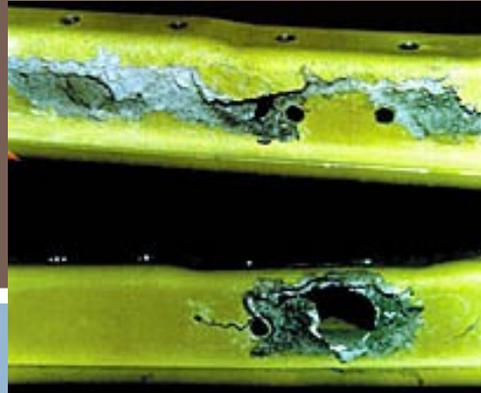


CORROSION





CORROSION



CORROSION AND DEGRADATION OF MATERIALS

3

□ Cost of Corrosion

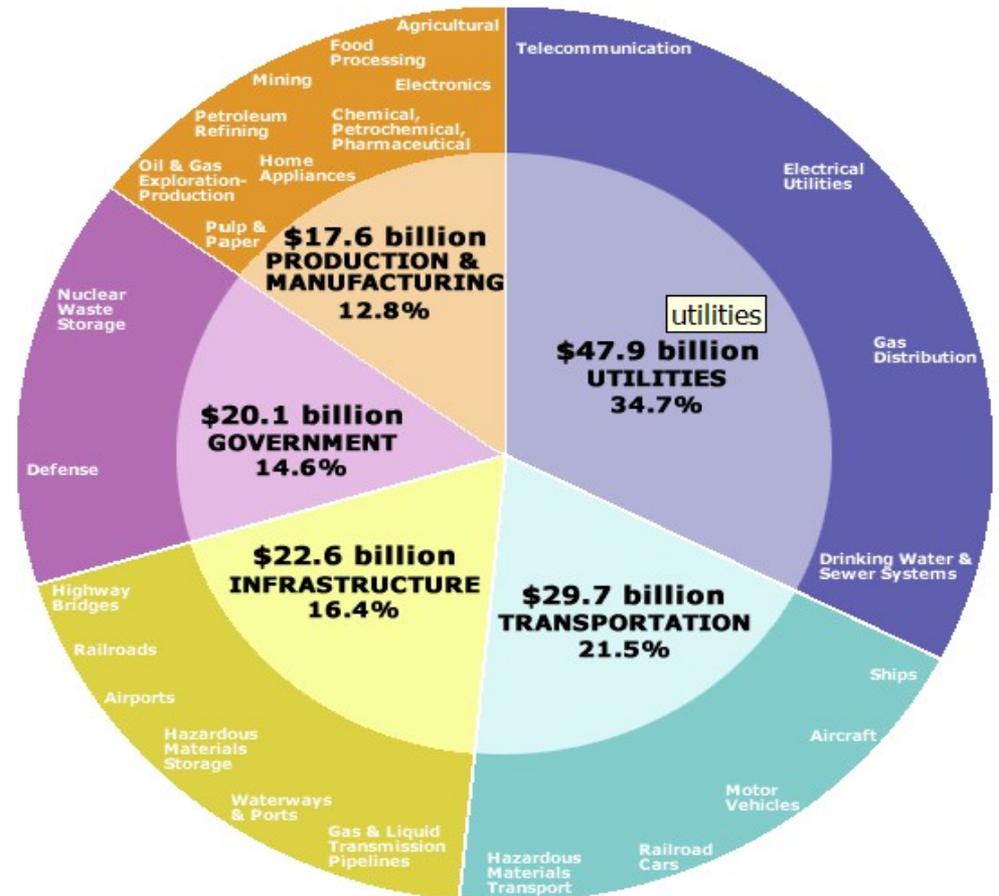
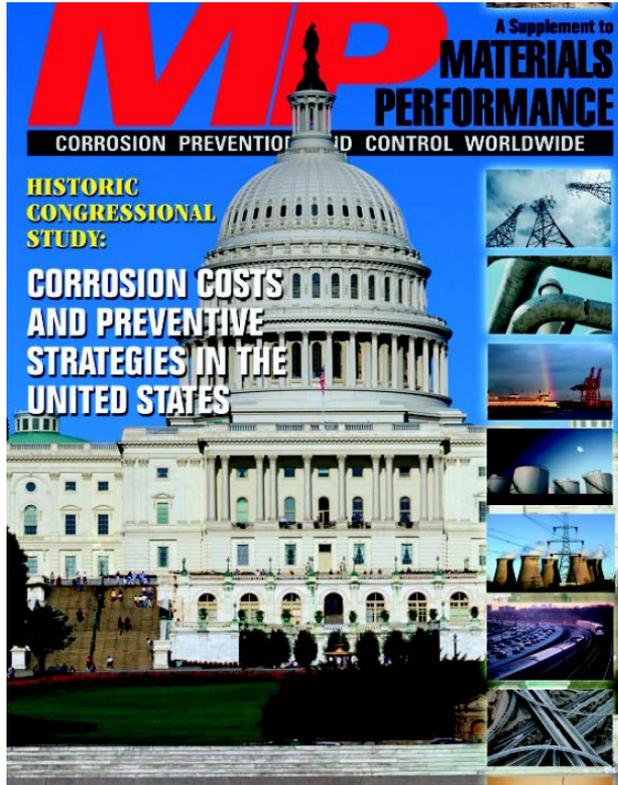
- Fundamentals of Corrosion
- Electrochemical reactions
- EMF and Galvanic Series
- Concentration and Temperature (Nernst)
- Corrosion rate
- Corrosion prediction (likelihood)
- Polarization
- Protection Methods

A heavy-duty metal chain with a large padlock is shown on a dark, textured surface. The chain and padlock are heavily rusted, with a reddish-brown patina covering most of their surfaces. The background is a dark, mottled grey with some lighter brown spots, suggesting a weathered metal or concrete surface. The lighting is dramatic, casting deep shadows and highlighting the texture of the rust and the metallic links.

