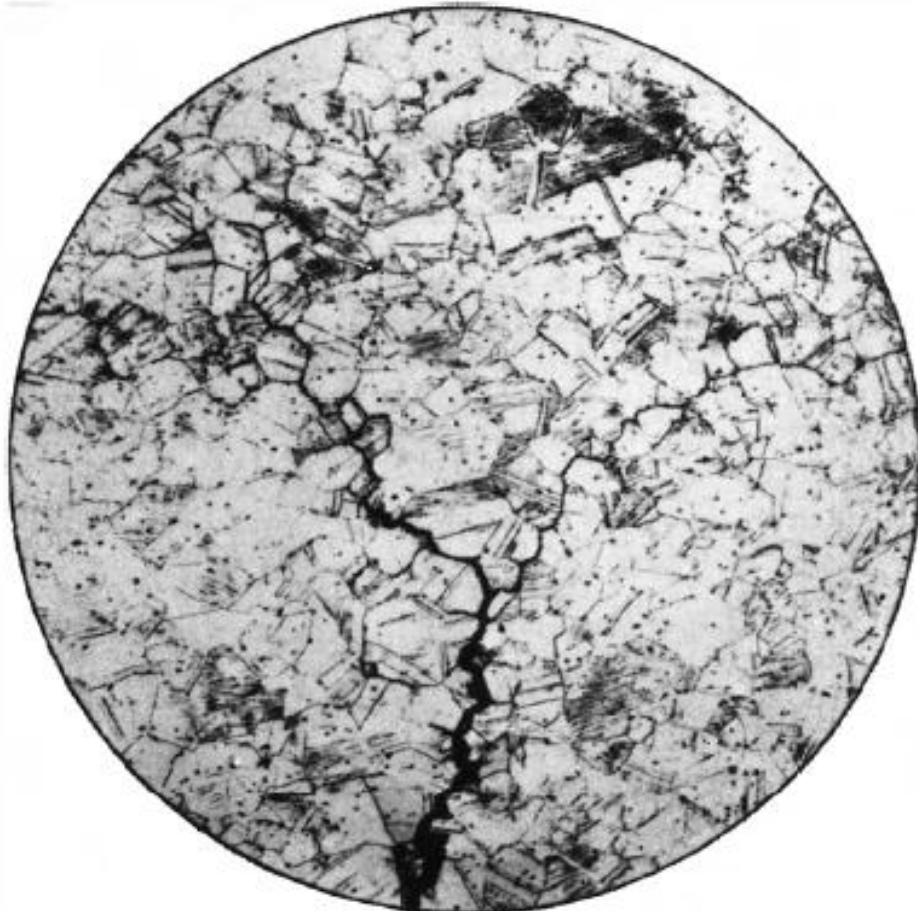
- The best measure to take in reducing or totally eliminating stress corrosion is to lower the magnitude of the stress.

  – Reducing the external load or increasing the cross-sectional area perpendicular to the applied stress.

  – An appropriate heat treatment may be used to anneal out any residual thermal stresses.

Hydrogen Embrittlement

- *Various metal alloys, specifically some steels, experience a significant reduction in ductility and tensile strength when atomic hydrogen (H) penetrates into the material. This phenomenon is referred to as **hydrogen embrittlement.***

Hydrogen Embrittlement Testing Methods

- *(NACE International) Resistance to Hydrogen-Induced Cracking*

- *(ISO)Test methods for selecting metallic materials resistant to hydrogen embrittlement*

- *ASTM F1940-07a- Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners*

- *ASTM F519-06e2-Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating/Coating Processes and Service Environments*

- *Hydrogen embrittlement is a type of failure; in response to applied or residual tensile stresses, brittle fracture occurs catastrophically as cracks grow and rapidly propagate.*

- *Hydrogen in its atomic form diffuses interstitially through the crystal lattice, and concentrations as low as several parts per million can lead to cracking.*

- *Hydrogeninduced cracks are most often transgranular, although intergranular fracture is observed for some alloy systems.*

- *Mechanisms are based on the interference of dislocation motion by the dissolved hydrogen.*

- *Hydrogen embrittlement is similar to stress corrosion in that a normally ductile metal experiences brittle fracture when exposed to both a tensile stress and a corrosive atmosphere. However, cathodic protection reduces or causes a cessation of stress corrosion, it may, on the other hand, lead to the initiation or enhancement of hydrogen embrittlement.*

