

CORROSION AND ITS EFFECTS

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Corrosion: “the gradual destruction of metals by the chemical or electrochemical reaction with the environment.

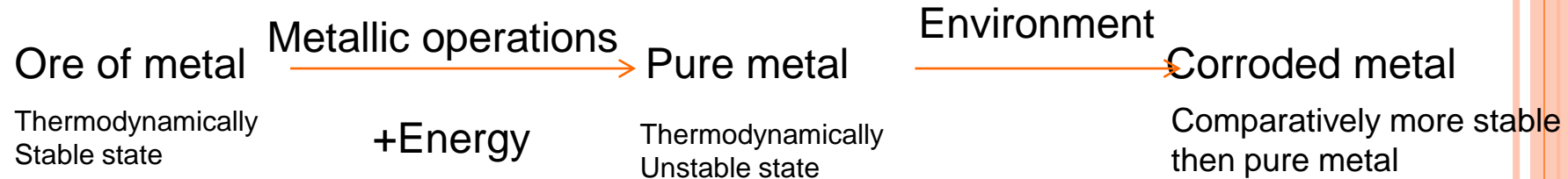
Eg. rusting of iron: formation of hydrated ferric oxide on the surface

Tarnishing of silver: formation of hydrated ferric oxide on the surface

formation of green film of basic copper carbonate on the surface of Cu, when exposed to moist air containing CO_2 .



Causes of corrosion



Consequences of corrosion

1. Deterioration/failure of machine & equipments, reduce efficiency
2. Cost increases --- Maintenance, replacement of corrode part, prevention of corrosion
3. Health hazards----contamination of water
4. Safety problem----- explosion, collapse of construction, leakage, inflammable gases from pipe lines
5. Pollution problem-----leakage of toxic gases



TYPES OF CORROSION

dry (direct) corrosion


- Direct chemical action of atmospheric gases such as O₂, halogens, H₂S, CO₂, SO₂, N₂, H₂ or liquid metals on metal surface in the absence of moisture.

There are 3 types of chemical corrosion.

- a. Oxidation corrosion
- b. Liquid metal corrosion
- c. Corrosion by other gases



Oxidation corrosion (corrosion by O₂)



- “direct action of O₂ present in the atmosphere on metals at low or medium temperature in the absence of moisture to form metallic oxides.
- Alkali and alkaline earth metals -----rapidly oxidised even at low temperature.
- all metals except (Ag, Au, Pt, Pd) -----high temperature



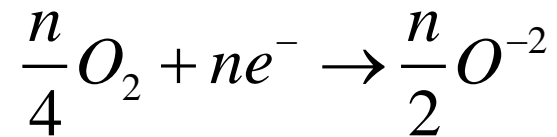
Mechanism of oxidation corrosion (Wagner's theory)

Step 1: Loss of electron by metal (at anode)

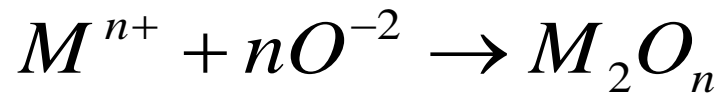


Step 2: Electron from step 1 transported to cathode

Step 3: Gain of electron by oxygen



Step 4: Formation of metal oxide by direct chemical reaction



- Stable oxide film-Al,Cu,Pb, etc
- Unstable oxide film-Ag,Au,Pt
- Volatile oxide film-Mo
- Porous oxide film-Alkali metals,alkaline earth metals



PILLING –BEDWORTH RULE

- The ratio of volume of the oxide formed to the volume of metal consumed is called Pilling Bedworth ratio

$$PB_{ratio} = \frac{V_{oxide}}{V_{metal}}$$

$$PB_{ratio} \propto Oxidation$$

Case1: $V_{oxide} > V_{metal}$  Non-porous layer (Al, Cu)

Case 2: $V_{oxide} < V_{metal}$  Porous layer (Li, Na, K, Mg)



Liquid metal corrosion



- “action of liquid metal at high temperature on solid metal or alloy”
- eg. In nuclear power plants. (weakening of metal)

Corrosion

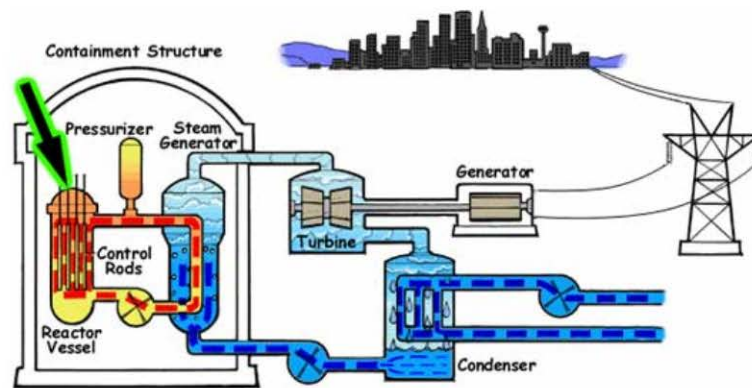
----- due to the dissolution of solid metal
by the liquid metal or

-----due to the penetration of liquid metal in to the
solid metal.