What is the....

ost of Corrosio

The Cost of Corrosion



FHWA funds Cost of Corrosion Study.
Total Direct Cost of Corrosion in Analyzed Sectors: \$137.9 billion/year (1998).
Extrapolated to U.S. Economy; Cost of Corrosion is \$275.7 billion/year (1998).

THE CONSEQUENCES OF CORROSION

- 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.

❑ Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localised zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.

❑ Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).

❑ Reduced value of goods due to deterioration of appearance.

❑ Contamination of fluids in vessels and pipes).

- ❑ Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations.
- ❑ Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.

- ❑ Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

Significance of Corrosion on Infrastructure





Engineer finds corrosion in collapsed bridge at North Carolina speedway (2000)





A Concrete bridge failure



WHAT IS 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. The most widely used metal is iron (usually as steel)

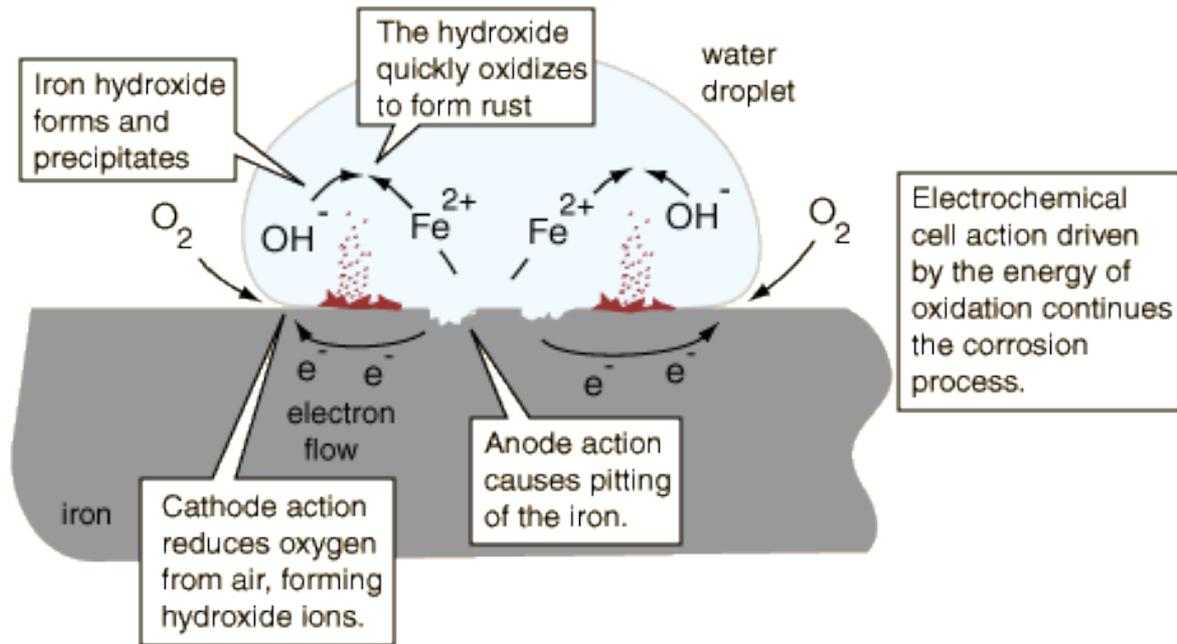
Fundamental Components

- **Corrosion** can be defined as the deterioration of material by reaction to its environment.
- Corrosion occurs because of the natural tendency for most metals to return to their natural state; e.g., iron in the presence of moist air will revert to its natural state, iron oxide.
- **4 required components** in an electrochemical corrosion cell: 1) An **anode**; 2) A **cathode**; 3) A conducting environment for ionic movement (**electrolyte**); 4) An **electrical connection** between the anode and cathode for the flow of electron current.
- If any of the above components is missing or disabled, the electrochemical corrosion process will be stopped.

CHEMISTRY OF CORROSION

Virtually all corrosion reactions are **electrochemical in nature**, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the **anodic reaction**. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a **cathodic reaction** is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal.

Mechanism of corrosion





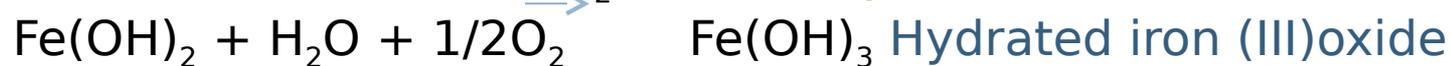
The corroding piece of metal is described as a “mixed electrode” because simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

Electrochemical reactions

Anodic reaction



Cathodic reaction



Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements which are present.

TYPES OF CORROSION

ELECTROCHEMICAL CORROSION

HIGH TEMPERATURE CORROSION

GENERAL SURFACE CORROSION

PITTING CORROSION.

CONCENTRATION CELL CORROSION.

Metal Ion Concentration Cells.

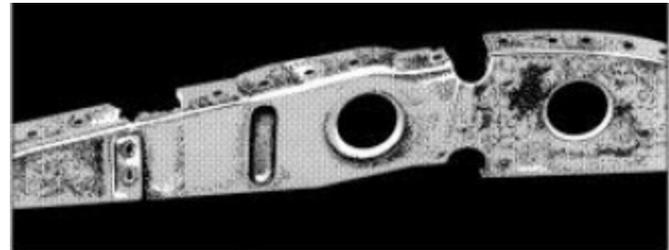
Oxygen Concentration Cells.