- *For hydrogen embrittlement to occur, some source of hydrogen must be present, and, in addition, the possibility for the formation of its atomic species. including: pickling of steels in sulfuric acid; electroplating; and the presence of hydrogen-bearing atmospheres (including water vapor) at elevated temperatures such as during welding and heat treatments.*

- *Also, the presence of what are termed "poisons" such as sulfur (i.e.,H2S) and arsenic compounds accelerates hydrogen embrittlement; these substances retard the formation of molecular hydrogen and thereby increase the residence time of atomic hydrogen on the metal surface.*

- *High-strength steels are susceptible to hydrogen embrittlement, and increasing strength tends to enhance the material's susceptibility.*

- *Martensitic steels are especially vulnerable to this type of failure; bainitic, ferritic, and spheroiditic steels aremore resilient.*

- *FCC alloys (austenitic stainless steels, and alloys of copper, aluminum, and nickel) are relatively resistant to hydrogen embrittlement,.*

- *Strain hardening these alloys will enhance their susceptibility to embrittlement.*

- *Some of the techniques commonly used to reduce the likelihood of hydrogen embrittlement include*
  - *reducing the tensile strength of the alloy via a heat treatment,*
  - *removal of the source of hydrogen,*
  - *"baking" the alloy at an elevated temperature to drive out any dissolved hydrogen,*
  - *and substitution of a more embrittlement resistant alloy.*

17.8 CORROSION PREVENTION

- General techniques
  - Material selection
    - *Inhibitors* are substances that, when added in relatively low concentrations to the environment, decrease its corrosiveness.
    - *The equilibrium of corrosion resistance and cost*
  - Environmental alteration
  - Design
    - *Especially with regard to galvanic and crevice corrosion and erosion–corrosion.*
  - Coatings
  - Cathodic protection

Cathodic Protection

- *Used for all eight different forms of corrosion*

- *Oxidation or corrosion of a metal M occurs by*

$$M \longrightarrow M^{n+} + ne^{-}$$

- ***Cathodic protection*** *simply involves supplying, from an external source, electrons to the metal to be protected, making it a cathode; the reaction above is thus forced in the reverse (or reduction) direction.*

Cathodic protection techniques

- **Sacrificial anode**
  - *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.*


(a)
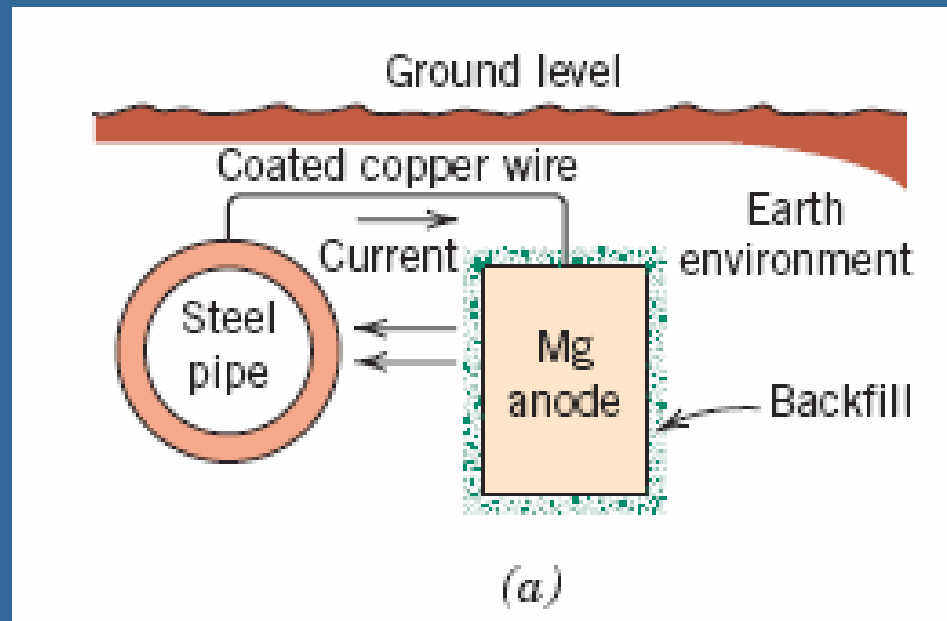
- *Galvanizing*
  - *The process of galvanizing is simply one in which a layer of zinc is applied to the surface of steel by hot dipping. In the atmosphere and most aqueous environments, zinc is anodic to and will thus cathodically protect the steel if there is any surface damage.*
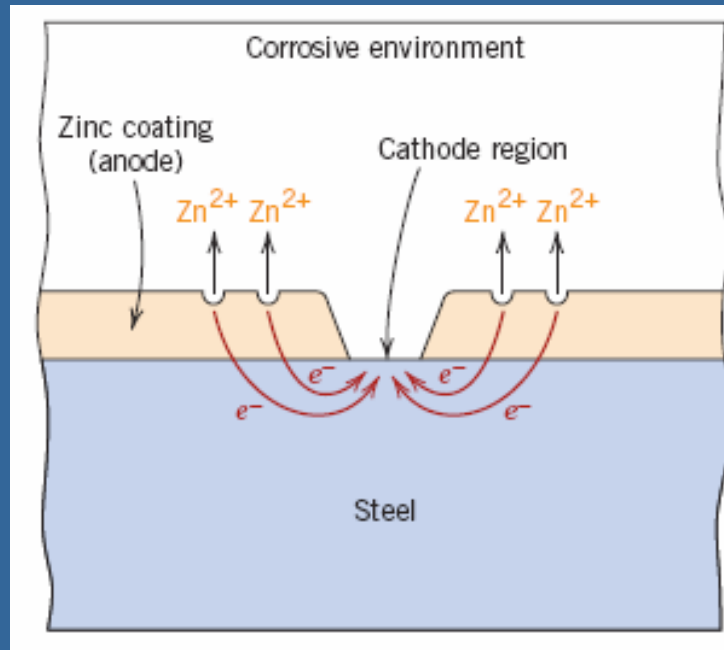
Figure 17.23 Galvanic protection of steel as provided by a coating of zinc.