NUCLEAR REACTOR WITH HOLE IN THE HEAD (COOLANT SODIUM METAL LEADS CORROSION OF CADMIUM)

Nuclear Reactor with a Hole in the Head



Corrosion by other gases



- "SO₂, H₂S, Cl₂, F₂ etc
- Film form on the surface

Porous----- allow gases to penetrate & spoil entire metal
eg. Steel by H₂S

Non-porous-----restrict the penetration , protect some
underlying metal, eg. Silver by Cl₂



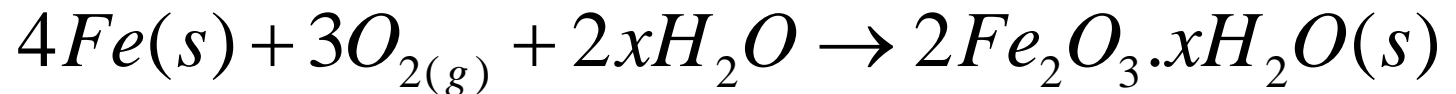
Wet(electrochemical) corrosion

- Involve transfer of electrons from anodic parts of metal to cathodic part through a conductive solution

This type of corrosion occurs when :

1. A metal is in contact with a conducting liquid,
2. Two dissimilar metals or alloys are immersed partially in a conducting solution.

Eg. Rusting of iron: reddish brown coating on surface



Takes place under wet or moist condition



MECHANISM (ELECTROCHEMICAL THEORY)

Involves

- Separate anodic and cathodic area
- anodic reaction involves the dissolution of metal to metallic ions with the liberation of electrons.
- Non-metallic ions at cathode
- Diffusion of metallic and non-metallic ions towards each other

.

At anodic area, M



$M^{n+} + ne^-$ (oxidation)

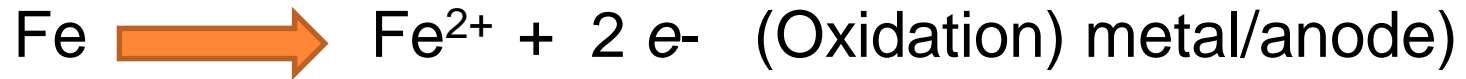
Cathodic reaction consumes e^- ns with either by the

1. evolution of H_2 or
2. absorption of O_2

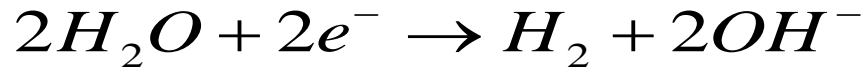


a. Evolution of H₂ (Absence of Dissolved oxygen)

(a) Acidic medium (H⁺ present)

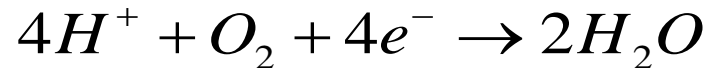


(b) Neutral or alkaline medium



B. Absorption of O₂ (presence of Dissolved oxygen)

(a) Acidic medium:



(b) neutral or slightly alkaline medium



Rusting of Iron

Diffuse of ions from cathode and anode:



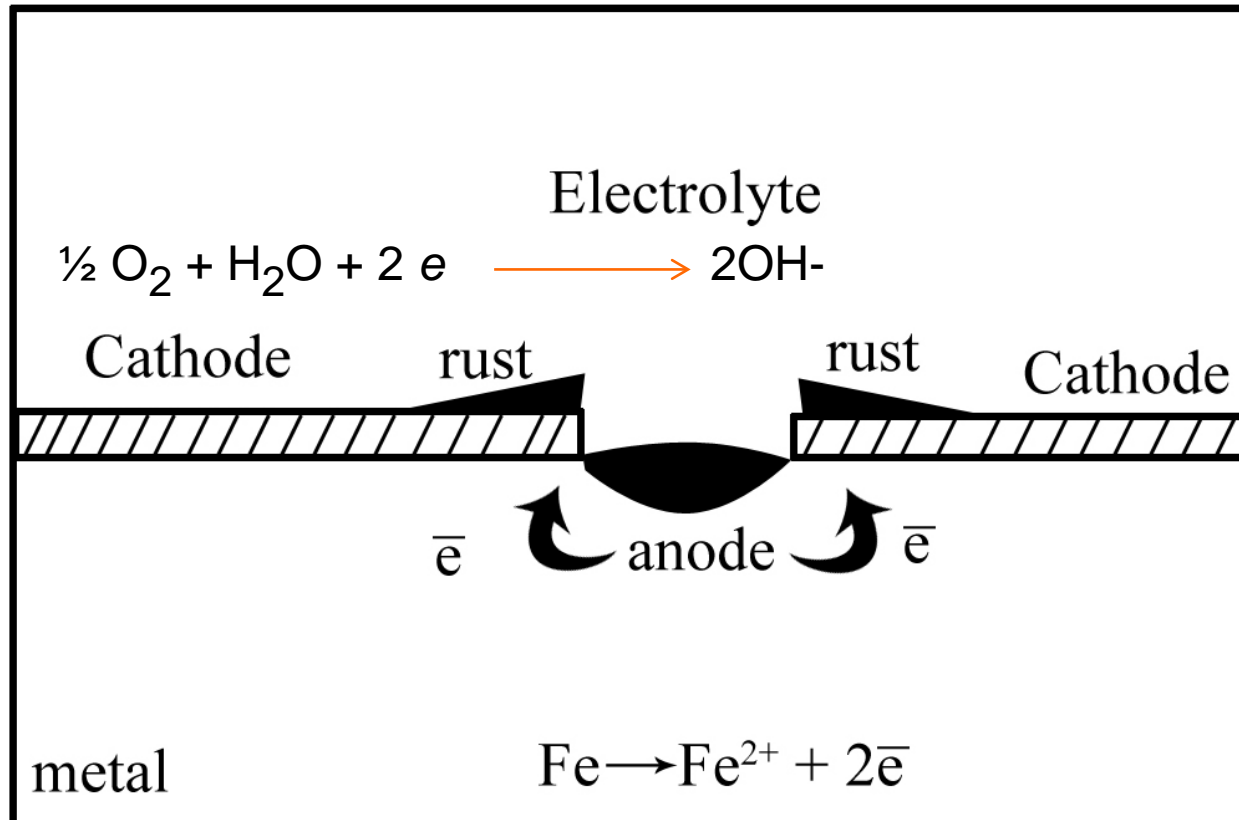
Excess of O_2



Factors govern rusting:

1. Presence of Air
2. Presence of moisture
3. Presence of CO_2
4. Presence of impurities of less electropositive metals in iron
5. Presence of electrolytes in water





Oxide film

Mechanism of rusting of iron



TYPES OF ELECTROCHEMICAL CORROSION

1. Galvanic corrosion or Bimetallic corrosion
2. Pitting corrosion
3. Water line corrosion
4. Differential aeration corrosion
5. Stress corrosion



Galvanic(Bimetallic) corrosion

- When two dissimilar metals or alloys are electrically connected and exposed to an electrolyte, the metal higher in the electrochemical series undergoes corrosion.

Higher in electrochemical series-----Anode----Corrosion

Eg.

- Zn & Cu galvanic cell

Zn-----Anode---Corrosion,
Copper-----Cathode---protected

- Steel pipe connected to copper plumbing
- Lead – antimony solder around copper wire.