GALVANIC CORROSION.

STRESS CORROSION CRACKING

1. GENERAL SURFACE CORROSION

General surface corrosion (also referred to as **Uniform Etch or Uniform Attack Corrosion**) is the most common form of corrosion and results from a direct chemical attack on a metal surface and involves only the metal surface. General surface corrosion usually occurs over a wide area and is more or less equal in dispersion. On a polished surface, this type of corrosion is first seen as a general dulling of the surface, and if allowed to continue, the surface becomes very rough



Uniform Corrosion

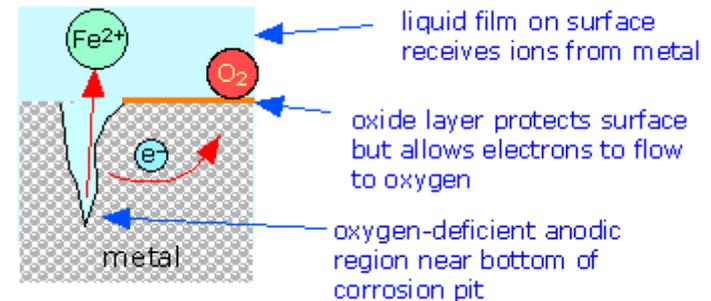
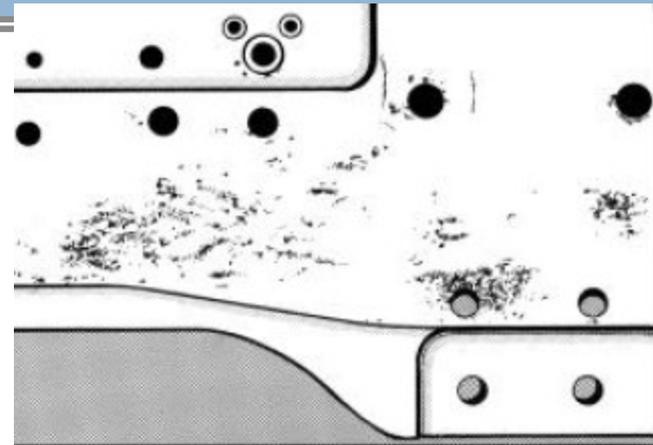
22



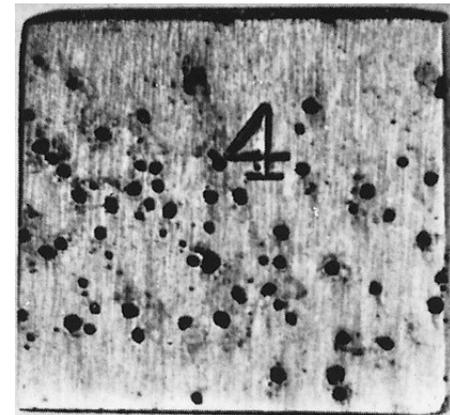
Formerly a ship

2. PITTING CORROSION.

Pitting corrosion is one of the most **destructive and intense** forms of corrosion. It can occur in any metal but is most common on metals that form protective oxide films, such as aluminum and magnesium alloys. It is first noticeable as a white or gray powdery deposit, similar to dust, which blotches the surface. When the deposit is cleaned away, tiny holes or pits can be seen in the surface. These small surface openings may penetrate deeply into structural members and cause damage



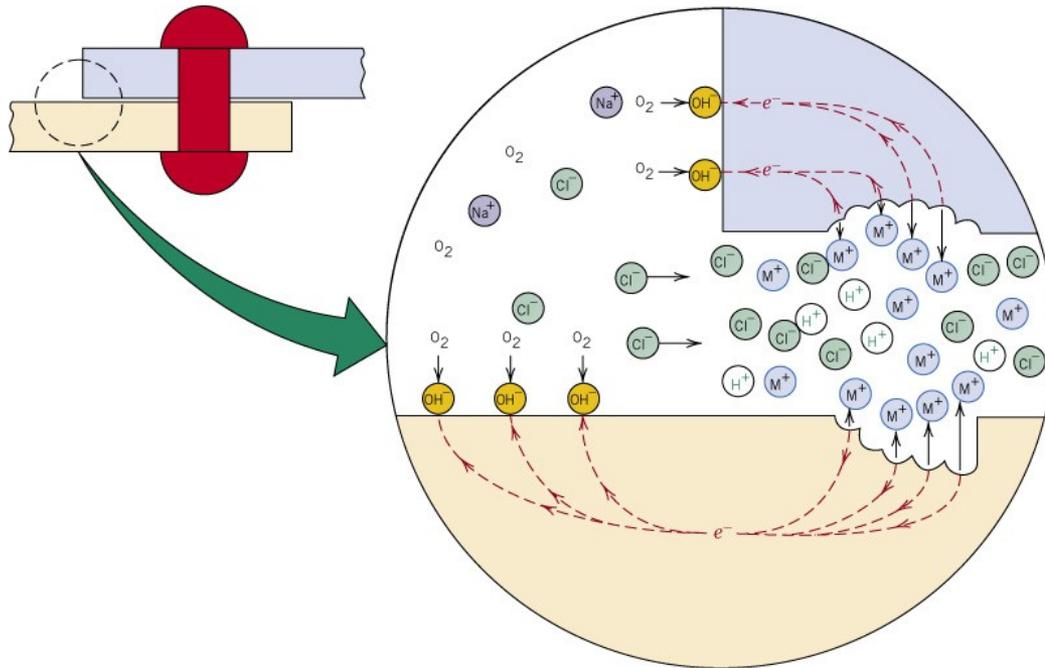
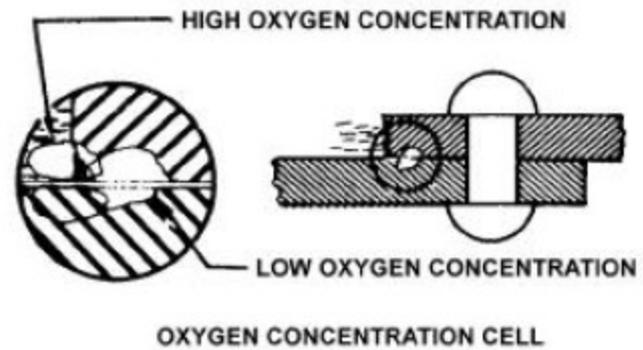
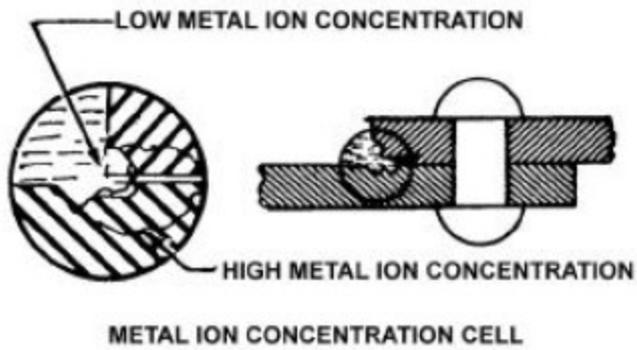
Pitting can cause failure, yet the total corrosion, as measured by weight loss, may be minimal.



