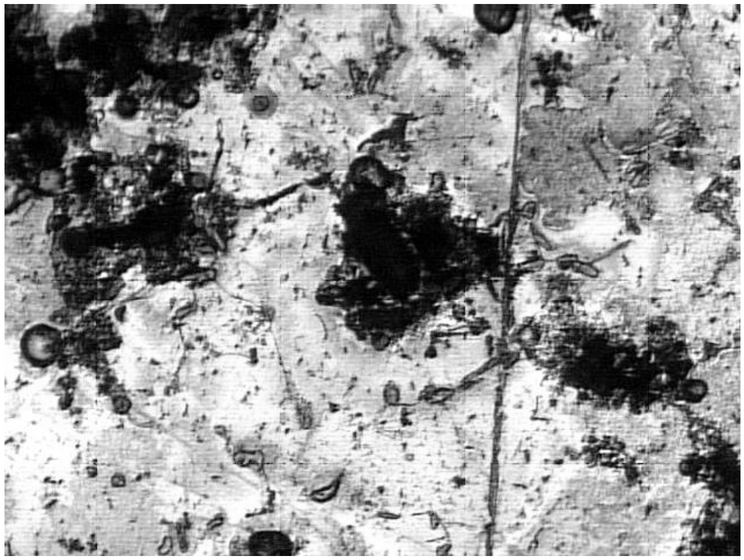
CHAPTER 23:
CORROSION AND DEGRADATION



CORROSION

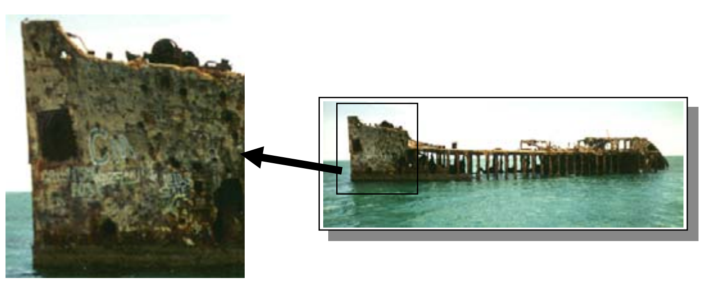
Corrosion:

The corrosion is the deterioration of the metals (oxidation) in different environments in presence of oxygen.

Anodic reaction: $M \longrightarrow M^{+n} + ne^-$

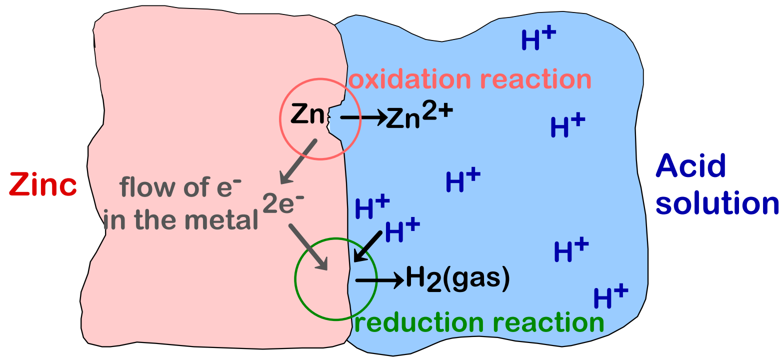
Cathodic reaction: $2H^+ + 2e^- \longrightarrow H_2$ (acid environment)

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



Example: CORROSION OF ZINC IN ACID

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



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

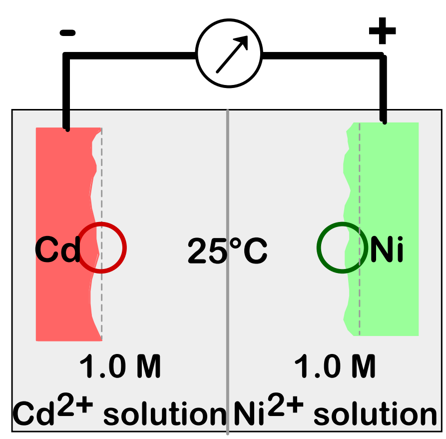
STANDARD EMF SERIES

- EMF series

	metal	V^o_{metal}
more cathodic ↑	Au	+1.420 V
	Cu	+0.340
	Pb	- 0.126
	Sn	- 0.136
	Ni	- 0.250
	Co	- 0.277
	Cd	- 0.403
more anodic ↓	Fe	- 0.440
	Cr	- 0.744
	Zn	- 0.763
	Al	- 1.662
	Mg	- 2.262
	Na	- 2.714
	K	- 2.924