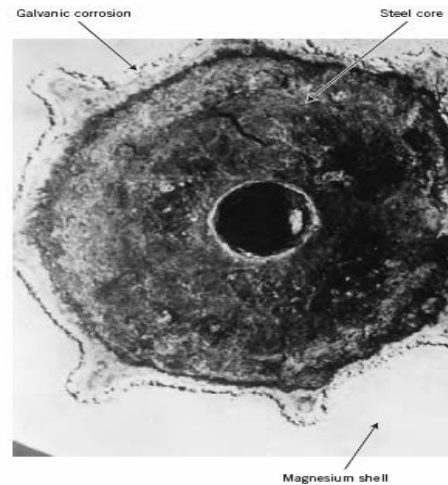
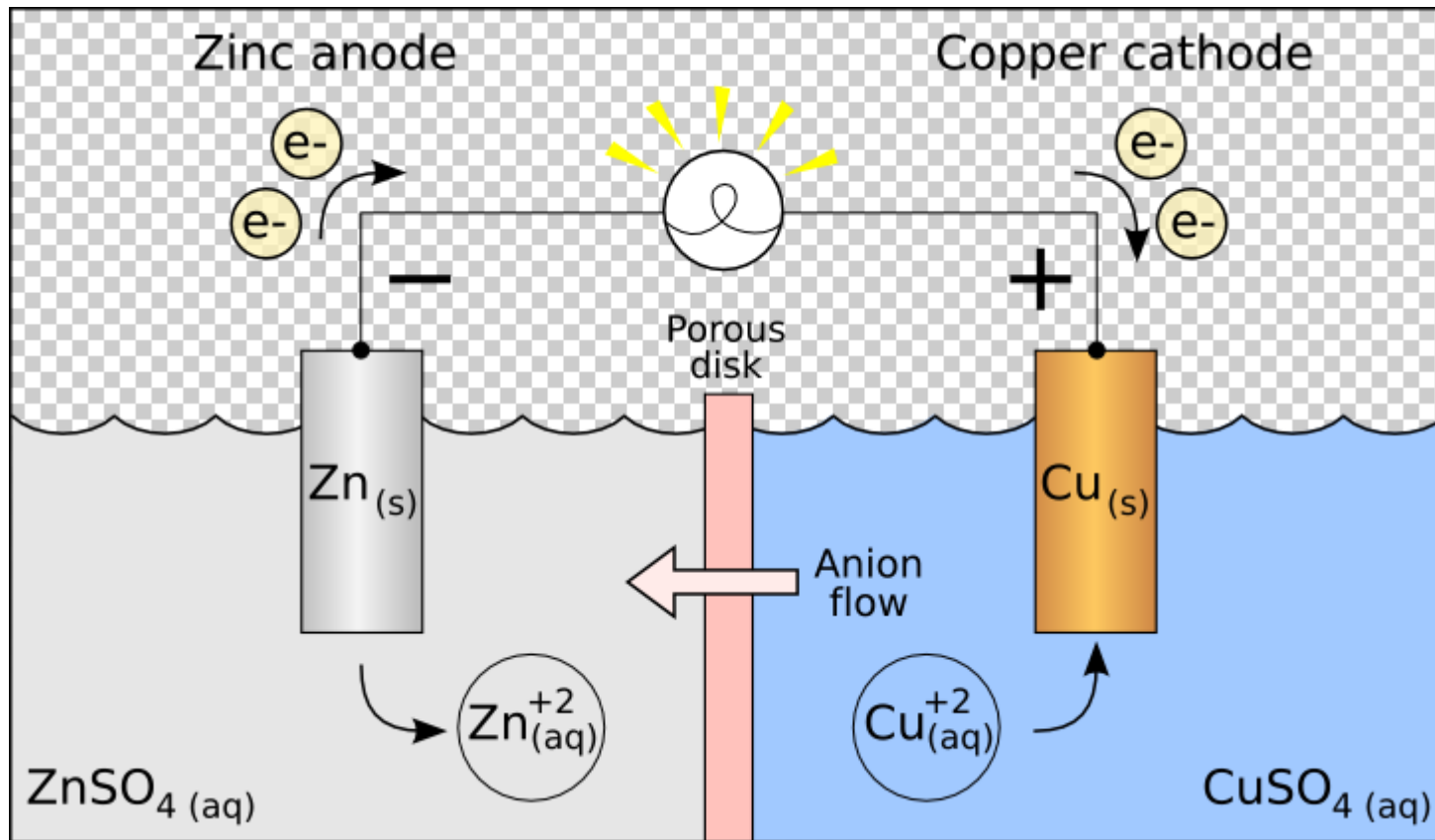


Figure 17.14 Photograph showing galvanic corrosion around the inlet of a single-cycle bilge pump that is found on fishing vessels. Corrosion occurred between a magnesium shell that was cast around a steel core. (Photograph courtesy of LaQue Center for Corrosion Technology, Inc.)





Pitting corrosion

- localized accelerated attack resulting in the formation of pin holes, pits and cavities on the metal surface

due to

- breakdown or cracking of the protective film on the metal at specified points (external impurities like sand, dust, water drops etc)
- -----formation of small anodic & large cathodic areas.
- -----small Pit form-----rate of corrosion increases (growing of pit)

