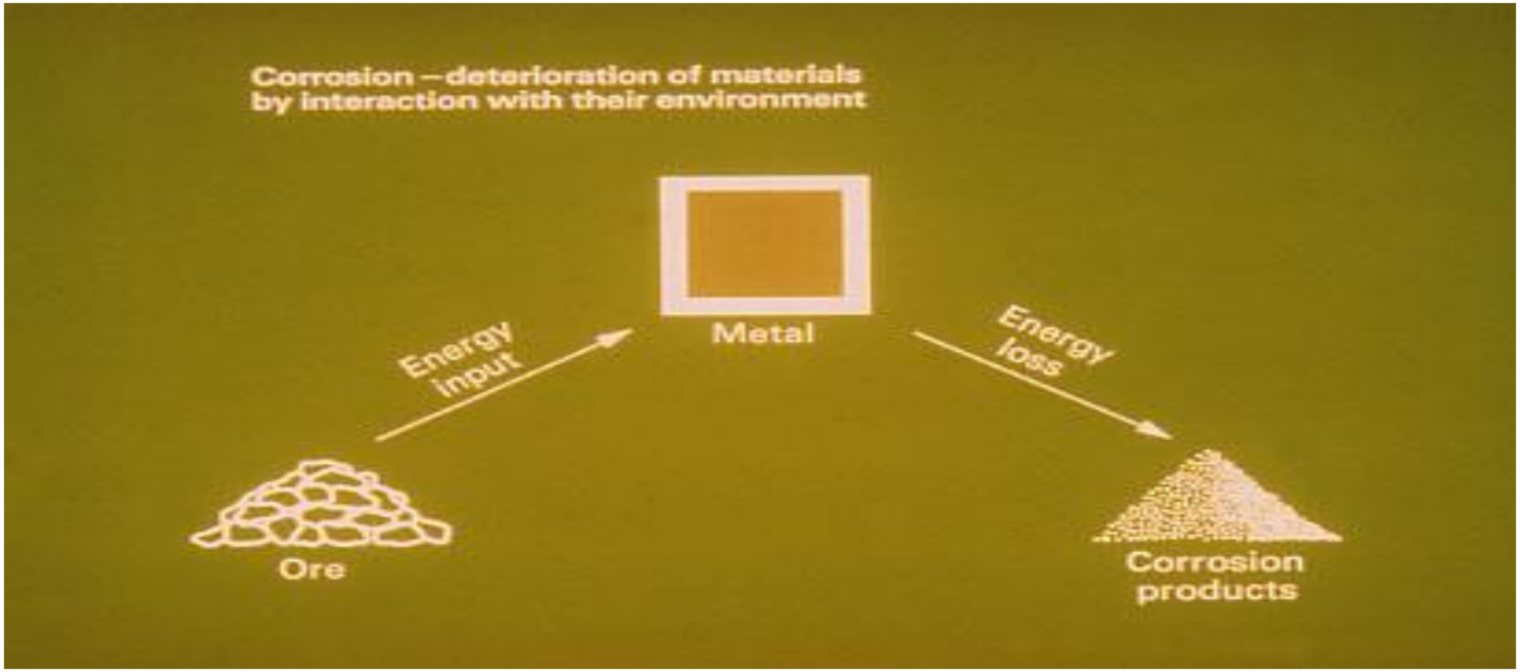
Introduction to Corrosion

Definition

- Corrosion may be defined as the destruction of a metal or an alloy because of chemical or electrochemical reaction with its surrounding environment or medium

Definition of Corrosion

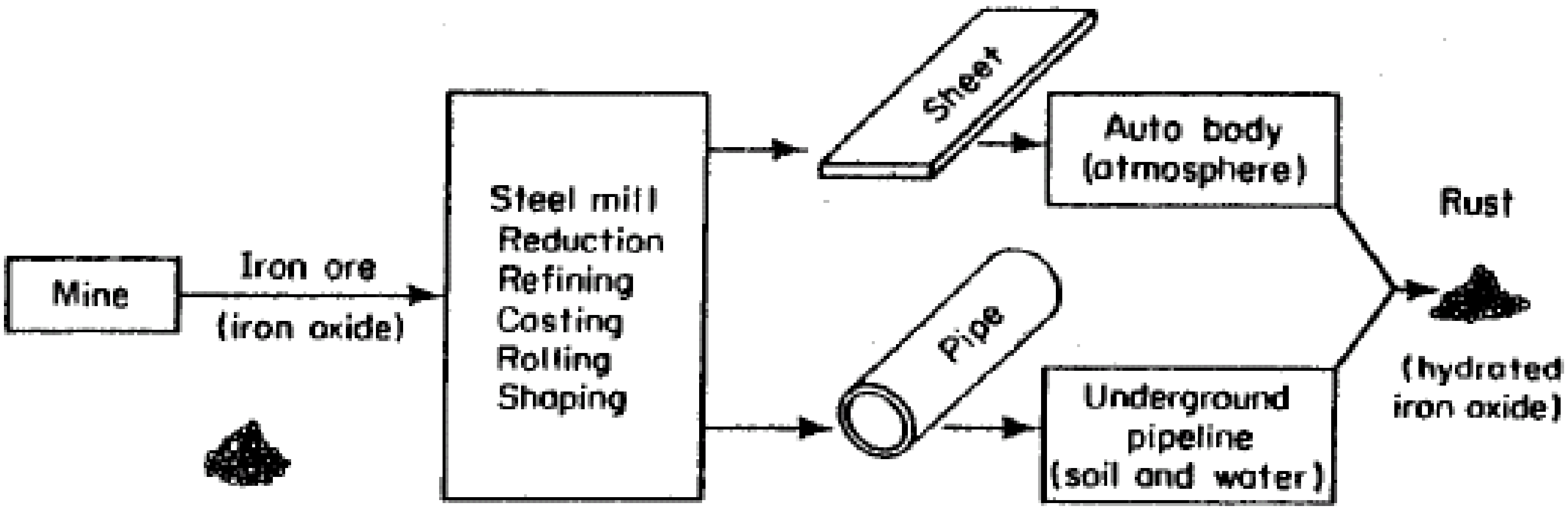


Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals.

So……Why Study Corrosion?

- Materials are precious resources
- Engineering design is incomplete without knowledge of corrosion
- Applying knowledge of corrosion protection can minimize disasters
- Corrosion – contaminate products such as pharmaceutical, food and dairy products or luxury items like soap
- Corrosion products – threat to the environment
- Artificial implants for the human body!!!

Corrosion: Metallurgy in Reverse[2]



[2]Fontana, M.G., *Corrosion Engineering*. 3rd ed. 1986, New York: McGraw-Hill.