3. CONCENTRATION CELL CORROSION.

Concentration cell corrosion, (also known as **Crevice Corrosion**) is corrosion of metals in a metal-to-metal joint, corrosion at the edge of a joint even though the joined metals are identical, or corrosion of a spot on the metal surface covered by a foreign material.

Metal ion concentration cells and oxygen concentration cells are the two general types of concentration cell corrosion.



a. Metal Ion Concentration Cells

Metal Ion Concentration Cells.

The solution may consist of water and ions of the metal which is in contact with metal. A high concentration of the metal ions will normally exist under faying surfaces where the solution is stagnant, and a low concentration of metal ions will exist adjacent to the crevice which is created by the faying surface. An electrical potential will exist between the two points; the area of the metal in contact with the low concentration of metal ions will be anodic and corrode, and the area in contact with the high metal ion concentration will be cathodic and not show signs of corrosion.

b. Oxygen Concentration Cells

Oxygen Concentration Cells.

The solution in contact with the metal surface will normally contain dissolved oxygen. An oxygen cell can develop at any point where the oxygen in the air is not allowed to diffuse into the solution, thereby creating a difference in oxygen concentration between two points. Typical locations of oxygen concentration cells are under gaskets, wood, rubber, and other materials in contact with the metal surface. Corrosion will occur at the area of low oxygen concentration (anode). Alloys are particularly susceptible to this type of crevice corrosion.

4. GALVANIC CORROSION

GALVANIC CORROSION.

Galvanic corrosion occurs when **two dissimilar metals** make contact in the presence of an electrolyte. It is usually recognizable by the presence of a build-up of corrosion at the joint between the metals

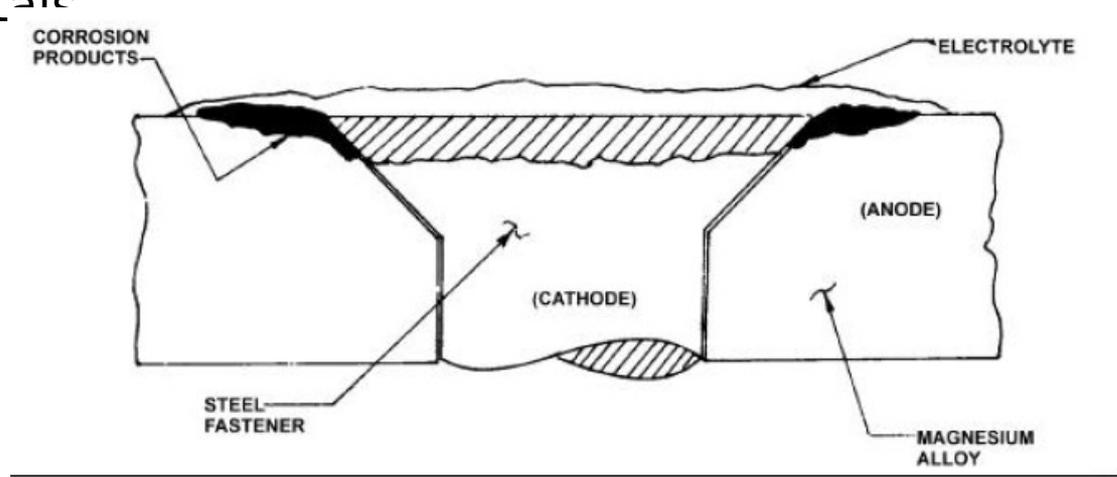
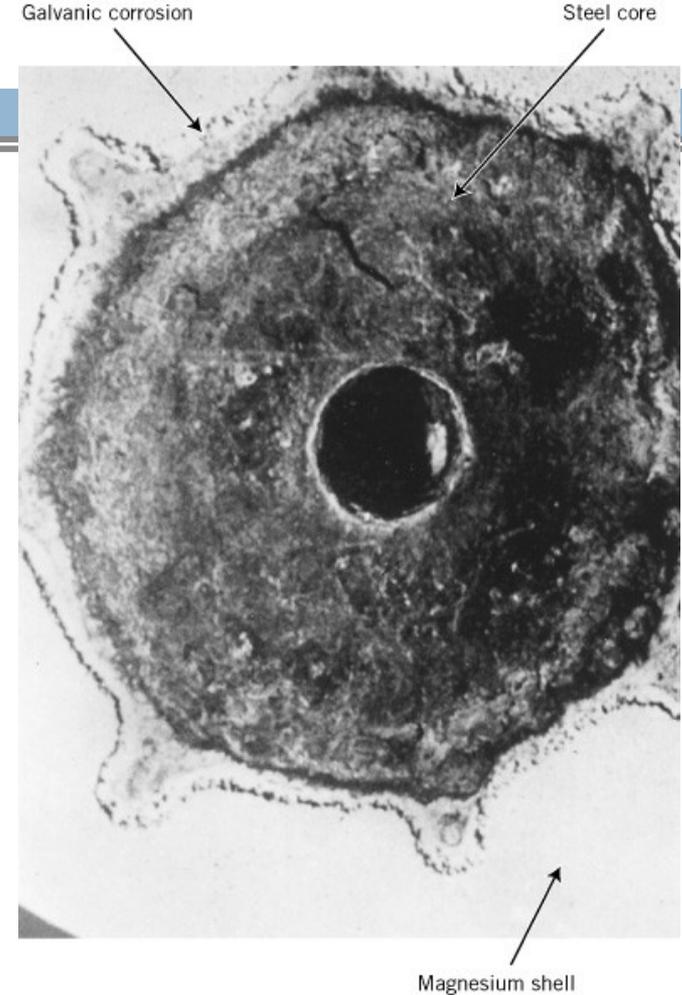
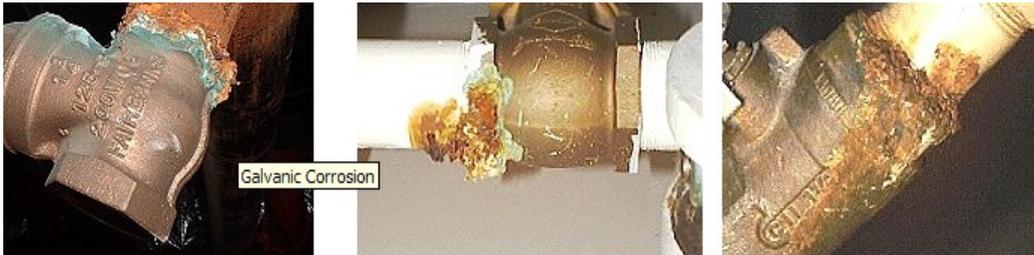