Anode-----small part below the impurity

Cathode-----rest of the metal

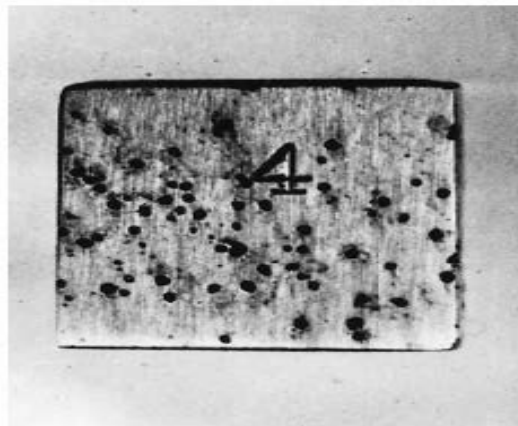
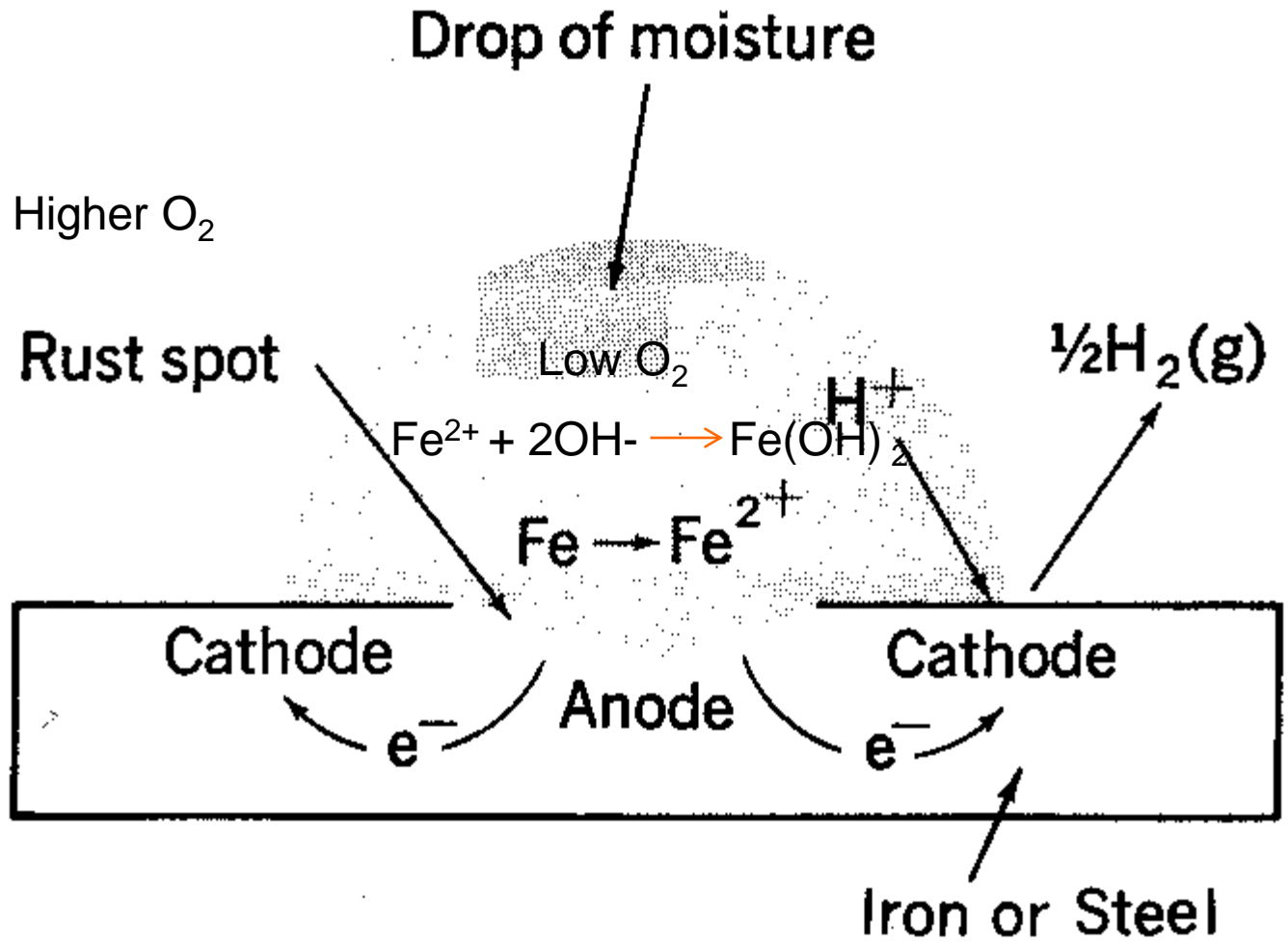


Figure 17.17 The pitting of a 304 stainless steel plate by an acid-chloride solution. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)





Cause

1. Chemical attack
2. Turbulent flow of solution over a metal surface
3. Alternating stress
4. Sliding under load
5. Non-uniform stresses causing straining of metal
6. Scratches or cut edges

Prevention

1. Use of pure metal devoid of impurities
2. Proper polishing of metal surface
3. Proper designing of metal structures



DIFFERENTIAL AERATION CORROSION

“One part of the metal is exposed to an electrolyte of varying concentration or of varying aeration”

This causes a difference in potential between differently aerated areas.