Anodic & Cathodic Reactions

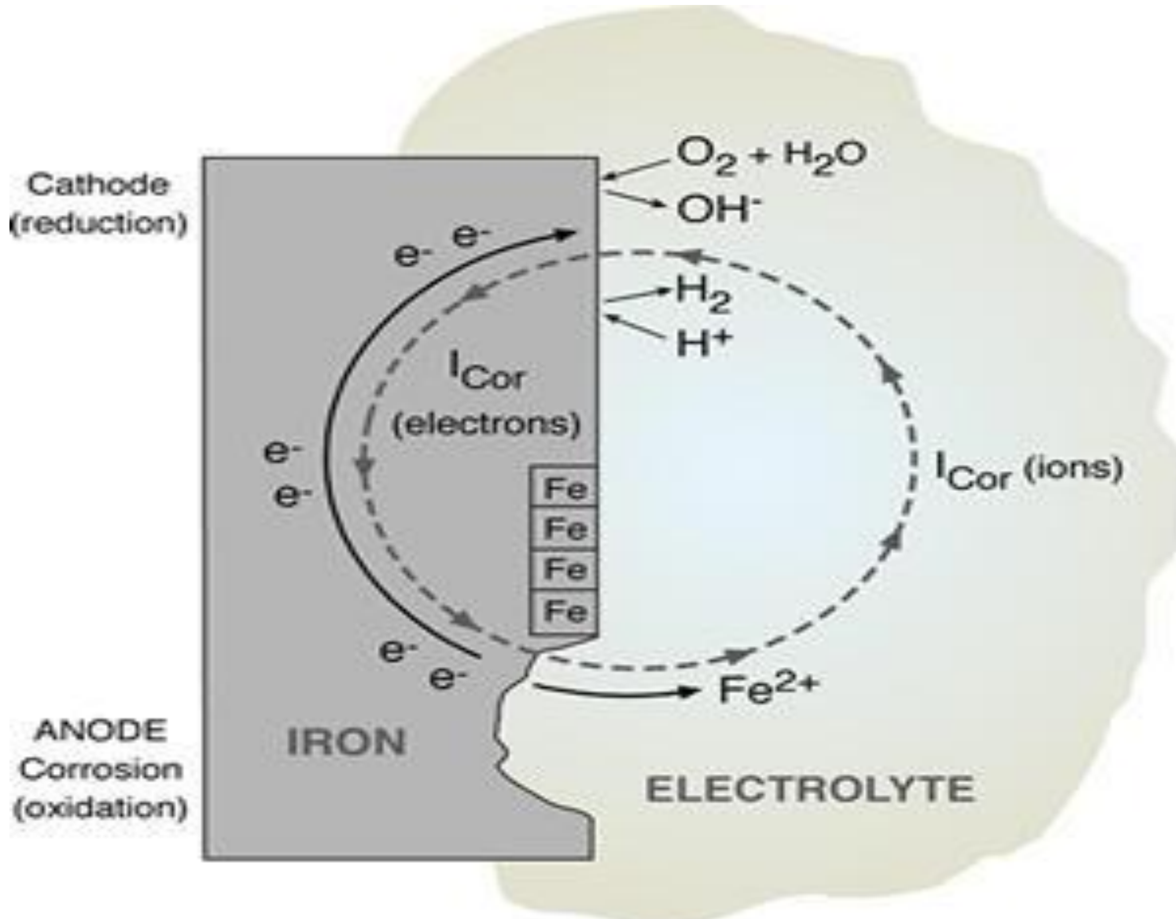
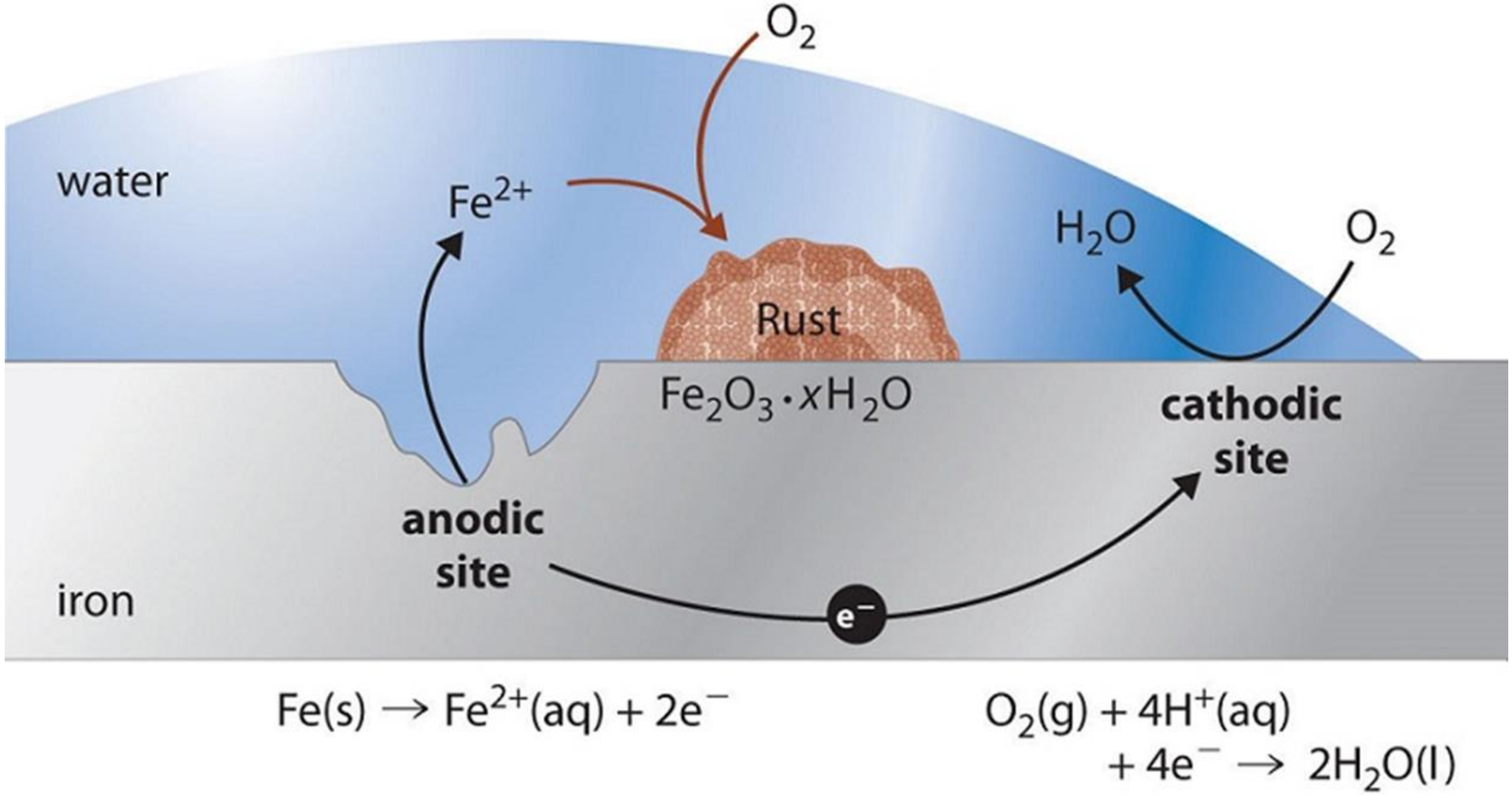


Figure 2



O2
water
Fe2+
H2O
O2
Rust
Fe2O3 · xH2O
cathodic
site
anodic
site
iron
e−
Fe(s) → Fe2+(aq) + 2e−
O2(g) + 4H+(aq)
+ 4e− → 2H2O(l)

Types of Corrosion

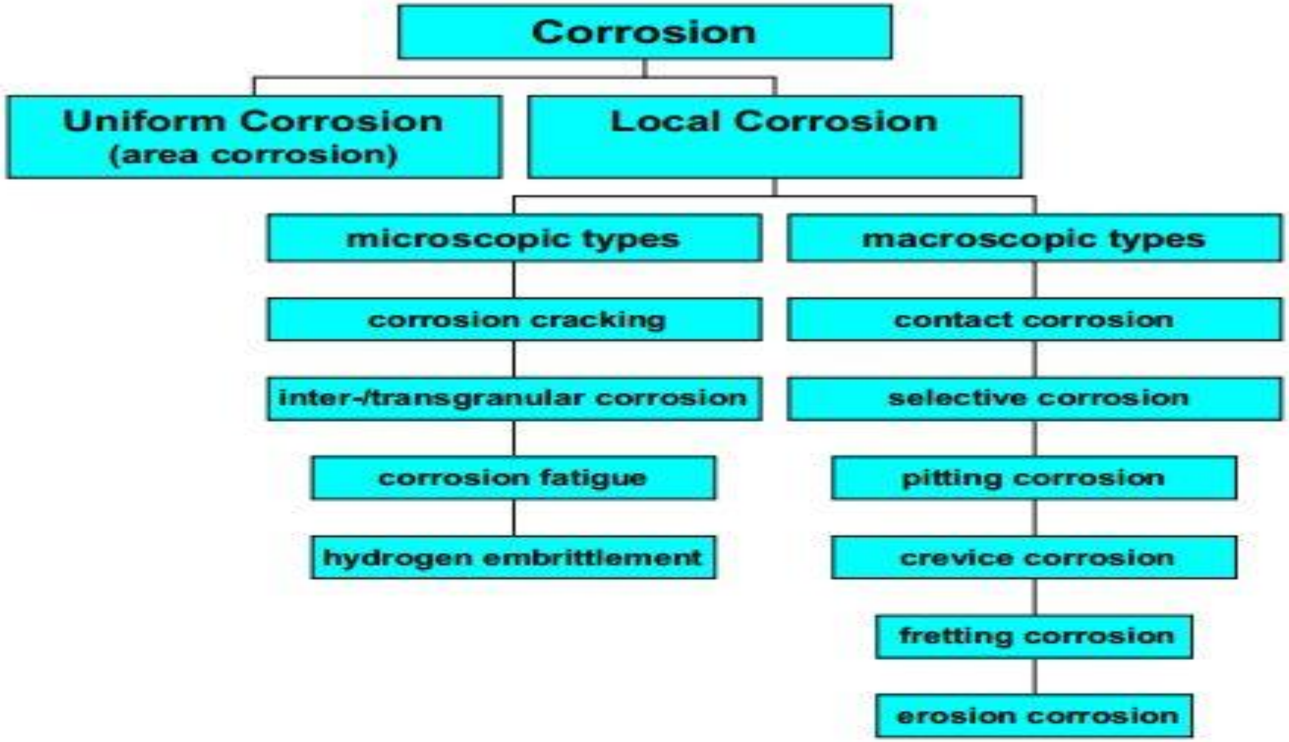
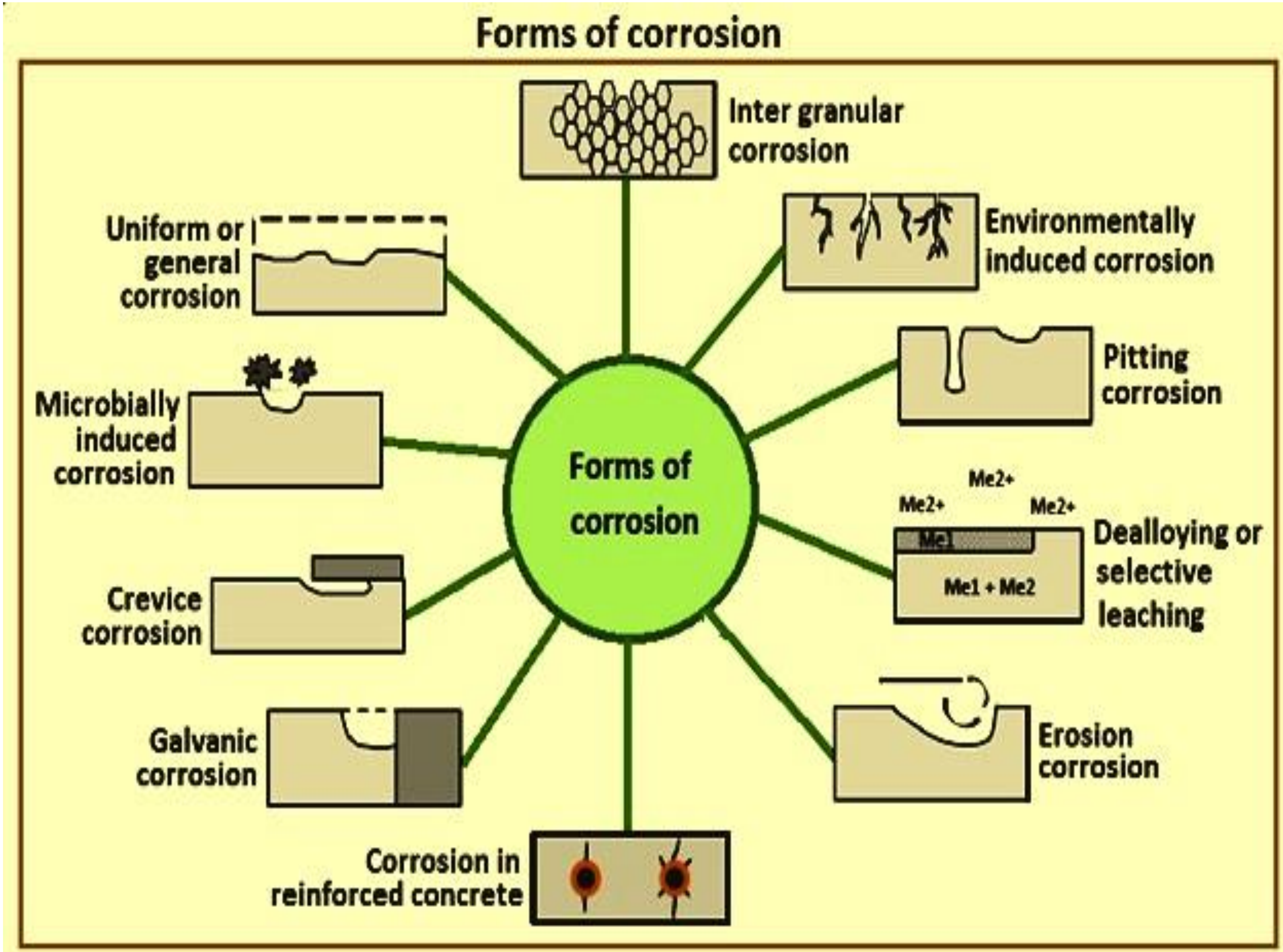


Figure 2. Outline of corrosion types.