Ni – Cd: DV^o = 0.153V

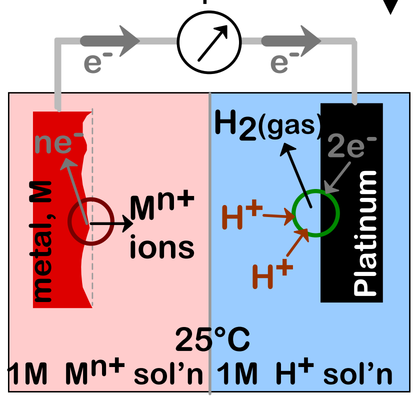
- Metal with smaller V^o_{metal} corrodes.
- Ex: Cd-Ni cell

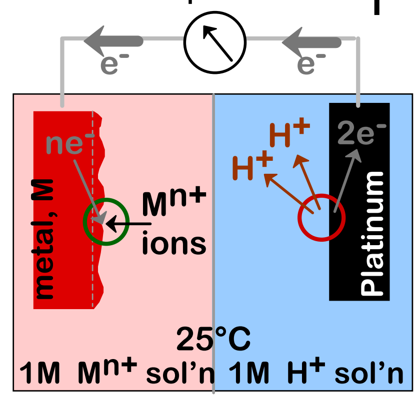


This is how we measure the potentials in the EMF Series:

- Two outcomes:

--Metal sample mass ↓ --Metal sample mass ↑





--Metal is the anode (-) --Metal is the cathode (+)

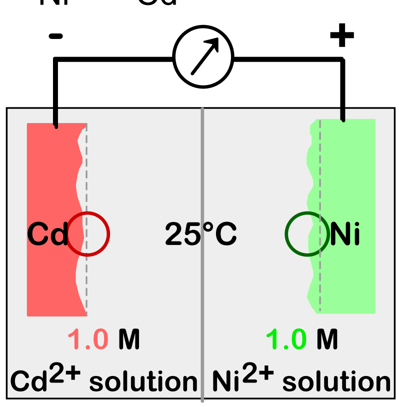
$V^o_{metal} < 0$ (relative to Pt) $V^o_{metal} > 0$ (relative to Pt)

Standard Electrode Potential

EFFECT OF SOLUTION CONCENTRATION

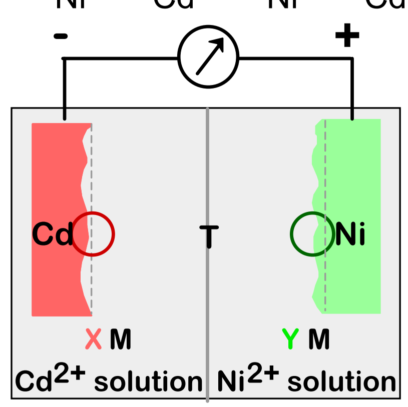
- Ex: Cd-Ni cell with standard 1M solutions

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



- 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

Nernst equation is used to measure the potential difference:

$$V = V^0 + \frac{RT}{nF} \ln C_{ion}$$

Where:

V = New potential of half-cell, V

V^0 = Standard potential, V

R = Real gas constant, 8.3143 J/mol °K

T = Temperature, °K

n = Number of electrons transferred.

F = Faraday constant, 96,500 C/mol or A· s/mol

C_{ion} = Molar concentration of ions

If we need to measure the amount of mass lost by corrosion we use Faraday equation:

$$w = \frac{ItM}{nF} = \frac{iAtM}{nF}$$

Where:

w = lost weight, g

M = Atomic mass of the metal, g/mol

t = time, sec

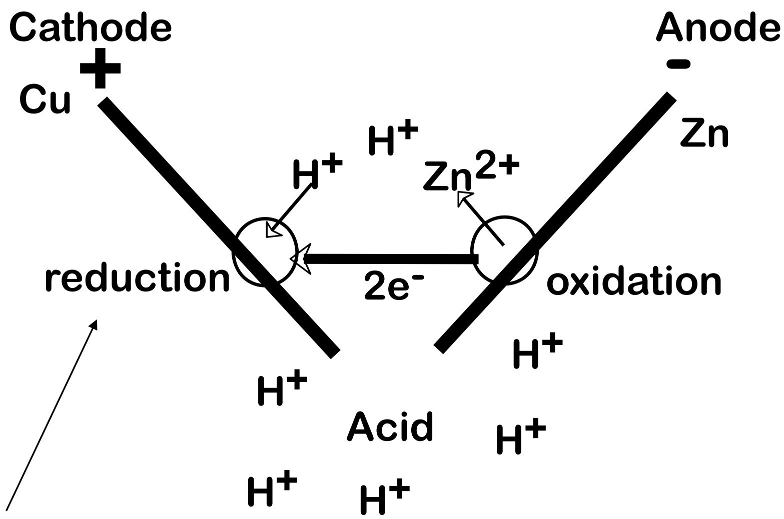
I = current density, A/cm^2

n = number of electrons transferred

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

A = area, cm^2

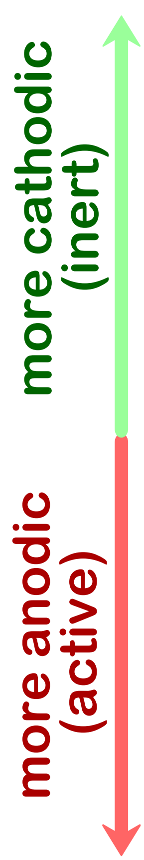
Example: Corrosion in a grapefruit



$$2H^+ + 2e^- \rightarrow H_2(gas)$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

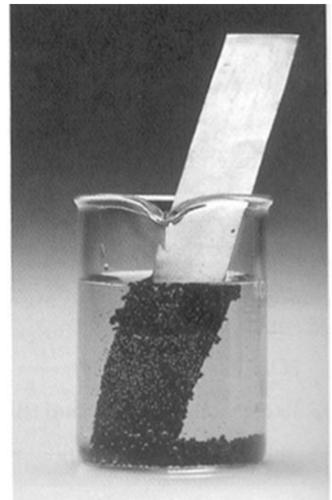
GALVANIC SERIES

Ranks the reactivity of metals/alloys in seawater

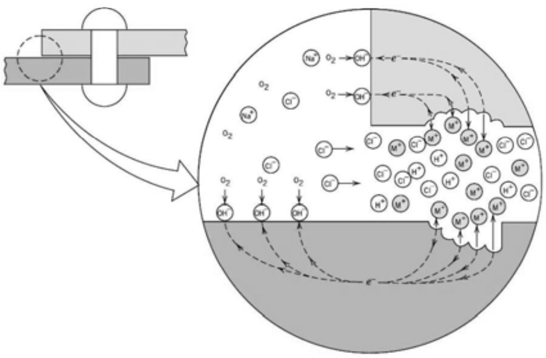


Platinum
Gold
Graphite
Titanium
Silver
316 Stainless Steel
Nickel (passive)
Copper
Nickel (active)
Tin
Lead
316 Stainless Steel
Iron/Steel
Aluminum Alloys
Cadmium
Zinc
Magnesium

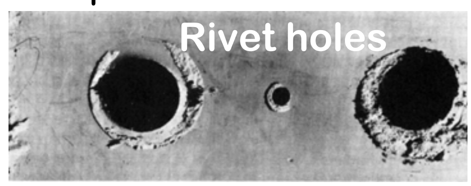
FORMS OF CORROSION



- **Uniform Attack**
  Oxidation & reduction occur uniformly over surface.

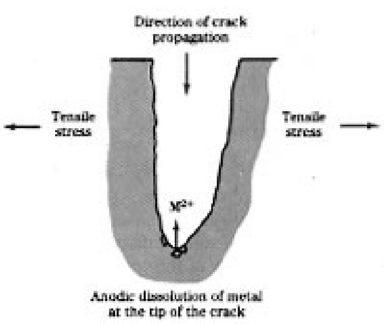


- **Crevice** **Between two pieces of the same metal.**



FORMS OF CORROSION (cont.)

- **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.