- Anode-----less oxygenated part
- Cathode-----more oxygenated part

Promoted by:

1. Accumulation of dirt, sand , scale
2. Partially covering metals with block of wood or piece of glass
3. Wire fence kind structure

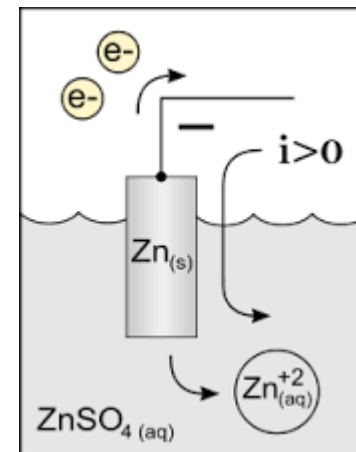




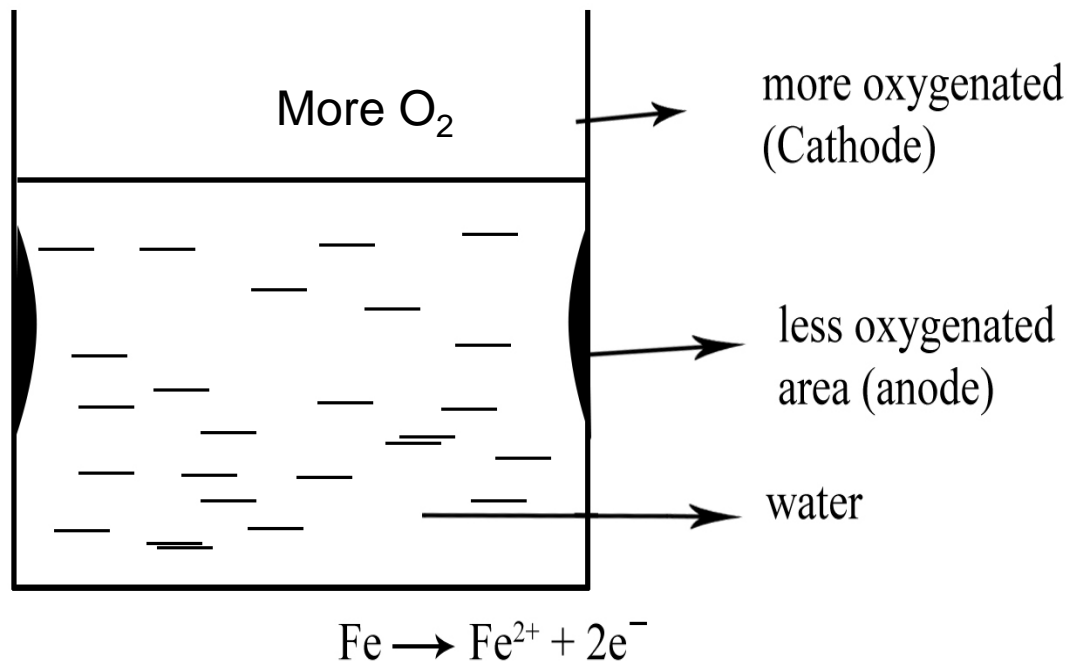
Figure 17.20 Impingement failure of an elbow that was part of a steam condensate line. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)



WATER LINE CORROSION

“The differential aeration corrosion of metals in metallic tanks partly filled with water just below the water line”

Example-Water stored in a steel tank.



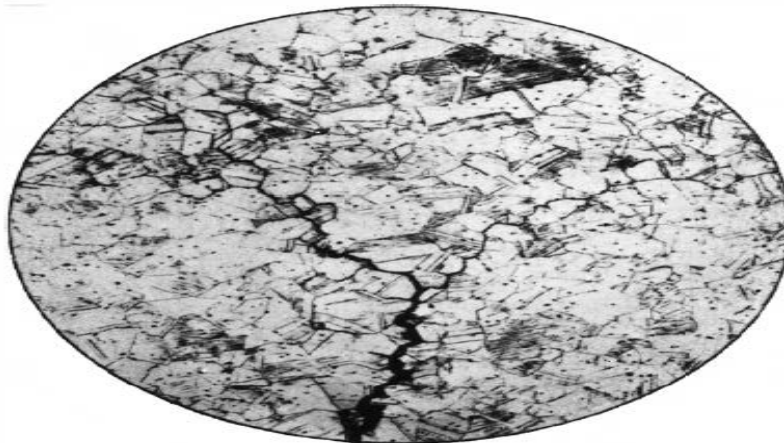
STRESS CORROSION

Tensile stress + Specific corrosion environment

Eg

- Pure metals ----- donot undergo stress corrosion
Fabricated metal-----undergo stress corrosion---eg zinc brass, nickel brass
- Caustic Embrittlement in boilers

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.)