8 Forms of Corrosion:

- Uniform
- Pitting
- Crevice Corrosion or Concentration Cell
- Galvanic or Two-Metal
- Stress Corrosion Cracking
- Intergranular
- Dealloying
- Erosion Corrosion

http://www.intercorr.com/failures.html


Forms of corrosion
Inter granular corrosion
Environmentally induced corrosion
Pitting corrosion
Me2+
Me2+
Me2+
Me1
Me1 + Me2
Dealloying or selective leaching
Erosion corrosion
Corrosion in reinforced concrete
Galvanic corrosion
Crevice corrosion
Microbially induced corrosion
Uniform or general corrosion
Forms of corrosion

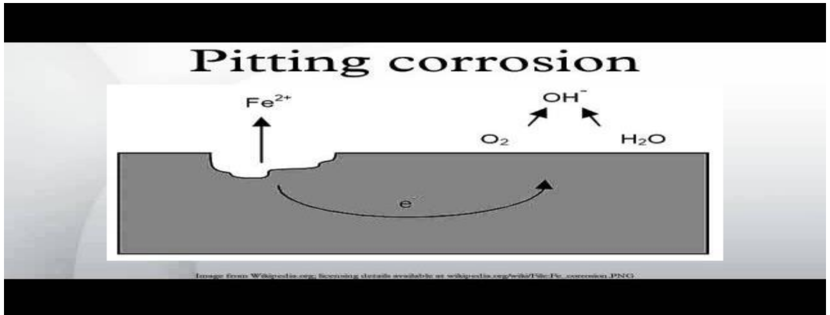
Uniform corrosion

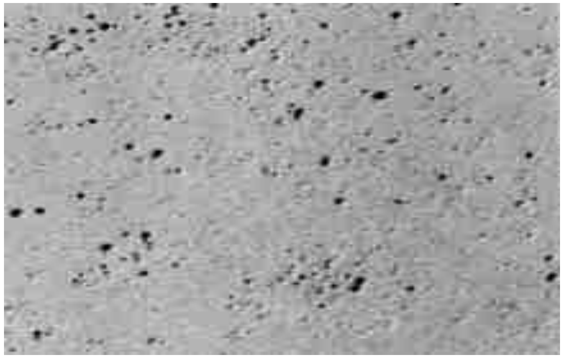
- The **reaction starts at the surface** and proceeds uniformly.


Pitting Corrosion

Pitting corrosion is a **localized type of corrosion that may either be shallow or deep but is often difficult to identify**.

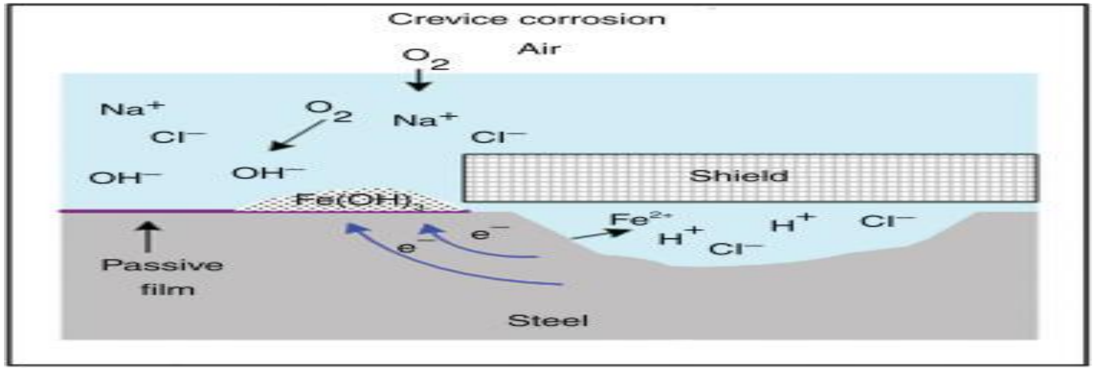
By the **time pitting corrosion is visible to humans, the damage is often extensive**. **Stainless steel** is affected by pitting corrosion rather than uniform corrosion due to the passivation layer.



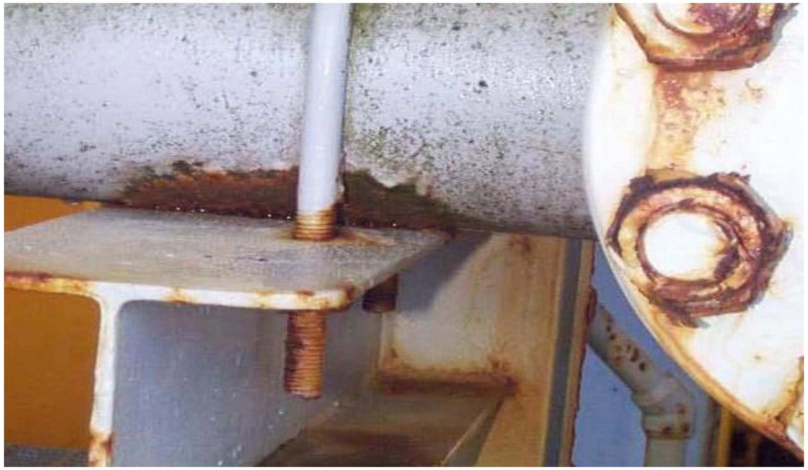


Crevice corrosion

- refers to corrosion occurring in confined **spaces to which the access of the working fluid from the environment is limited**. These spaces are generally called crevices.
- Examples of **crevices** are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles.



Crevice corrosion between pipe and I-beam:



Rubber pads just accelerated the attack – why???

Galvanic Corrosion:

- Possibility when two dissimilar metals are electrically connected in an electrolyte*
- Results from a difference in oxidation potentials of metallic ions between two or more metals. The greater the difference in oxidation potential, the greater the galvanic corrosion.
- Refer to Galvanic Series (Table 13-1)
- The less noble metal will corrode (i.e. **will act as the anode**) and the more noble metal will not corrode (**acts as cathode).**
- Perhaps the best known of all **corrosion** types is galvanic **corrosion**, which occurs at the contact point of two metals or alloys with different electrode potentials.

GALVANIC **SERIES**

Galvanic Series in Seawater (supplements Faraq Table 3.1 , page 65), EIT Review Manual, page 38-2

Tendency to be protected from corrosion, cathodic, more noble end

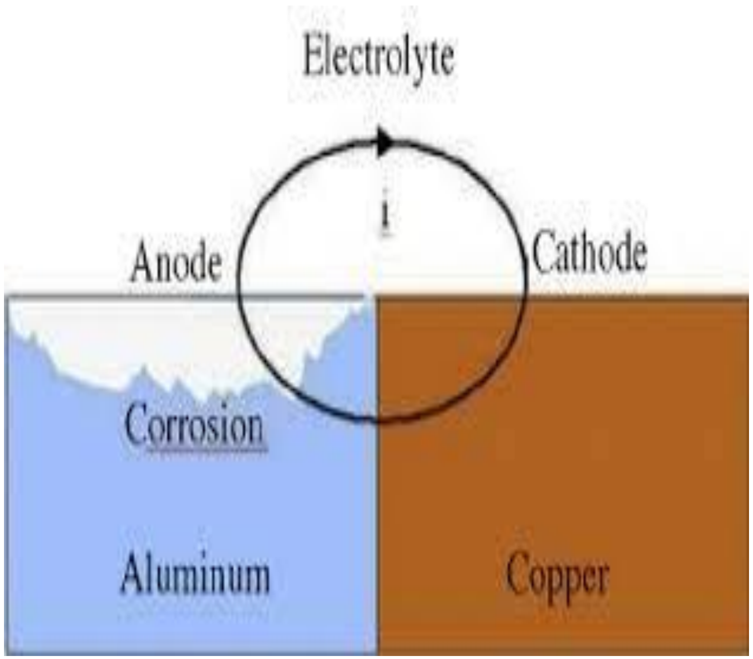
Mercury
Platinum
Gold
Zirconium Graphite
Titanium
Hastelloy C Monel
Stainless Steel (316-passive)
Stainless Steel (304-passive)
Stainless Steel (400-passive)
Nickel (passive oxide)
Silver
Hastelloy 62Ni, 17Cr
Silver solder
Inconel 61Ni, 17Cr
Aluminum (passive Al_20_3)
70/30 copper-nickel
90/10 copper-nickel
Bronze (copper/tin)
Copper
Brass (copper/zinc)
Alum Bronze Admiralty Brass
Nickel
Naval Brass Tin
Lead-tin
Lead
Hastelloy A
Stainless Steel (active)
316 404 430 410
Lead Tin Solder
Cast iron
Low-carbon steel (mild steel)
Manganese Uranium
Aluminum Alloys
Cadmium
Aluminum Zinc
Beryllium
Magnesium

PASSIVE – will not corrode – act as cathode. These elements are least likely to give up electrons!