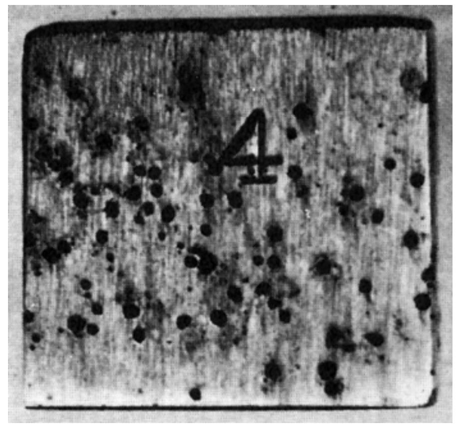
FORMS OF CORROSION (cont.)

- Selective Leaching

Preferred corrosion of
one element/constituent
(e.g., Zn from brass (Cu-Zn)).

- Pitting

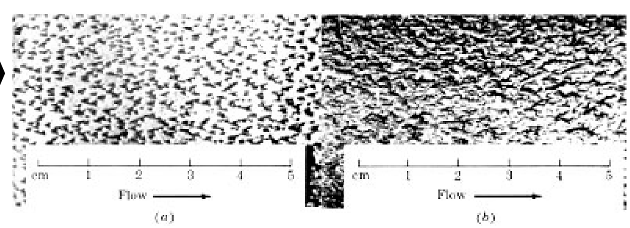
Downward propagation
of small pits & holes.

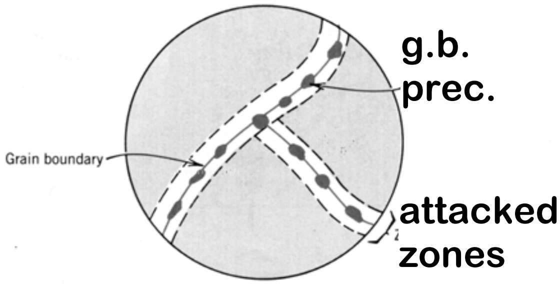


FORMS OF CORROSION (cont.)

- Erosion-corrosion

Break down of passivating
layer by erosion (pipe
elbows).



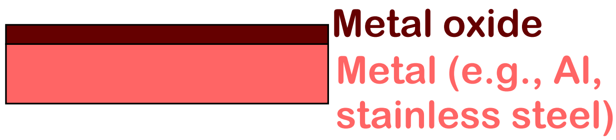


- Intergranular

Corrosion along
grain boundaries,
often where special
phases exist.

CONTROLLING CORROSION

- **Self-protecting metals!**
  --Metal ions combine with O
  to form a thin, adhering oxide layer that slows corrosion.



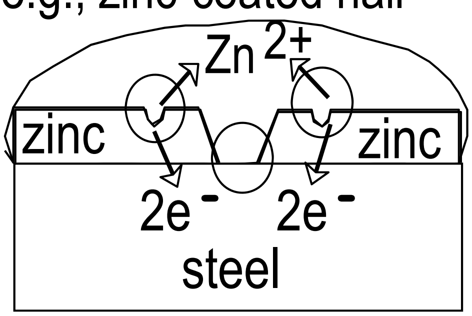
- **Reduce T** **(slows kinetics of oxidation and reduction)**

- Add inhibitors
  --Slow oxidation/reduction reactions by removing reactants
  (e.g., remove O_2 gas by reacting it w/an inhibitor).
  --Slow oxidation reaction by attaching species to
  the surface (e.g., paint it!).

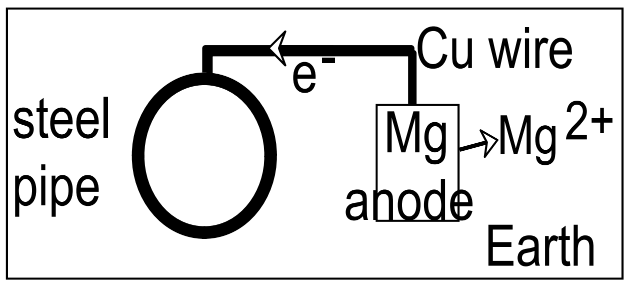
CONTROLLING CORROSION (cont.)