Tensile stresses:

Caused by welding, thermal treatment, heavy working like rolling, drawing, quenching, annealing etc

Corrosive environment:

Specific and selective

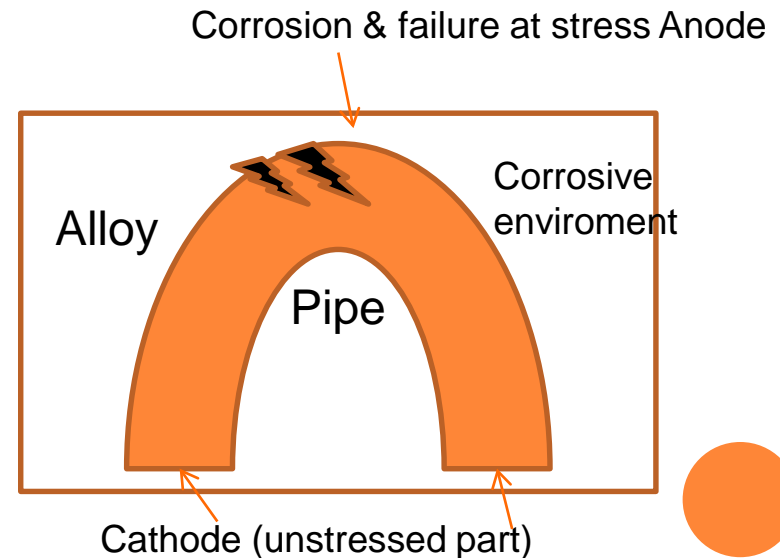
1. Acid chloride solution for corrosion of brass
2. Traces of ammonia for corrosion of brass
3. Caustic alkalis and strong nitrate solution

Mechanism:

Localised Electrochemical Phenomenon

Type:

1. **Season cracking**—Brass (Alloy of Cu, Zn) in ammonia
2. **Caustic embrittlement**—Irregular cracks at joints/bend
3. **Corrosion fatigue**—repeated cyclic stresses—shaking, vibration, flexing



UNDERGROUND OR SOIL CORROSION

Different type of soil---different corrosive property---
corroded underground structure & pipe

The corrosiveness of the soil depend upon

1. Its acidity
2. Degree of aeration
3. Electrical conductivity
4. Its moisture and soil contents
5. Presence of bacteria and micro-organism
6. Soil Texture



Soil corrosion-----electrochemical corrosion

Classification of Soil:

- a) Gravelly or sandy soil---very porous, strongly aerated, moisture. Wet corrosion type
- b) Water logged soil---less free O₂, large bacteria and micro-organisms, evolution of hydrogen type corrosion (Acidic medium), depend upon
 - i) pH of the soil
 - ii) Presence of salts
 - iii) Presence of oxygen etc.
- c) Intermediate character soil---presence of Air ----localized and intense corrosion.



MICROBIOLOGICAL CORROSION

By metabolic activities of various micro-organisms

Classification of Micro-organisms:

Aerobic----can develop in an environment of oxygen

----consume O_2 ---decrease concentration of O_2 on surface of metal

---differential aeration corrosion

----eg. Iron & manganese bacteria form insoluble hydretes of iron and Manganese.

Anaerobic----can develop in an environment without oxygen.

Eg

- (1) Sulphate reducing bacteria---anaerobic corrosion of iron and steel.----*Microspira* & *vibrio desulfuricans*---require sulphur---when die release H_2S ---corrosion of Fe(FeS)



FACTORS AFFECTING CORROSION

The rate and extent of corrosion depends mainly upon two factors—

1. Nature of the metal
2. Nature of the environment



I. NATURE OF THE METAL OR METALLIC CONDITIONS

1. Position in Galvanic Series

higher in the galvanic series----more corrosion.

2. Relative anodic and cathodic areas

Small Anodic area----more demand for electrons by the larger cathodic area– rapid Corrosion

Rate of corrosion \propto Cathodic area/anodic area



3. Purity of the metal

Impurities in a metal form minute electrochemical cells ---the anodic part gets corroded.

4. Physical state of metal

- size, orientation of crystals, stress, and presence of internal defects, etc.
- smaller the size----greater corrosion
- More stressed portion-----more corrosion.
- More internal defects-----more corrosion.



5. Nature of corrosion product

Fe, Mg ----non protective porous oxide film---
more corrosion

Al, Cr, Ni etc ----protective coating lower
corrosion.

6. Solubility of corrosion product

electrochemical corrosion,
corrosion product is soluble in the medium---
faster rate.



7. Reactivity of the metal

Passive metals like Ni, Co, Cr, --- highly protective layer --- do not undergo corrosion frequently.

▪



II. NATURE OF THE ENVIRONMENT

1. Temperature

rate of corrosion \propto temperature

2. Humidity

rate of corrosion \propto humidity

humid condition----atmospheric gases easily form electrochemical cell

3. Effect of PH

acidic media is $\text{pH} < 7$ ---more corrosive than alkaline and neutral media.