FIGURE 6-11 Galvanic corrosion of magnesium adjacent to steel fastener

Galvanic

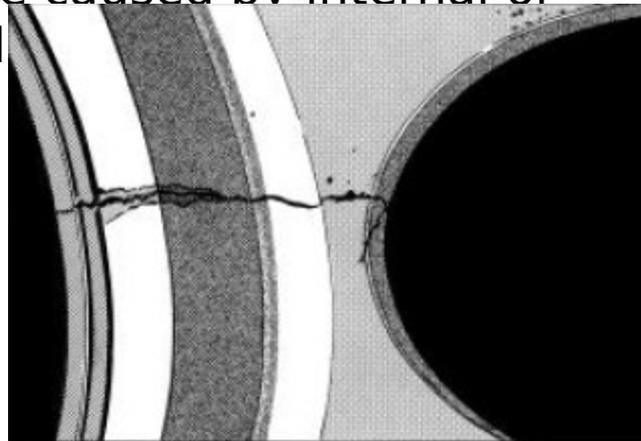
- ❑ Dissimilar metals are physically joined in the presence of an electrolyte.
- ❑ The more anodic metal corrodes.



Bilge pump -
Magnesium shell cast
around a steel core.

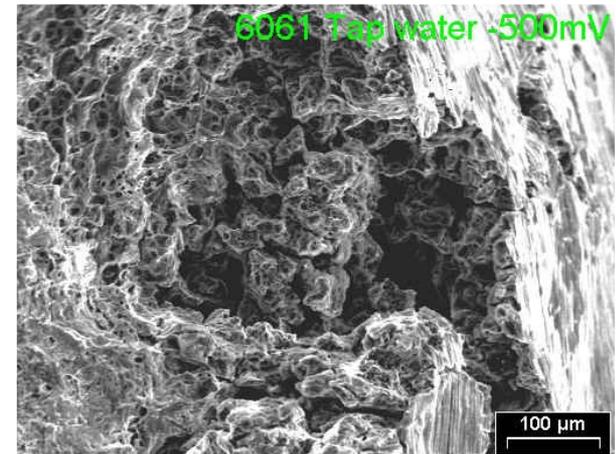
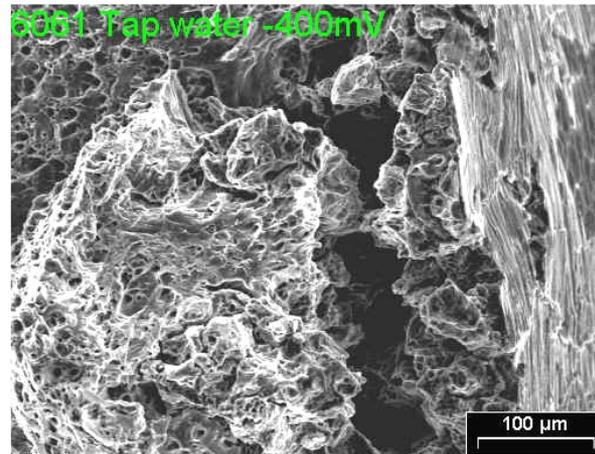
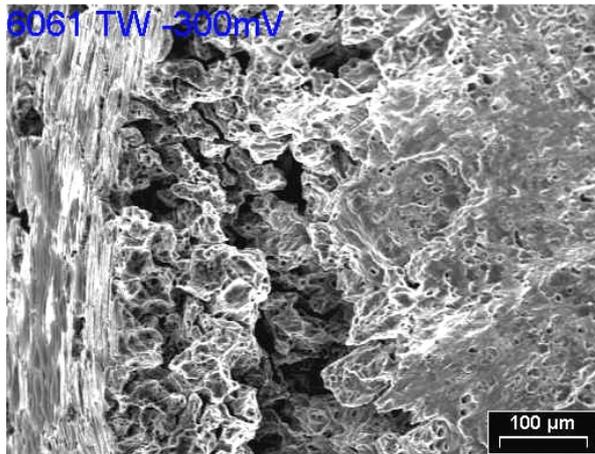
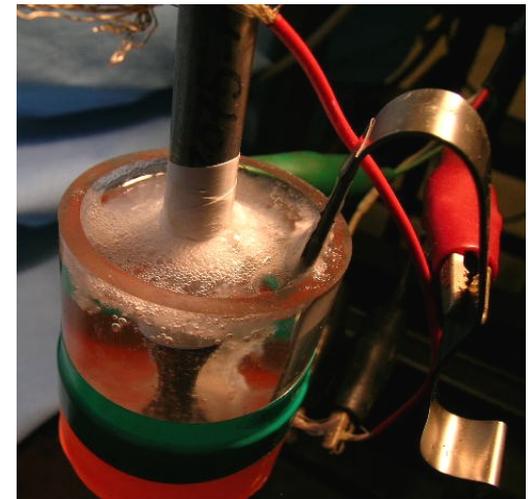
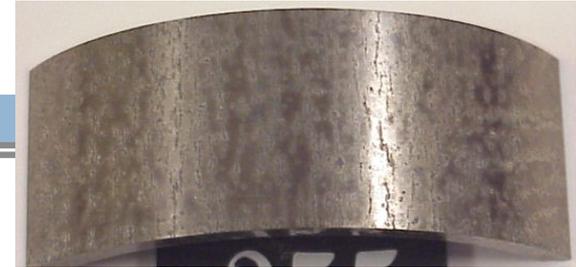
5. STRESS CORROSION CRACKING.

This form of corrosion involves constant or cyclic stress, acting in conjunction with a damaging chemical environment. The stress may be caused by internal or external load



Stress Corrosion Cracking, SCC

- A structure that has **SCC sensitivity**, if subjected to **stresses** and then exposed to a **corrosive environment**, may initiate cracks.
- Consequently, no corrosion products are visible, making it difficult to detect or prevent; fine cracks can penetrate deeply into the part.



a. Internal stress

Internal stress may be trapped in a part of structure during manufacturing processes such as cold working or by unequal cooling from high temperatures. Most manufacturers follow up these processes with a stress relief operation. Even so, sometimes stress remains trapped.

b. External stress

The stress may be externally introduced by welding, clamping, press fit, etc.

c16f20

