CHAPTER 17:
CORROSION AND DEGRADATION

ISSUES TO ADDRESS...

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

THE COST OF CORROSION

- **Corrosion:**
  --the destructive electrochemical attack of a material.
  --Al Capone's ship, Sapona, off the coast of Bimini.

Photos courtesy L.M. Maestas, Sandia National Labs. Used with permission.

- **Cost:**
  --4 to 5% of the Gross National Product (GNP)*
  --this amounts to just over $400 billion/yr**

*** H.H. Uhlig and W.R. Revie, *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering*, 3rd ed., John Wiley and Sons, Inc., 1985.**
****Economic Report of the President (1998).**

The Rusting Mechanism (Peel)

$4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3$

gives ferric hydroxide

$2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot 3H_2O$

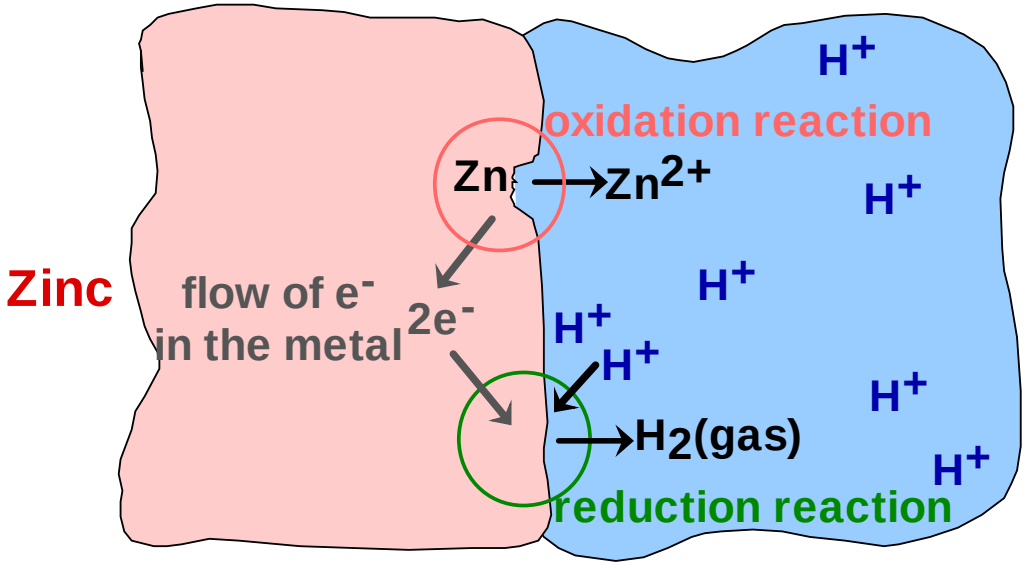
gives iron oxide (rust) and water

Basic "rusting" or corrosion requirements

1. The metal is oxidized at the anode of an electrolytic cell
2. Some ions are reduced at the cathode
3. There is a potential or voltage difference between the anode and cathode
4. An electrolyte (fluid) must be present
5. The electrical path must be completed

CORROSION OF ZINC IN ACID

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



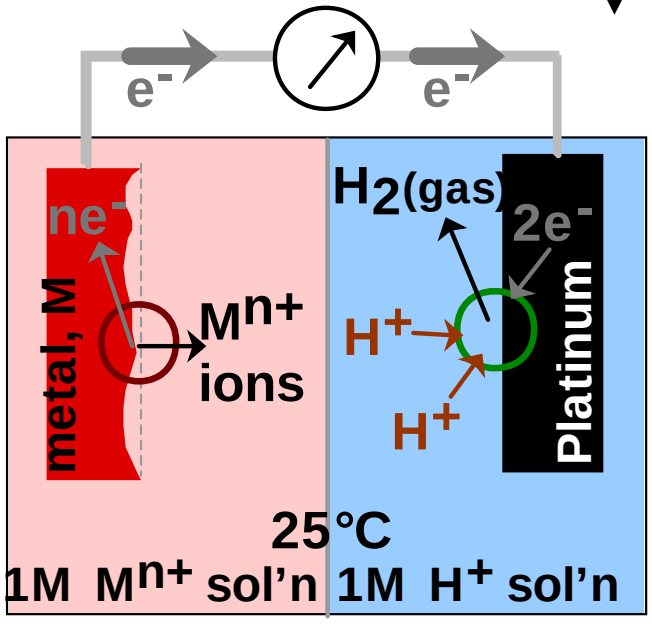
Adapted from Fig. 17.1, *Callister 6e.* (Fig. 17.1 is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