ACTIVE – will corrode – act as anode. These elements most likely to give up electrons!

Note, positions of ss and al**

Galvanic corrosion of Aluminium



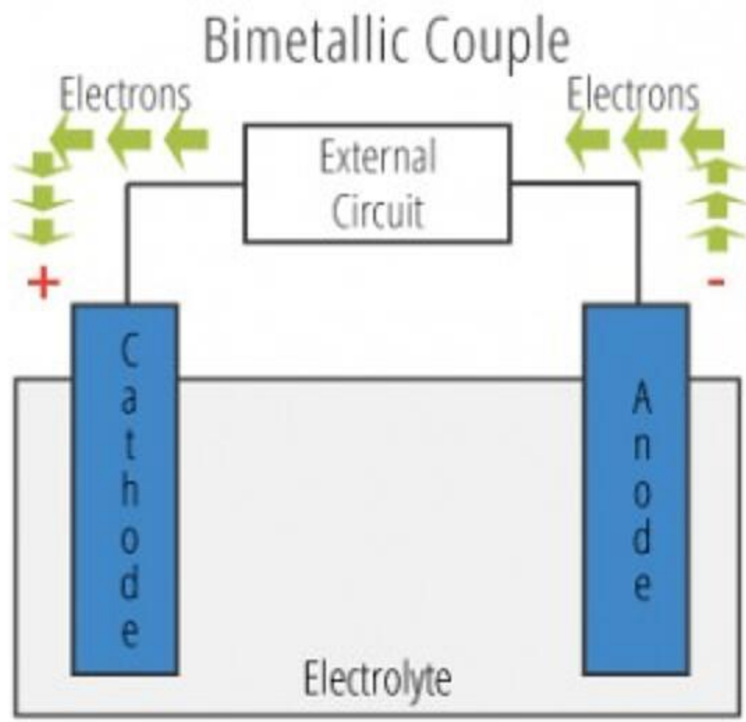


Table 13–1
Galvanic series of some metals in seawater

↑	Magnesium and magnesium alloys
	CB75 aluminum anode alloy
	Zinc
	B605 aluminum anode alloy
	Galvanized steel or galvanized wrought iron
	Aluminum 7072 (cladding alloy)
	Aluminum 5456, 5086, 5052
	Aluminum 3003, 1100, 6061, 356
	Cadmium
Anodic	2117 aluminum rivet alloy
or least	Mild steel
noble	Wrought iron
(active)	Cast iron
	Ni-Resist
	13% chromium stainless steel, type 410 (active)
	50–50 lead tin solder
	18-8 stainless steel, type 304 (active)
	18-8 3% Mo stainless steel, type 316 (active)
	Lead
	Tin
	Muntz metal
	Manganese bronze
	Naval brass (60% copper, 39% zinc)
	Nickel (active)
	78% Ni, 13.5% Cr, 6% Fe (Inconel) (active)
	Yellow brass (65% copper, 35% zinc)
	Admiralty brass
	Aluminum bronze
	Red brass (85% copper, 15% zinc)
	Copper
	Silicon bronze
Cathodic	5% Zn, 20% Ni, 75% Cu
or most	90% Cu, 10% Ni
noble	70% Cu, 30% Ni
(passive)	88% Cu, 2% Zn, 10% Sn (composition G-bronze)
	88% Cu, 3% Zn, 6.5% Sn, 1.5% Pb (composition M-bronze)
	Nickel (passive)
	78% Ni, 13.5% Cr, 6% Fe (Inconel) (passive)
	70% Ni, 30% Cu
	18-8 stainless steel type 304 (passive)
	18-8 3% Mo stainless steel, type 316 (passive)
	Hastelloy C
	Titanium
	Graphite
	Gold
↓	Platinum

Source: F. L. LeQue, *Introduction to Corrosion,* National Association of Corrosion Engineers, Houston, TX, 1970, p. 27.

Galvanic Series:

Questions:

1. Worst combination?
2. Aluminum and steel?
3. Titanium and Zinc?
4. Stainless Steel and Copper?
5. Mild steel and cast iron?

Show Demo!

Galvanic Corrosion Potentials:

Figure 1 illustrates the idea of an electro-chemical reaction. **If a metal is placed in a conducting solution like salt water**, it dissociates into ions, releasing electrons, as the iron is shown doing in the figure, via the *ionization reaction*

$$Fe \leftrightarrow Fe^{++} + 2e^{-}$$

The electrons accumulate on the iron giving it a **negative charge that grows until the electrostati**c attraction starts to pull the Fe^{++} ions back onto the metal surface, stifling further dissociation. At this point the iron has a potential (relative to a standard, the *hydrogen standard*) of –0.44 volts.

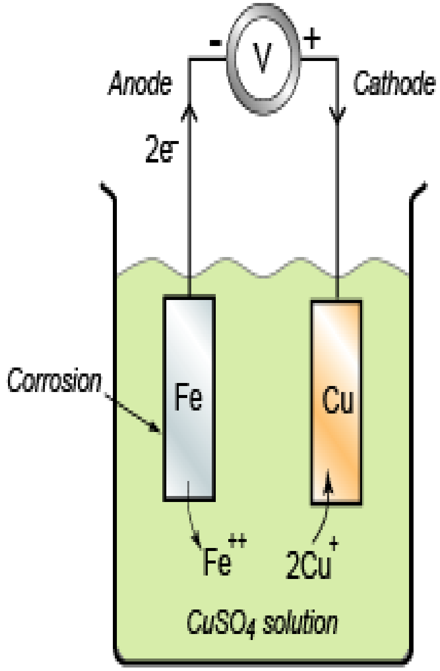


Figure 1. A bi-metal corrosion cell. The corrosion potential is the potential to which the metal falls relative to a hydrogen standard.

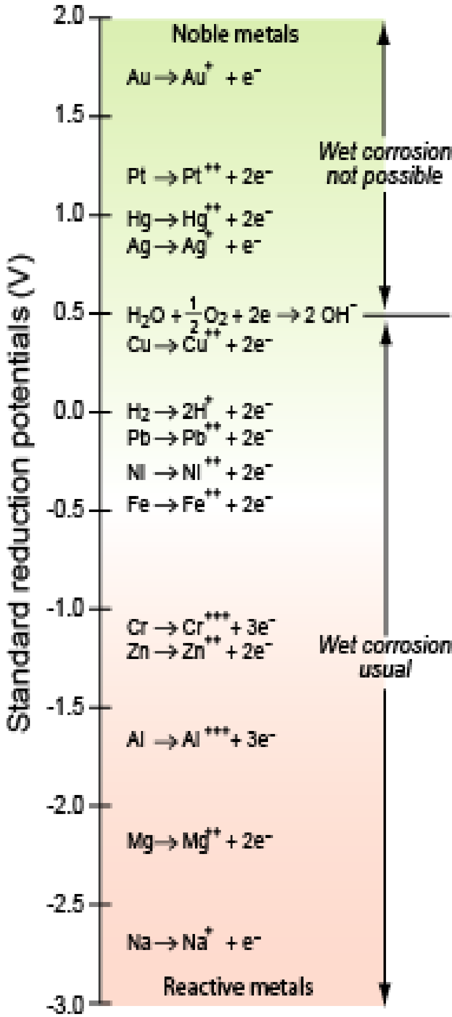
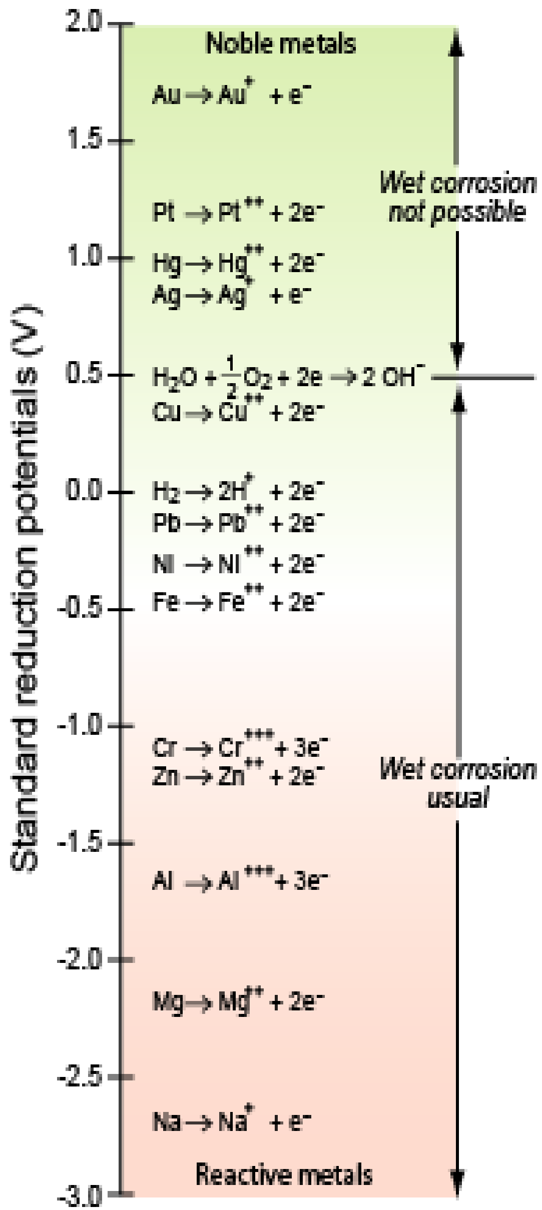