Erosion-corrosion

Combined chemical attack and mechanical wear (e.g., pipe elbows).



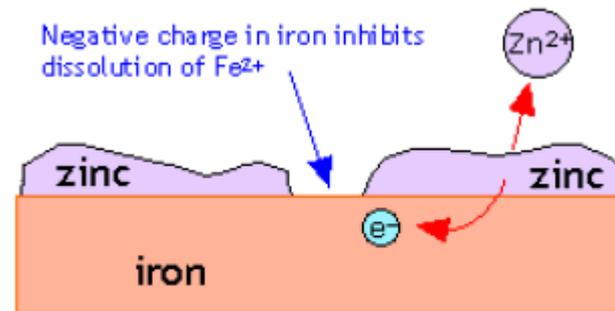
Corrosion protection

- Electroplating
- Galvanization
 1. Galvanization of Zinc
 2. Galvanization of Tin
- Cathodic protection
 1. Sacrificial anode
 2. Impressed current
- Anodizing
- Phosphatizing

Galvanization of Zinc

- This a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as **galvanizing**.
- The zinc coating, **being less noble than iron**, tends to corrode selectively. Dissolution of this sacrificial coating leaves behind electrons which concentrate in the iron, making it **cathodic** and thus inhibiting its dissolution

Zinc plating

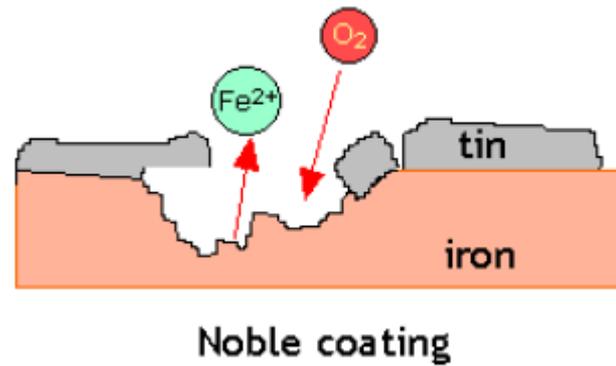


Sacrificial coating

Galvanization of Tin

- The effect of plating iron with a **less active metal** provides an interesting contrast. The common tin-plated can is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the **iron more anodic** so now the tin is actively promoting corrosion of the iron!
- **Example: tin cans disintegrate very rapidly when left outdoors.**

Tin plating



Cathodic protection

The approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction $M \rightarrow M^{2+} + 2 e^-$ to take place.

This can be done by using a **sacrificial anode** made from a more reactive metal, or using an **external power supply** to change the amount of charge on the metal surface.