- **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:**

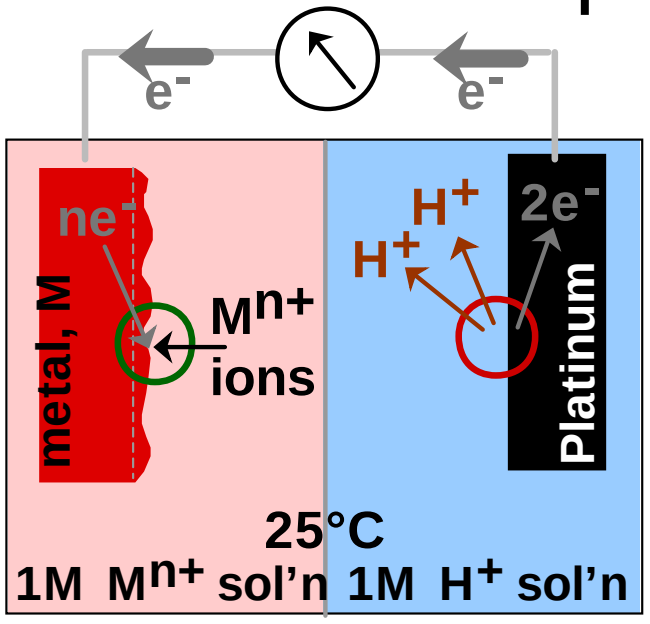
--Metal sample mass ↓



--Metal is the anode (-)

$V^{o}_{metal} < 0$ **(relative to Pt)**

--Metal sample mass ↑



--Metal is the cathode (+)