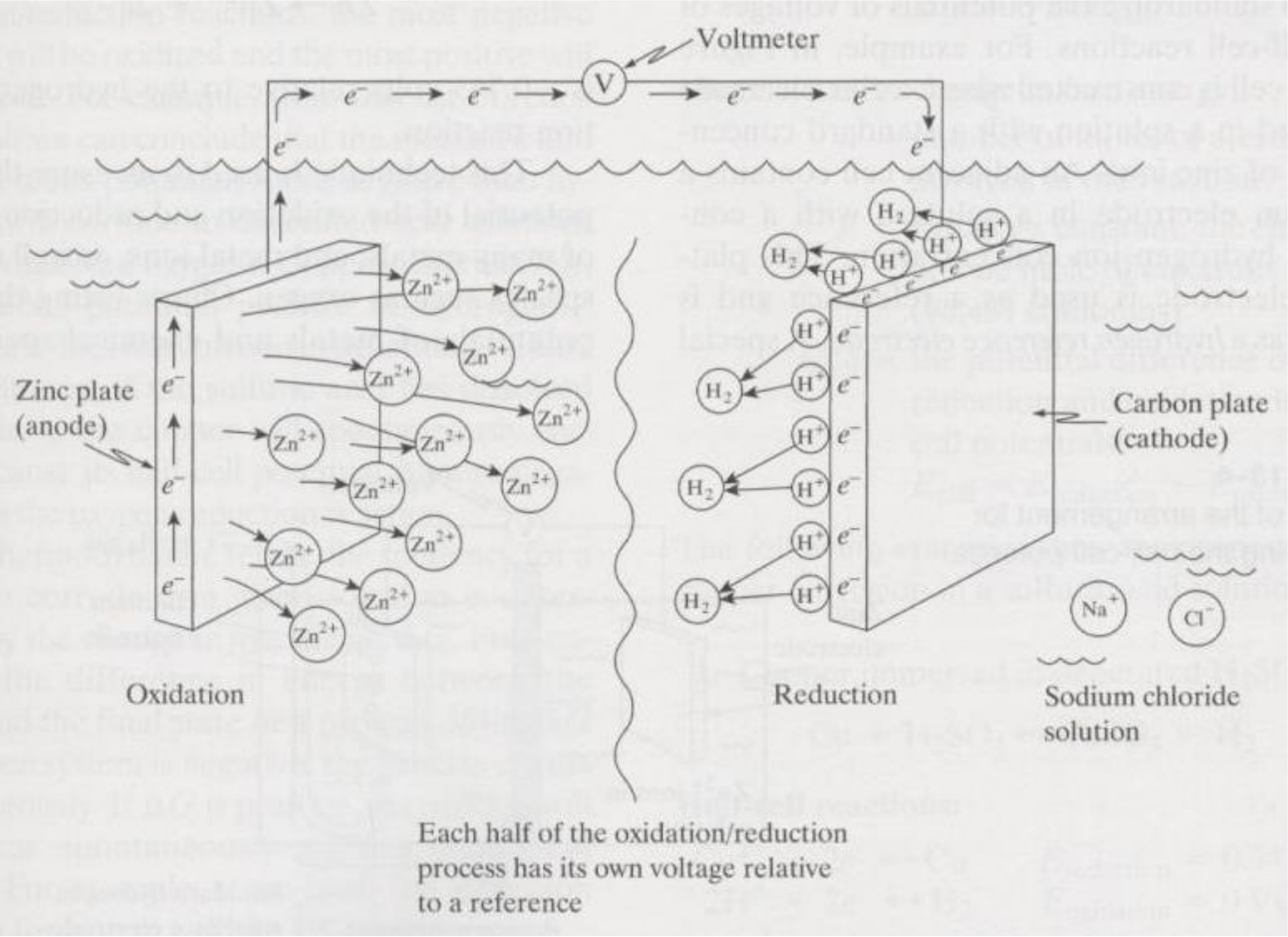
Figure 2. Standard reduction potentials of metals.

. **Each metal has its own characteristic corrosion potential (called the standard reduction potential**), as plotted in Figure 2. **If two metals are connected together in a cell, like the iron and copper samples in Figure 1**, a potential difference equal to their separation on Figure 2 appears between them.

The corrosion potential of iron, -0.44, differs from that of **copper, +0.34** , by 0.78 volts, so if no current flows in the connection the voltmeter will register this



Liquid Cell Battery:

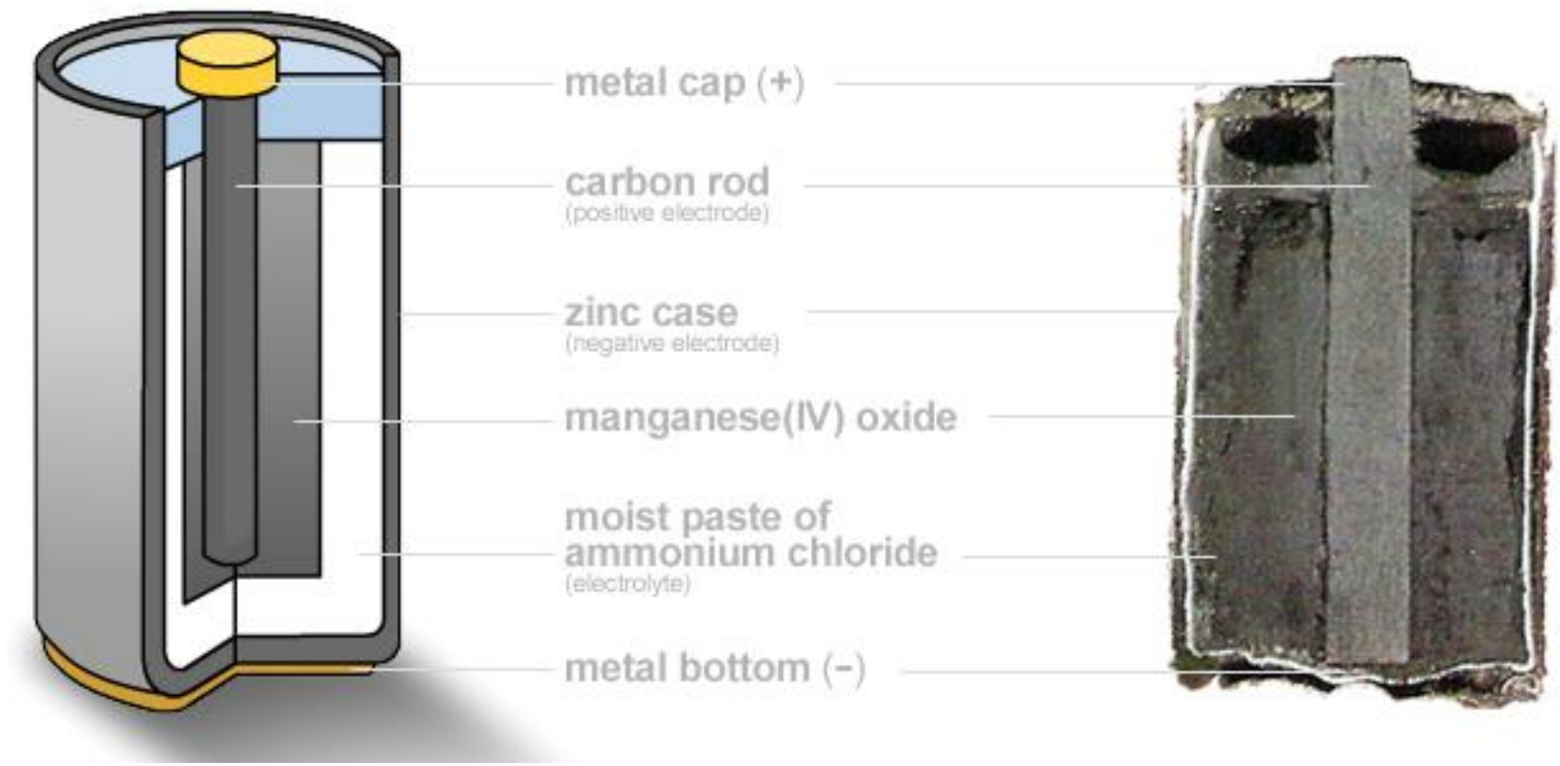


dry cell is a galvanic electrochemical cell with a pasty low-moisture electrolyte. A wet cell, on the other hand, is a cell with a liquid electrolyte, such as the lead-acid batteries in most cars

Dry Cell - Zinc-carbon battery

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$ - oxidation reaction that happens at zinc = anode

$2MnO_2(s) + 2\ H^+(aq) + 2\ e^- \rightarrow Mn_2O_3(s) + H_2O(l)$ - reduction reaction at carbon rod = cathode



Stress Corrosion Cracking:

- **Spontaneous corrosion** induced **cracking of a material under static (or residual) *tensile* stress.**

- **Environmentally assisted cracking (EAC**), other forms:
  - Hydrogen embrittlement
  - Caustic embrittlement
  - Liquid metal corrosion

Stress Corrosion Cracking:

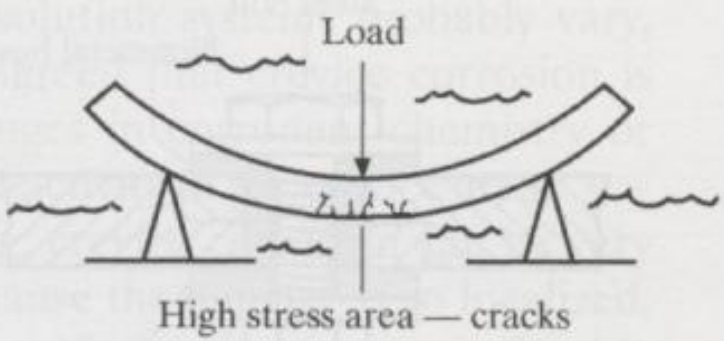
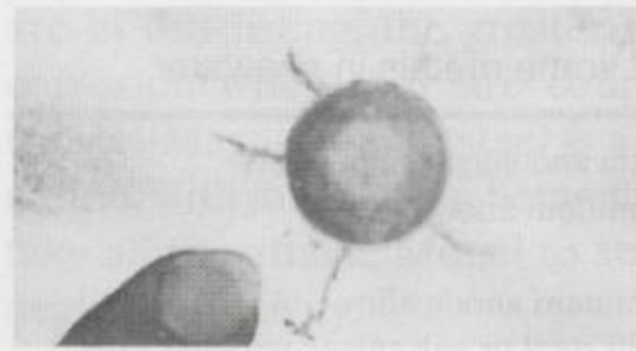


Figure 13–16
Stress corrosion cracking of stainless steel



See handout, review HO hydron!