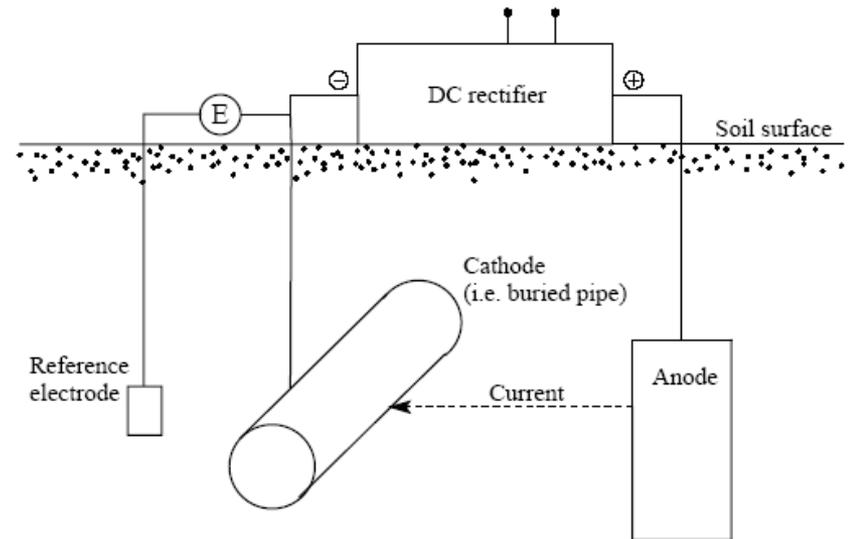
Cathodic protection is well suited to steel structures in marine or underground environments.

a. Impressed current

This technique is widely used for the protection of buried pipelines and the hulls of ships immersed in seawater.

The negative terminal of the current source is connected to the metal requiring protection. The positive terminal is connected to an auxiliary anode immersed in the same medium to complete the circuit. The electric current charges the structure with excess electrons and hence changes the electrode potential in the negative direction.

It is important that the anode be completely separated from the cathode so that a true electric circuit is established with the current flow from



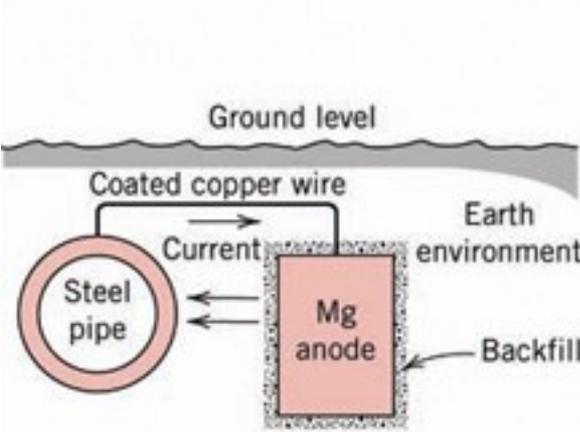
b. Sacrificial anode

This technique is frequently used for ships in seawater and for offshore oil and gas production Platforms.

The principle here is to use a more reactive metal in contact with the steel structure. **Zinc is often used as the sacrificial anode.** If a zinc electrode is now attached, it produces an anodic dissolution current at a more negative potential.

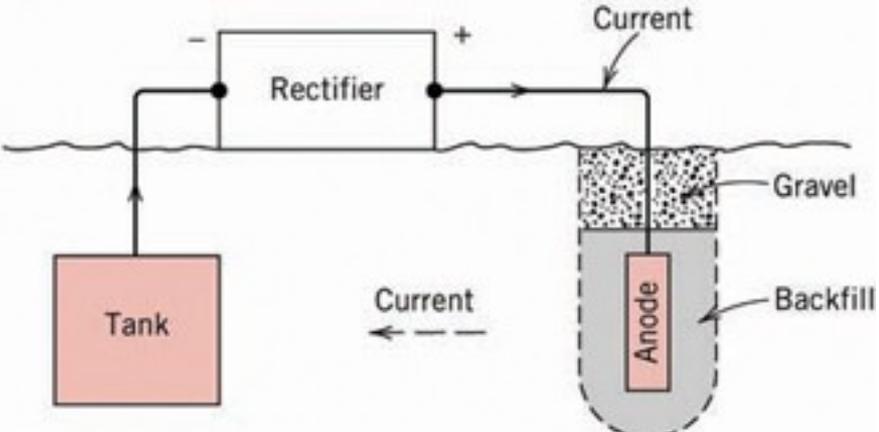
Corrosion prevention

Sacrificial Anode

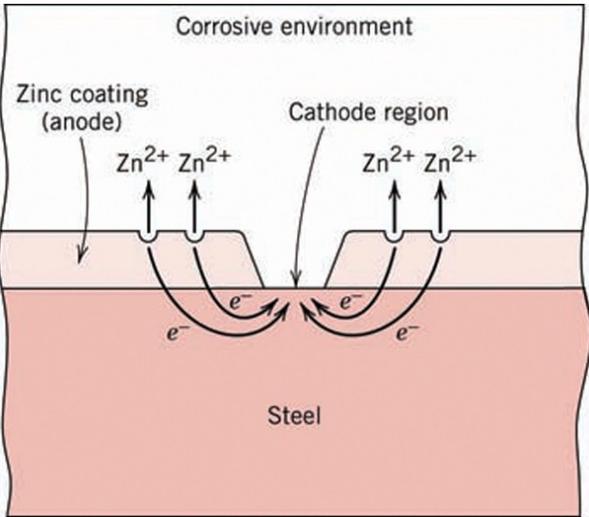


(a)

Applied Voltage



(b)



Anodizing & Phosphatizing

- They provides an **effective base or key** for supplementary protection such as **paints**. In some instances, these treatments can also be a preparatory step prior to painting.
- They help to prevent the spreading of rust under layers of paint.