- ## Impressed current

  – *The source of electrons is an impressed current from an external dc power source .*
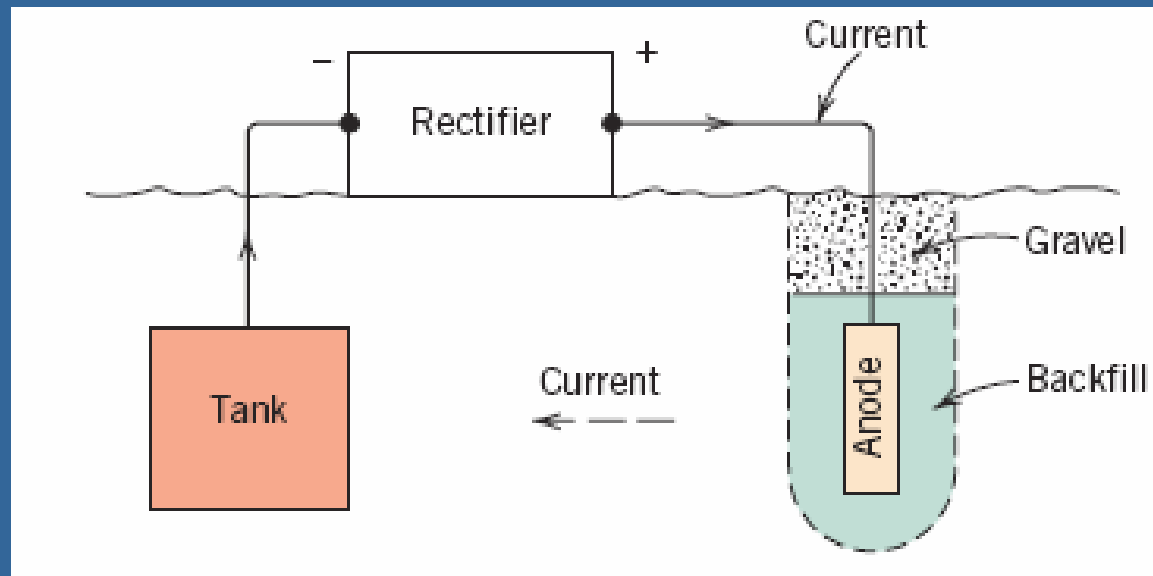
The negative terminal of the power source is connected to the structure to be protected. The other terminal is joined to an inert anode (often graphite), high-conductivity backfill material provides good electrical contact between the anode and surrounding soil. A current path exists between the cathode and anode through the intervening soil, completing the electrical circuit.