Factors:

- **Must consider metal and environment**.
- What to watch for:
  - **Stainless steels** at elevated temperature in chloride solutions.
  - **Steels** in caustic solutions
  - **Aluminum** in chloride solutions
- 3 Requirements for SCC:
  1. Susceptible alloy
  2. Corrosive environment
  3. High tensile stress or residual stress

Design for Stress Corrosion Cracking:

- Material selection for a given environment (Table 13-2).
- Reduce applied or residual stress - Stress relieve to eliminate residual stress (i.e. stress relieve after heat treat).
- Introduce residual compressive stress in the service.
- Use corrosion alloy inhibitors.
- **Apply protective coatings**.

Intergranular Attack:

- **Corrosion** which occurs preferentially at grain boundries.
- Why at grain boundries?
  - Higher energy areas which may be more anodic than the grains.
  - **The alloy** chemistry might make the grain boundaries dissimilar to the grains.
  - **The grain** can act as the cathode and material surrounding it the anode.

Intergranular Attack:

- How to recognize it?
  - Near surface
  - Corrosion only at grain boundries (note if only a few gb are attacked probably pitting)
  - Corrosion normally at uniform depth for all grains.

Example-1: Intergranular Attack:

- **Sensitization of stainless steels**:
  - Heating up of **austenitic stainless steel**(*alloy of iron, usually containing at least 8 per cent of nickel and 18 per cent of chromium,)* (750 to 1600 F) causes chromuim carbide to form in the grains. **Chromuim is therefore depleted near the grain boundries** causing the material in this area to essentially act like a low-alloy steel which is anodic to the chromium rich grains.
  - **Preferential Intergranular Corrosion** will occur parallel to the grain boundary – eventually grain boundary will simply fall out!!

Intergranular Attack:

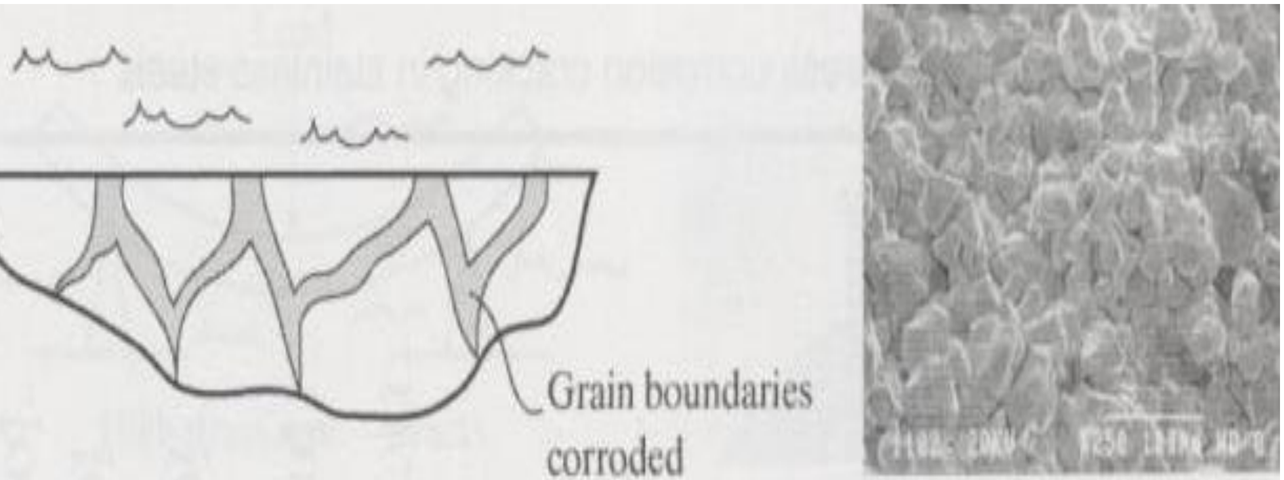


Figure 13–17

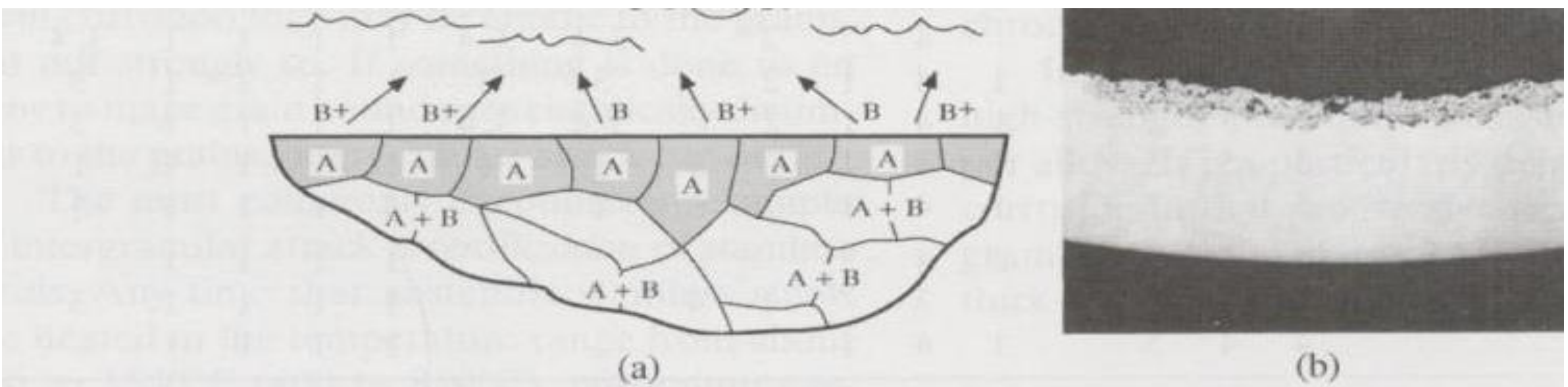
Scanning electron photomicrograph of intergranular corrosion on the surface of sensitized austenitic stainless steel. Improper annealing caused the sensitization. Note the gaps between the grain boundaries. The corrodent dissolved the material adjacent to the grain boundaries allowing the grains to fall out of the surface. ASTM A 262 describes susceptibility tests (×250 original magnification).

Example 2: Intergranular Attack:

- **Exfoliation of high strength Aluminum alloys**.
  - **Corrosion** that preferentially attracts the elongated grains of rolled aluminum.
  - Corroded grains usually near surface
  - **Grain swells** due to **increase in volume** which causes drastic separation to occur in a pealing fashion.

Dealloying:

- When one element in an alloy is anodic to the other element.
- Example: Removal of zinc from brass (called dezincification) leaves spongy, weak brass.
- Brass alloy of zinc and copper and zinc is anodic to copper (see galvanic series).

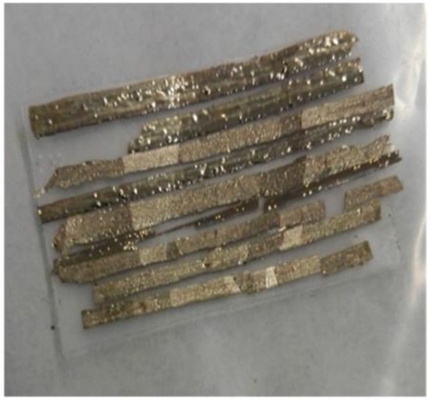


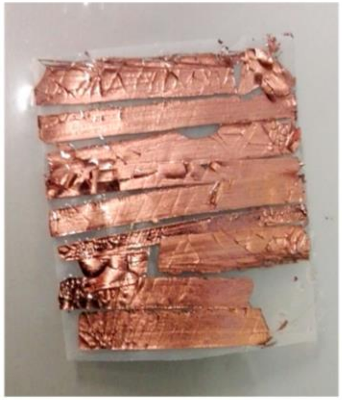
igure 13–18
) Dealloying in the form of dezincification of a brass part; zinc has been removed from e surface, which leaves weak copper, (b) (×40)

Dealloying:

- **1.** **Dezincification** – preferential removal of **zinc** in brass
  - Try to limit Zinc to 15% or less and add 1% tin.
  - Cathodic protection

2. **Graphitization** – preferential **removal** of Fe in Cast Iron leaving graphite (C).

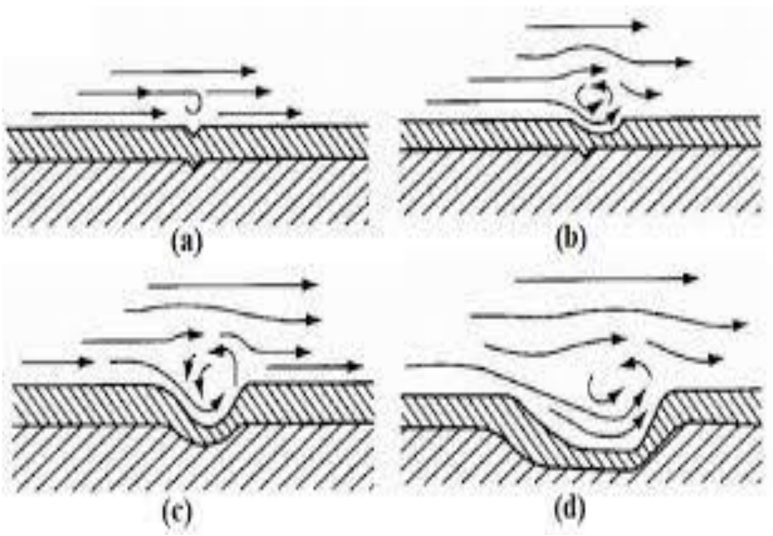




Examples of the external aspect of the Cu-Mg-Ca ribbons before and after chemical dealloying in 0.04 M H_2SO_4 for 30 min

Erosion:

- **Forms of Erosion:**
- **Erosion is the movement of particles away from their source. Errosion of metal is the gradual wearing away of a metal surface by a combination of both corrosion and abrasion from an impinging water stream**, such that the higher the velocity of the impinging stream, the greater the rate of erosion corrosion.
  - 1. Liquid Impingement
  - 2. Liquid erosion
  - 3. Slurry Erosion
  - 4. Cavitation



Methods to Control Corrosion

There are five methods to control corrosion:

- material selection
- coatings
- changing the environment
- changing the potential
- design

How to avoid (or control) Corrosion?