$V^{o}_{metal} > 0$ **(relative to Pt)**

Standard Electrode Potential

STANDARD EMF SERIES

- EMF series

more cathodic

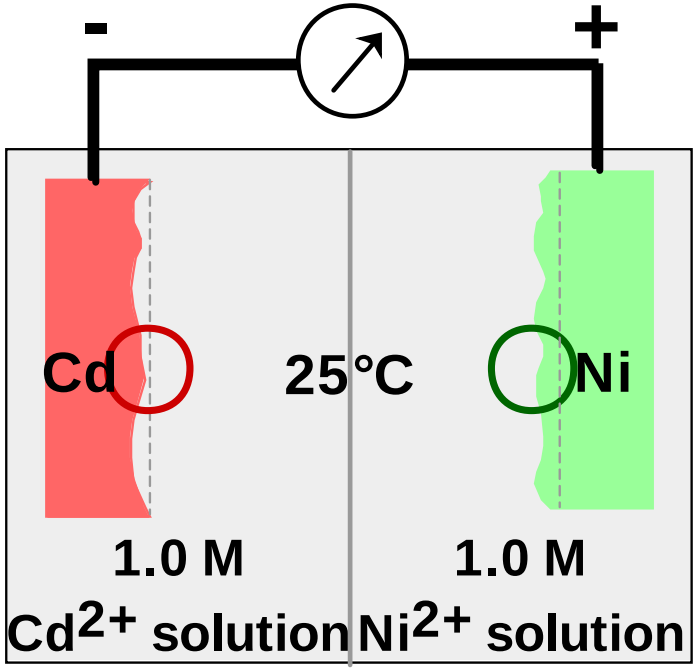
more anodic

metal	V^o_{metal}
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

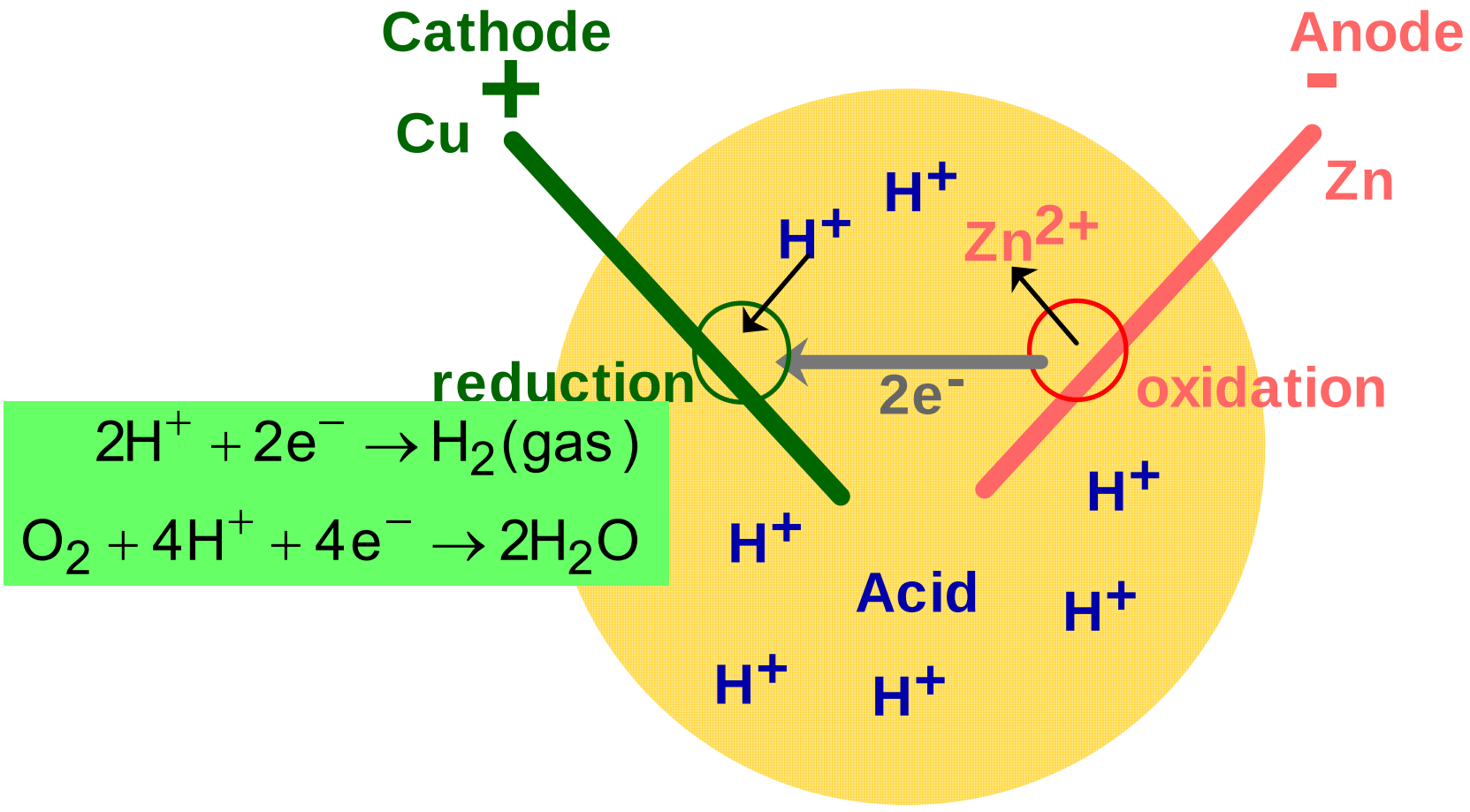
ΔV^o = 0.153V

Data based on Table 17.1, *Callister 6e.*

- Metal with smaller V^o_{metal} corrodes.
- Ex: Cd-Ni cell



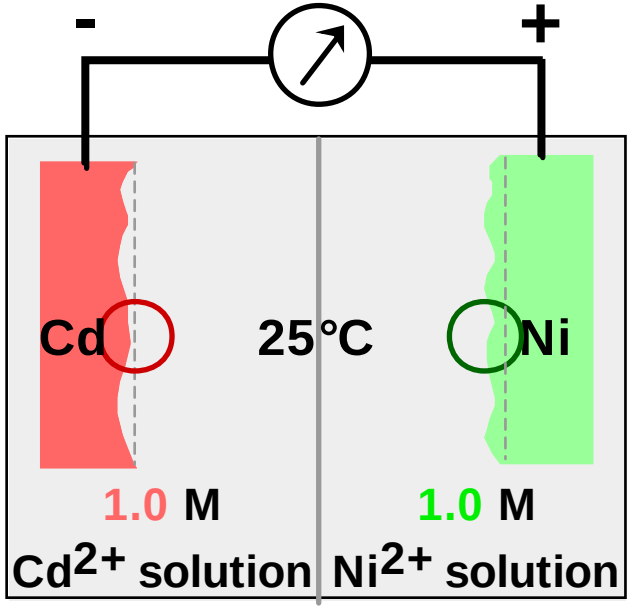
CORROSION IN A GRAPEFRUIT



EFFECT OF SOLUTION CONCENTRATION

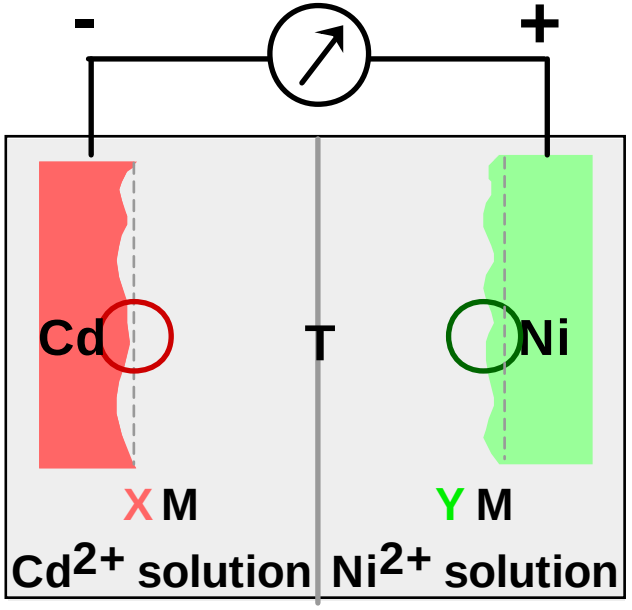
- **Ex: Cd-Ni cell with standard 1M solutions**

$$V^o_{Ni} - V^o_{Cd} = 0.153$$



- **Ex: Cd-Ni cell with non-standard solutions**

$$V_{Ni} - V_{Cd} = V^o_{Ni} - V^o_{Cd} - \frac{RT}{nF}\ln\frac{X}{Y}$$



n = #e- per unit oxid/red reaction (=2 here)

F = Faraday's constant =96,500 C/mol.

- **Reduce $V_{Ni} - V_{Cd}$ by**
  - **--increasing X**
  - **--decreasing Y**

Factors affecting Corrosion (Peel)

- Material properties
- Metallurgical factors
- Passivity
- Environment

Metallurgical factors

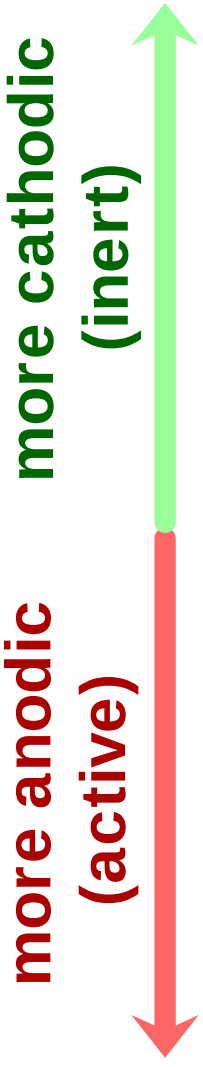
- Chemical segregation
- Presence of multiple phases
- Inclusions
- Cold Work
- Non-uniform stresses

Passivity