- Cathodic (or sacrificial) protection
  --Attach a more anodic material to the one to be protected.

e.g., zinc-coated nail



e.g., Mg Anode



Rate of oxidation

Rate of oxidation and the tendency of the film to protect the metal from further oxidation are related to the relative volumes of the oxide and metal.

$$P-B\,ratio=\frac{A_0\rho_M}{A_M\,\rho_0}$$

Where:

P-R ratio = Pilling-Bedworth ratio

A_0 = is the molecular (or formula) weight of the oxide

A_M = is the atomic weight of the metal

ρ_0 = oxide density

ρ_0 = metal density

Oxidation rate (kinetics)

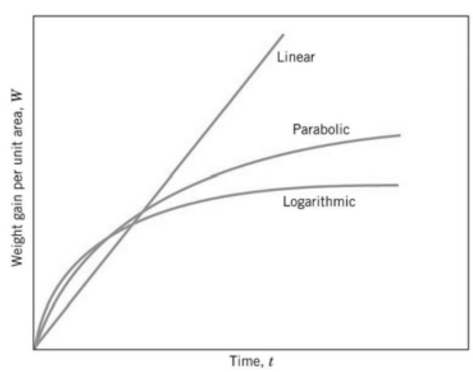
Where:

ω = weight gain per unit area

t = time

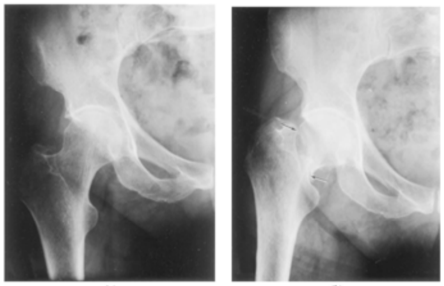
κ_L, κ_p and κ_e are the constant linear, parabolic and logarithmic respectively.

C and A are constant.

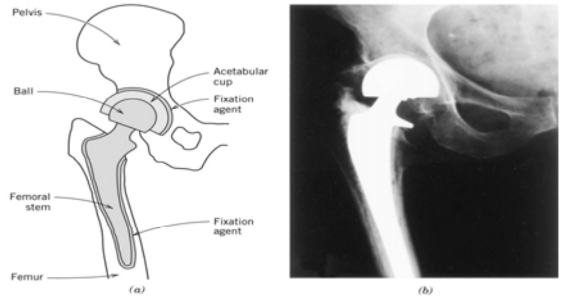


Linear:	$\omega = \kappa_L t$
Parabolic	$\omega^2 = \kappa_p t + C$
Logarithmic	$\omega = \kappa_e \log(C\cdot t + A)$

Example: Artificial total hip replacement



X-rays of a normal hip joint and fractured hip joint



Schematic diagram and x-ray of an artificial total hip replacement

Artificial total hip joint replacement designs

Artificial total hip replacement (cont.)

Three types of biomaterials are used for hip implants:

- Austenitic stainless steel - 316L with low sulfur content (< 0.002 wt%) and extremely low carbon
- Cobalt-nickel-chromium-molybdenum – MP35N with a composition 35 wt% Co, 35 wt% Ni, 20 wt% Cr, and 10 wt% Mo.
- Titanium – Ti-6Al-4V with a composition 90 wt% Ti, 6 wt% Al and 4 wt% V

Artificial Total Hip replacement

Mechanical and Corrosion Characteristics of Three Metal Alloys That Are Commonly Used for the Femoral Stem Component of the Prosthetic Hip

Alloy	*Elastic Modulus* [*GPa* (*psi*)]	*0.2% Yield Strength* [*MPa* (*ksi*)]	*Tensile Strength* [*MPa* (*ksi*)]	*Elongation at Fracture* (%)	*Fatigue Strength or Limit, 10^7 Cycles* [*MPa* (*ksi*)]	*Corrosion Rate* (*mpy*)[a]
316L Stainless steel (cold worked)	196 (28.4×10^6)	700 (102)	875 (127)	12	383 (55.5)	0.001–0.002
MP35N (hot forged)	230 (33.4×10^6)	1000 (145)	1200 (174)	13	500 (72.5)	0.0012–0.002
Ti-6Al-4V (hot forged)	120 (17.4×10^6)	950 (138)	1075 (156)	13	580 (84.1)	0.007–0.04

[a] mpy means mils per year, or 0.001 in./yr

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.