- **Material Selection**! Remember – environment key. Look at potential pH diagrams!!!
- Eliminate any one of the 4 req'ments for corrosion!
- **Galvanic** - Avoid using dissimilar metals.
  - Or close together as possible
  - Or electrically isolate one from the other
  - Or MAKE ANODE BIG!!!

How to avoid (or control) Corrosion?

- **Pitting/Crevice**: Watch for stagnate water/ electrolyte.
  - Use gaskets
  - Use good welding practices
- **Intergranular –** watch grain size, environment, temperature, etc.. Careful with Stainless Steels and AL.

How to avoid (or control) Corrosion?

- **Consider organic coating** (paint, ceramic, chrome, etc.) – DANGER IF IT GETS SCRACTHED!!

- OR BETTER YET, **consider cathodic protection**:
  - such as **zinc** (or galvanized) plating on steel
  - **Mg** sacrificial anode on steel boat hull

Corrosion Control:

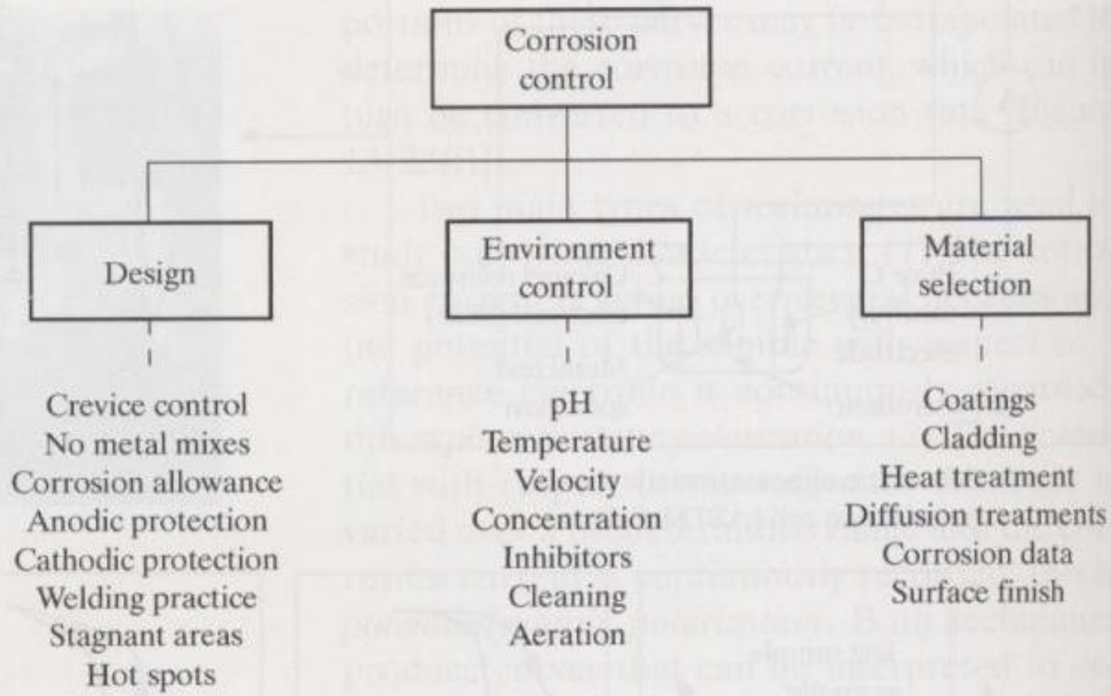


Figure 13–24
Techniques for corrosion control

Anodic Protection – Zinc coating of steel. KNOW HOW THIS WORKS!!

Surface Treatment (Coatings)

1. Organic paints

2. Chromating and phosphating:

- The Process - **chromating and phosphating are surface-coating processes** that enhance the corrosion resistance of metals.
- **Both** involve soaking the component in a heated bath based on chromic or phosphoric acids.
- The **acid reacts with the surface**, dissolving some of the surface metal and **depositing a thin protective layer of complex chromium or phosphorous compounds**

3. Anodizing (aluminum, titanium)

- The Process - **Aluminum is a reactive metal**, yet in everyday objects it does not corrode or discolor.
- That is because of a **thin oxide film - Al2O3** - that forms spontaneously on its surface, and this film, though invisible, **is highly protective.**
- The film can be thickened and its structure controlled by the process of anodizing.
- **The process is electrolytic;** the electrolyte, typically, is dilute (15%) sulfuric acid.
- **Anodizing** is most generally applied to
- , but magnesium, titanium, zirconium and zinc can all be treated in this way.
- The **oxide formed by anodizing is hard**, abrasion resistant and resists corrosion well.
- The film-surface is micro-porous, allowing it to absorb dyes, giving metallic reflectivity with an attractive gold, viridian, azure or rose-colored sheen; and it can be patterned.
- **The process is cheap**, an imparts both corrosion and wear resistance to the surface.

Surface Treatment (Coatings)

1. **Electro-plating**
   - The Process -Metal coating process wherein a thin metallic coat is deposited on the workpiece by means of an ionized electrolytic solution.
   - **The workpiece (cathode)** and the **metallizing source material (anode)** are **submerged in the solution** where a direct electrical current causes the **metallic ions to migrate** from the source material to the workpiece.
   - The **workpiece** and **source** metal are suspended in the ionized electrolytic solution by insulated rods.

Reasons for Plating :

- Thorough surface cleaning precedes the plating operation.
- **Plating is carried out for many reasons**:
- corrosion resistance,
- improved appearance,
- wear resistance,
- higher electrical conductivity,
- better electrical contact,
- greater surface smoothness and better light reflectance.

2. Bluing

- **Bluing** is a passivation process in which steel is partially protected against rust, and is named after the blue-black appearance of the resulting protective finish.
- True **gun bluing** is an electrochemical conversion coating resulting from an oxidizing chemical reaction with iron on the surface selectively forming magnetite (Fe_3O_4), the **black oxide of iron, which occupies the same volume as normal iron.**
- Done for bolts called "blackening"

3. Hot-dip Coating (i.e. galvanizing)

- Hot dipping is a process for **coating a metal, mainly ferrous metals,** with low melting point metals usually **zinc and its alloys**.
- The component is **first degreased in a caustic bath**, then **pickled (to remove rust and scale) in a sulfuric acid bath**, immersed (dipped) in the liquid metal and, after **lifting out**, it is **cooled in a cold air stream**.
- The **molten metal alloys** with the surface of the component, **forming a continuous thin coating**.
- When the **coating is zinc** and the **component is steel**, the process is known as **galvanizing.**
- **The process is very versatile** and can be applied to components of any shape, and sizes up to 30 m x 2 m x 4 m.
- The **cost** is comparable with that of **painting**, but the **protection offered by galvanizing is much greater**, because if the coating is scratched it is the **zinc** not the **underlying steel** that corrodes ("galvanic protection").
- **Properly galvanized** steel will survive outdoors for **30-40 years without further treatment.**

Material Selection:

- **Importance of Oxide films**
- The fundamental **resistance of stainless steel to corrosion** occurs because of its **ability to form an oxide protective coating on its surface.**
- This **thin coating is invisible**, but generally **protects the steel in oxidizing environments** (air and nitric acid).
- However, this **film loses its protectiveness** in environments such as **hydrochloric acid and chlorides**.
- **In stainless steels**, lack of oxygen also ruins the corrosion protective oxide film, therefore these debris ridden or stagnant regions are susceptible to corrosion.