- Example with steel in nitric acid…dilute solutions will cause rapid attack, strong solutions have little visible effect.
- Surface film can be formed
- Some types of steel may do this with rust
- Aluminum does this
- Need to watch passive film, but can be used for simple protection

GALVANIC SERIES

- Ranks the reactivity of metals/alloys in seawater



Platinum
Gold
Graphite
Titanium
Silver
316 Stainless Steel
Nickel (passive)
Copper
Nickel (active)
Tin
Lead
316 Stainless Steel
Iron/Steel
Aluminum Alloys
Cadmium
Zinc
Magnesium

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

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.

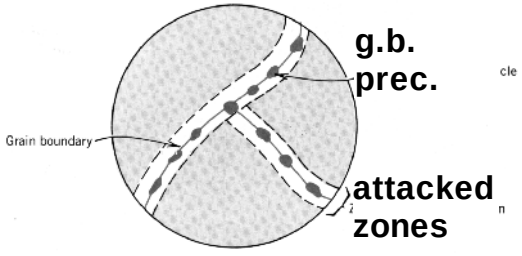


Fig. 17.9, *Callister 6e*.

- **Stress corrosion**
  Stress & corrosion work together at crack tips.
- **Galvanic**
  Dissimilar metals are physically joined. The more anodic one corrodes.(see Table 17.2) Zn & Mg very anodic.
- **Erosion-corrosion**
  Break down of passivating layer by erosion (pipe elbows).
- **Pitting**
  Downward propagation of small pits & holes.

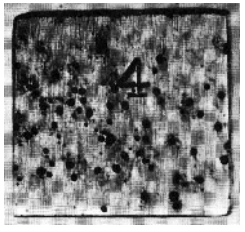


Fig. 17.8, *Callister 6e*. (Fig. 17.8 from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

- **Crevice** Between two pieces of the same metal.