Concept Check 17.7

Tin cans are made of a steel the inside of which is coated with a thin layer of tin. The tin protects the steel from corrosion by food products in the same manner as zinc protects steel from atmospheric corrosion. Briefly explain how this cathodic protection of tin cans is possible, given that tin is electrochemically less active than steel in the galvanic series (Table 17.2).

SUMMARY

Electrochemical Considerations

Metallic corrosion is ordinarily electrochemical, involving both oxidation and reduction reactions. Oxidation is the loss of the metal atom's valence electrons; the resulting metal ions may either go into the corroding solution or form an insoluble compound. During reduction, these electrons are transferred to at least one other chemical species. The character of the corrosion environment dictates which of several possible reduction reactions will occur.

Not all metals oxidize with the same degree of ease, which is demonstrated with a galvanic couple; when in an electrolyte, one metal (the anode) will corrode, whereas a reduction reaction will occur at the other metal (the cathode). The magnitude of the electric potential that is established between anode and cathode is indicative of the driving force for the corrosion reaction.

The standard emf and galvanic series are simply rankings of metallic materials on the basis of their tendency to corrode when coupled to other metals. For the standard emf series, ranking is based on the magnitude of the voltage generated when the standard cell of a metal is coupled to the standard hydrogen electrode at 25°C (77°F). The galvanic series consists of the relative reactivities of metals and alloys in seawater.

The half-cell potentials in the standard emf series are thermodynamic parameters that are valid only at equilibrium; corroding systems are not in equilibrium. Furthermore, the magnitudes of these potentials provide no indication as to the rates at which corrosion reactions occur.

Corrosion Rates

The rate of corrosion may be expressed as corrosion penetration rate, that is, the thickness loss of material per unit of time. Mils per year and millimeters per year are the common units for this parameter. Alternatively, rate is proportional to the current density associated with the electrochemical reaction.

Prediction of Corrosion Rates

Corroding systems will experience polarization, which is the displacement of each electrode potential from its equilibrium value; the magnitude of the displacement is termed the overvoltage. The corrosion rate of a reaction is limited by polarization, of which there are two types—activation and concentration. Polarization data are plotted as potential versus the logarithm of current density. The corrosion rate for a particular reaction may be computed using the current density associated with the intersection point of oxidation and reduction polarization curves.

Passivity

A number of metals and alloys passivate, or lose their chemical reactivity, under some environmental circumstances. This phenomenon is thought to involve the formation of a thin protective oxide film. Stainless steels and aluminum alloys exhibit this type of behavior. The active-to-passive behavior may be explained by the alloy's S-shaped electrochemical potential-versus-log current density curve. Intersections with reduction polarization curves in active and passive regions correspond, respectively, to high and low corrosion rates.

Design Problem

- *Each student (or group of students) is to find a real-life corrosion problem that has not been solved*
  - *Conduct a thorough investigation as to the cause(s) and type(s) of corrosion;*
  - *Propose possible solutions for the problem, indicating which of the solutions is best and why;*
  - *Submit a report that addresses the above issues.*

Forms of Corrosion

Metallic corrosion is sometimes classified into eight different forms: uniform attack, galvanic corrosion, crevice corrosion, pitting, intergranular corrosion, selective leaching, erosion–corrosion, and stress corrosion. Hydrogen embrittlement, a type of failure sometimes observed in corrosion environments, was also discussed.

Corrosion Prevention

The measures that may be taken to prevent, or at least reduce, corrosion include material selection, environmental alteration, the use of inhibitors, design changes, application of coatings, and cathodic protection.

IMPORTANT TERMS AND CONCEPTS

Activation polarization

Anode

Cathode

Cathodic protection

Galvanic corrosion

Galvanic series

Hydrogen embrittlement

Inhibitor

Intergranular corrosion

Molarity

Concentration polarization

Corrosion

Corrosion penetration rate

Crevice corrosion

Oxidation

Passivity

Pilling–Bedworth ratio

Pitting

Polarization

Reduction

Degradation

Electrolyte

Electromotive force (emf) series

Erosion–corrosion

Sacrificial anode

Scission

Selective leaching

Standard half-cell

Stress corrosion

Weld decay