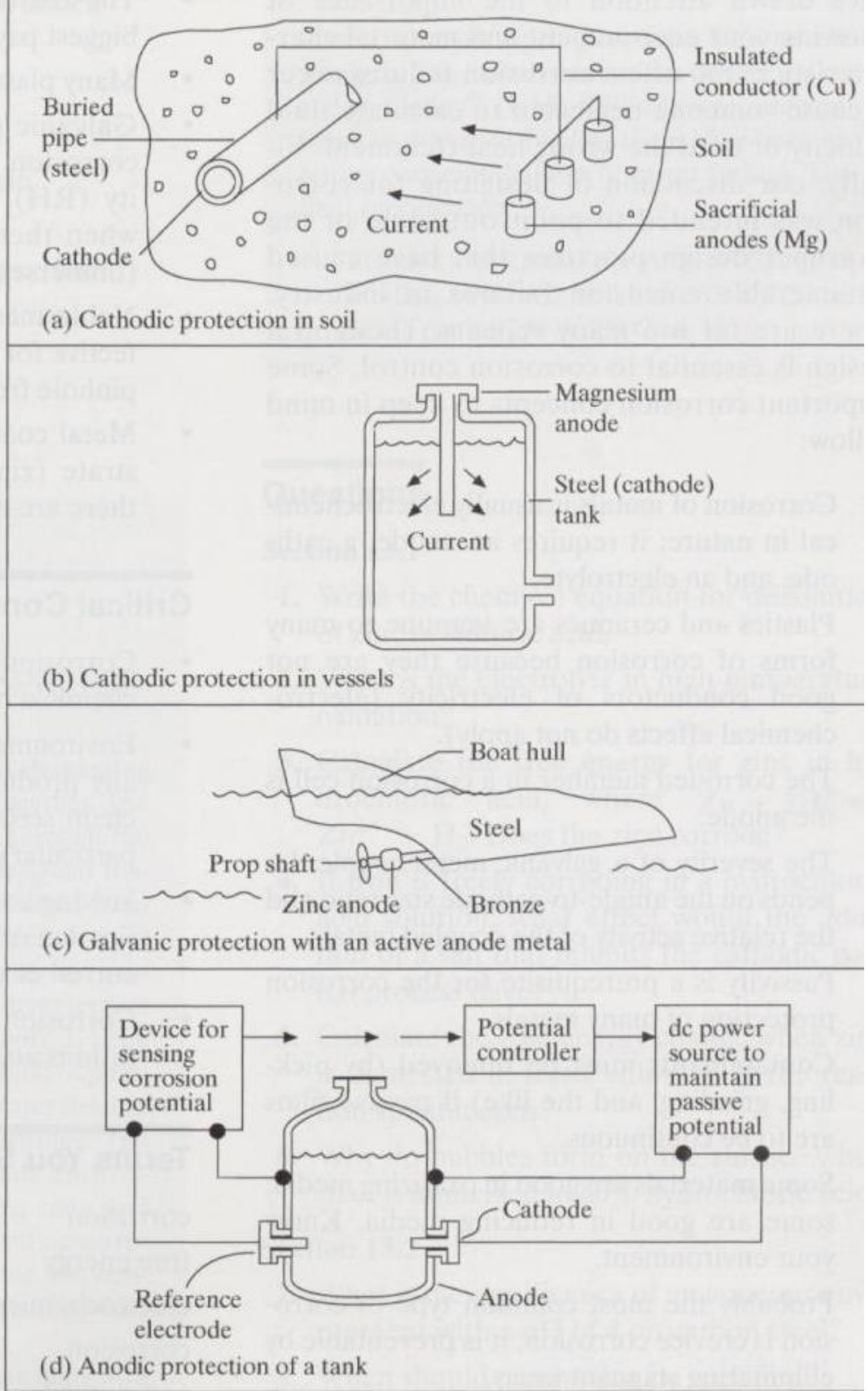
Cathodic Protection (CP)

- **Cathodic protection** (**CP**)
- Is a technique to control the corrosion of a metal surface by making it work as a cathode of an electrochemical cell.
- This is achieved by placing in contact with the **metal to be protected another more easily corroded metal** to act as the anode of the electrochemical cell.
- **Cathodic protection** systems are most commonly used to protect steel, water or fuel pipelines and storage tanks, steel pier piles, ships, offshore oil platforms and onshore oil well casings.

- Types of CP:
  - **1. Galvanic or sacrificial anodes** – zinc, magnesium or aluminum.
  - The sacrificial anodes are more active (**more negative potential)** than the metal of the structure they're designed to protect.
  - The **anode pushes the potential of the steel structure more negative** and therefore the **driving force for corrosion halts**.
  - **The anode continues to corrode until it requires replacement**,

2. Impressed current CP – done for large structures (pipes, offshore platforms, etc) where a galvanic (or sacrificial) anode can not economically deliver enough current.

  - **Galvanized steel** (see above slide) – again, **steel is coated with zinc** and if the **zinc coating is scratched** and steel exposed, the surrounding areas of **zinc coating form a galvanic cell with the exposed steel** and protects in from corroding.
  - The **zinc coating acts as a sacrificial anode**.



See Exxon Mobil example

Aluminium anodes mounted on a steel jacket structure – using galvanic corrosion for corrosion control! Called cathodic protection (aka sacrificial anode)

Effects of corrosion

Losses are economic and safety:

- Reduced Strength
- Downtime of equipment
- Escape of fluids
- Lost surface properties
- Reduced value of goods

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal.

Failures of **various kinds and the need for expensive replacements** may occur even though the amount of metal destroyed is quite small.

Underground corrosion

Buried gas or water supply pipes can suffer severe corrosion which is not detected until an actual leakage occurs, by which time considerable damage may be done.

Electronic components

In electronic equipment it is very important that there should be no raised resistance at low current connections. Corrosion products can cause such damage and can also have sufficient conductance to cause short circuits. These resistors form part of a radar installation.

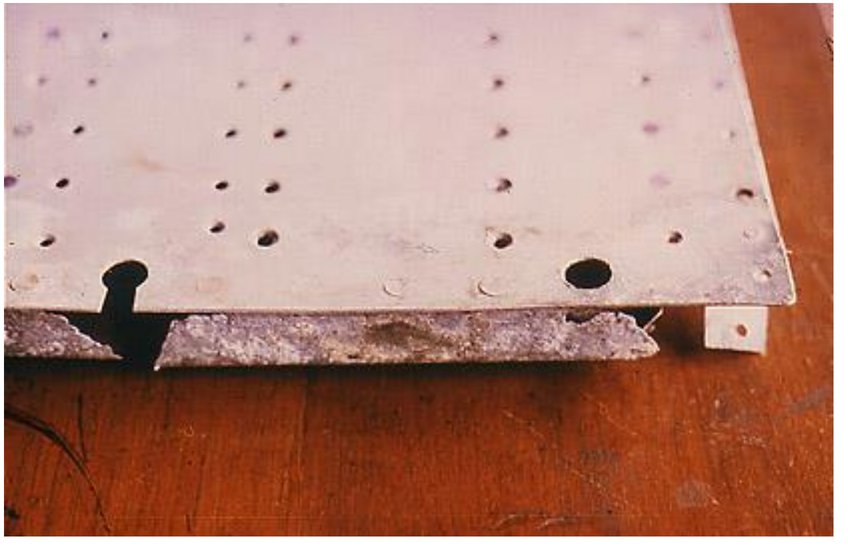
Corrosion influenced by flow-1

The cast iron pump impeller shown here suffered attack when acid accidentally entered the water that was being pumped. The high velocities in the pump accentuated the corrosion damage.

Corrosion influenced by flow – 2

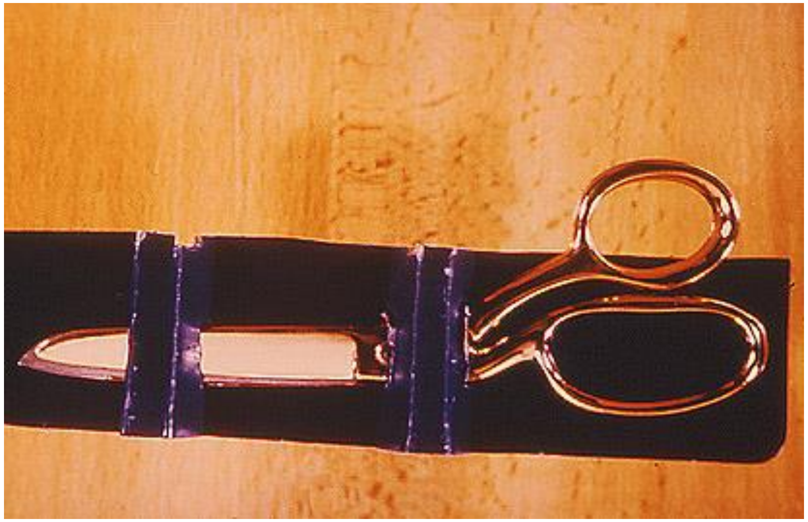
This is a bend in a copper pipe-work cooling system. Water flowed around the bend and then became turbulent at a roughly cut edge. Downstream of this edge two dark corrosion pits may be seen, and one pit is revealed in section.

Safety of aircraft



The lower edge of this aircraft skin panel has suffered corrosion due to leakage and spillage from a wash basin in the toilet. Any failure of a structural component of an aircraft can lead to the most serious results.

Influence of corrosion on value



A very slight amount of corrosion may not interfere with the usefulness of an article, but can affect its commercial value. At the points where these scissors were held into their plastic case some surface corrosion has occurred which would mean that the shop would have to sell them at a reduced price.

Motor vehicle corrosion and safety

The safety problems associated with corrosion of motor vehicles is illustrated by the holes around the filler pipe of this petrol tank. The danger of petrol leakage is obvious. Mud and dirt thrown up from the road can retain salt and water for prolonged periods, forming a corrosive "poultice".

Corrosion at sea

Sea water is a highly corrosive electrolyte towards mild steel. This ship has suffered severe damage in the areas which are most buffeted by waves, where the protective coating of paint has been largely removed by mechanical action.

Aluminium Corrosion

The current trend for aluminium vehicles is not without problems. This aluminium alloy chassis member shows very advanced corrosion due to contact with road salt from gritting operations or use in coastal / beach regions.

Damage due to pressure of expanding rust

The **iron reinforcing rods in this garden fence post** have been set too close to the surface of the concrete.

A small amount of corrosion leads to bulky rust formation which exerts a pressure and causes the concrete to crack.

For structural engineering applications all reinforcing metal should be covered by 50 to 75 mm of concrete.

“Corrosion” of plastics

Not only metals suffer “corrosion” effects. This dished end of a vessel is made of glass fibre reinforced PVC. Due to internal stresses and an aggressive environment it has suffered “environmental stress cracking”.

Galvanic corrosion

This rainwater guttering is made of aluminium and would normally resist corrosion well. Someone tied a copper aerial wire around it, and the localised bimetallic cell led to a “knife-cut” effect.

Galvanic corrosion

The tubing, shown here was part of an aircraft's hydraulic system. The material is an aluminium alloy and to prevent bimetallic galvanic corrosion due to contact with the copper alloy retaining nut this was cadmium plated. The plating was not applied to an adequate thickness and pitting corrosion resulted.

Corrosion prevention

Corrosion prevention

Treatment of metal
- Surface coating - zinc, tin, plastic, paint, phosphate
- Alloy - stainless steel

Treatment of environment
- Removal of oxygen
- Control of pH
- Inhibitors

Change of potential
- Cathodic protection
- Anodic protection