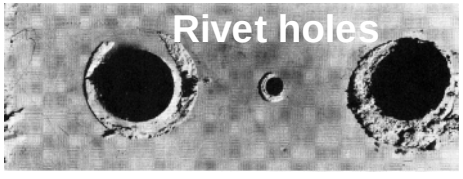
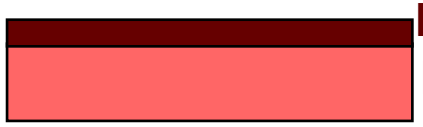


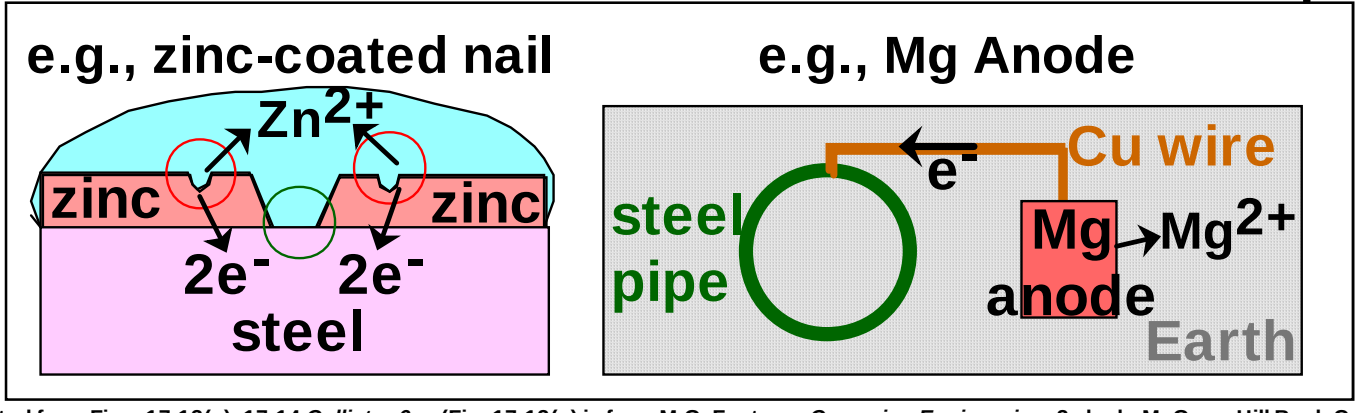
Fig. 17.6, *Callister 6e*. (Fig. 17.6 is courtesy LaQue Center for Corrosion Technology, Inc.)

CONTROLLING CORROSION

- **Self-protecting metals!**
  --Metal ions combine with O_2 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_2 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.



Adapted from Figs. 17.13(a), 17.14 *Callister 6e*. (Fig. 17.13(a) is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Co., 1986.)

SUMMARY

- **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.

Homework

17.10 This problem asks, for several pairs of alloys that are immersed in seawater, to predict whether or not corrosion is possible, and if it is possible, to note which alloy will corrode. In order to make these predictions it is necessary to use the galvanic series, Table 17.2. If both of the alloys in the pair reside within the same set of brackets in this table, then galvanic corrosion is unlikely. However, if the two alloys do not reside within the same set of brackets, then that alloy appearing lower in the table will experience corrosion.

(d) For the titanium-304 stainless steel pair, the stainless steel will corrode, inasmuch as it is below titanium in both its active and passive states.

(e) For the cast iron-316 stainless steel couple, the cast iron will corrode since it is below stainless steel in both active and passive states.

Homework

17.14 This problem asks for us to calculate the **CPR** in both mpy and mm/yr for a thick steel sheet of area 100 in.2 which experiences a weight loss of 485 g after one year. Employment of Equation (17.23) leads to

$$\text{CPR} = \frac{KW}{\rho A t} \qquad \text{CPR} = \frac{(534)(485\ \text{g})\left(10^3\ \text{mg/g}\right)}{\left(7.9\ \text{g/cm}^3\right)\left(100\ \text{in.}^2\right)(24\ \text{h/day})(365\ \text{day/yr})(1\ \text{yr})}$$

$$= 0.952\ \text{mm/yr}$$

Also

$$\text{CPR} = \qquad = \frac{(87.6)(485\ \text{g})\left(10^3\ \text{mg/g}\right)}{\left(7.9\ \text{g/cm}^3\right)\left(100\ \text{in.}^2\right)(2.54\ \text{cm/in.})^2(24\ \text{h/day})(365\ \text{day/yr})(1\ \text{yr})}$$

$$= 37.4\ \text{mpy}$$