Anodizing

This treatment change the immediate **surface layer of metal into a film of metallic oxide** or compound which has better corrosion resistance than the natural oxide film.

The difference between **plating and anodizing** is that the oxide coating is integral with the metal substrate as opposed to being a metallic coating deposition. The oxidized surface is **hard and abrasion resistant**, and it provides some degree of corrosion resistance.

Background

- Anodizing process first used in industry in 1923 to protect Duralumin seaplane parts from corrosion using chromic acid.
- Aluminum is most widely anodized metal
- Magnesium, Titanium, and Zinc are capable of being anodized but not used to a wide extent
- Other metals such as tin and copper can be anodized, but rarely practiced

Anodizing Basics

- Basic Concept
- Creates or thickens an oxide layer on surface of metal
- Allows electrical insulation of the given metal
- Creates opportunity of various decorative effects: dyeing, brightening, preservation of surface texture
- Increases hardness of the metal, improves corrosion and wear resistance

Areas of Application

□ Entertainment Industr



□ Military/Aerospace



□ Commercial



Purpose of Anodizing

- Grow an aluminum oxide layer on the aluminum so it can be dyed
- Corrosion and wear resistance
- Hardening
- Color – cosmetic



Photo by Ron Newman, <http://www.focuser.com/anodize.html>

Overview

- Aluminum part immersed in acid electrolyte
- Apply electrical current, DC, ~12V
- The part is the anode (+) (thus the name)
- Electrolysis and chemical reaction occurs
- Porous aluminum oxide layer grows on the aluminum
- Up to 3000 times thicker than naturally occurring Al_2O_3 layer
- Dye goes into pores, results in bright colors
- Place in boiling water to seal pores

Electrochemistry

- Electrolyte in Solution: Free ions ,conductive
 - Sulfuric, oxalic, or phosphoric acid typically used
- Anode
 - Evolution of oxygen
 - $2\text{Al} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$
- Cathode
 - Evolution of hydrogen
 - $6\text{H}_2\text{O} + 6\text{e}^- \rightleftharpoons 3\text{H}_2(\text{g}) + 6\text{OH}^-$

Pore growth

- Acid electrolyte acts as solvent for oxide
- Dissolves portions of barrier oxide layer
- Rate of growth dependent on current, concentration, temperature, voltage

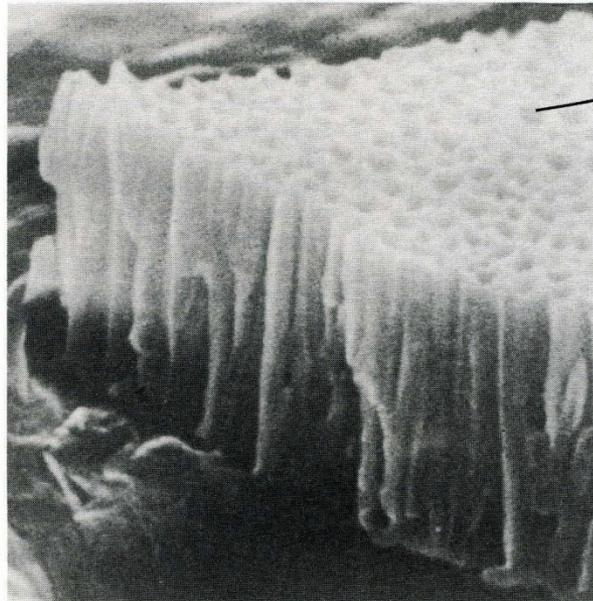


Photo from Artists Anodizing Aluminum, D. LaPlantz, 1988, p. 17

Reasons to anodize

- **Appearance:** Products look finished, cleaner, better
- **Corrosion resistance:** A smooth surface is retained while weathering is retarded. Useful for food handling and marine products
- **Abrasion resistance:** The treated metal is tough, harder than many abrasives.

Anodizing treatments are also available for magnesium and titanium

Phosphatizing

- **Phosphatizing** is a method of protecting a steel surface from corrosion and increasing its resistance to wear through the application of an electrochemical phosphate conversion coating.
- It cannot be used on non-ferrous metals such as aluminum, brass, or copper. It similarly cannot be applied to steels containing a large amount of nickel, or on stainless steel.

Phosphatizing

- They are applied by brushing, spraying or prolonged immersion in an **acid orthophosphate solution containing iron, zinc or manganese**. For example a solution might contain $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ with added H_3PO_4 . The coatings consist of a thick porous layer of fine phosphate crystals, tightly bonded to the steel. When forming steel sheet, the parts are often phosphatized in order to improve the surface properties of the sheet.

- It is commonly used on firearms as a more effective alternative to bluing (magnetite, Fe_3O_4), which is another electrochemical conversion coating that was developed earlier. It is also used extensively on automobiles to protect unfinished metal parts from corrosion

Prevention of Corrosion

Basic goal → • protect the metal • avoid localized corrosion

- ❑ When possible chose a nobler metal
- ❑ Avoid electrical / physical contact between metals with very different electrode potentials (avoid formation of a galvanic couple)
- ❑ If dissimilar metals are in contact make sure that the anodic metal has a larger surface area / volume
- ❑ In case of microstructural level galvanic couple, try to use a coarse microstructure (where possible) to reduce number of galvanic cells formed
- ❑ Modify the base metal by alloying
- ❑ Protect the surface by various means
- ❑ Modify the fluid in contact with the metal
 - Remove a cathodic reactant (e.g. water)
 - Add inhibitors which form a protective layer
- ❑ Cathodic protection
 - Use a sacrificial anode (as a coating or in electrical contact)
 - Use an external DC source in connection with a inert/expendable electrode