4. Formation of O₂ concentration cell

Difference in O₂ conc. around the metal---

Anode---less oxygenated metal part

Cathode----more oxygenated part

O₂ concentration cell is set up resulting corrosion.

5. Nature of ions

Presence of anions like silicate ions in the medium---
formation of insoluble reaction products---inhibit further
corrosion.

Cl⁻ ions, ammonium ions ----destroy the protective
surface film

-----exposing fresh metal surface for
corrosion.

----Rapid corrosion of Al in sea water is an
example.



6. Presence of suspended particulars or compounds

NaCl, $(\text{NH}_4)_2 \text{SO}_4$ etc along with moisture----powerful electrolyte---promote corrosion.

7. Conductance of the corroding medium

Underground & submerged structures

---Conductance (dry sandy soil < clayey & mineralized soil)

---- corrosion rate of metallic structures -- (dry sandy soil < clayey & mineralized soil)



CORROSION CONTROL OR PROTECTION FROM CORROSION

1. Material selection and proper designing:

1. Using pure metal

2. Using metal alloy

3. Proper Designing

a) Avoid the contact of dissimilar metals, in the presence of corroding solution.

b) If two dissimilar metals are in direct contact, anodic metal should have large area to reduce the corrosion.

c) If two dissimilar metals are in direct contact, they should be as close as possible in the electrochemical series.

d) An insulating fitting may be applied to joining two dissimilar metals.

e) The anodic part should not be painted or coated.

f) There should not be the occurrence of inhomogeneity in metal and in corrosive environment.

g) Sharp corners should be avoided.

h) Allow free air circulation to prevent the stagnation of water.



2. Barrier Protection

- a) Coating with paint—iron sheet in bicycles, cars, buses painted
- b) coating with paint or grease---iron tools and machinery parts
- c) coating with non corroding metal---Cromium by electroplating technique
- d) coating with chemicals---coating FePO_4 tough adherent insoluble film protect iron



3. Cathodic Protection(Electrical Protection)

Corroding metal is forced to behave like a cathode.

Types of cathodic protection:

- a) Sacrificial Anodic protection or Galvanic protection
- b) Impressed current cathodic protection



(A) SACRIFICIAL ANODIC PROTECTION ON GALVANIC PROTECTION

“ Protection of metal at the expense of some other more active(more electropositive) metal coated on its surface”

Metallic structure which is to be protected from corrosion is connected to a more anodic metal by a wire so that the entire corrosion is concentrated on this more active metal.

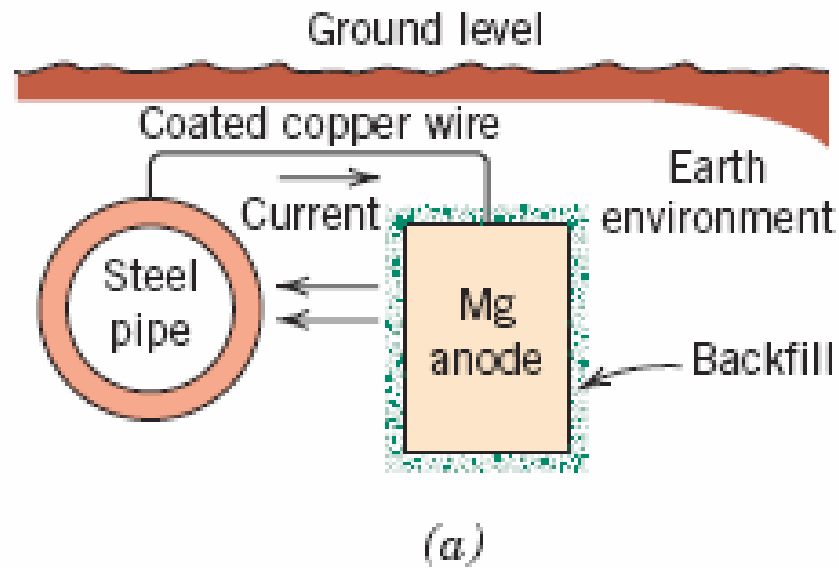
More active metal loses e^- & get corroded----**sacrificial anode.**

Example-Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys.

Applications-----protection of buried pipe lines, underground cables, marine structures etc.



SACRIFICIAL ANODIC PROTECTION OR GALVANIC PROTECTION



(B) IMPRESSED CURRENT CATHODIC PROTECTION

“Metal structure to be forced to act as cathode by applying impressed current in the opposite direction to nullify corrosion current so as to convert the corroding metal from anode to cathode”

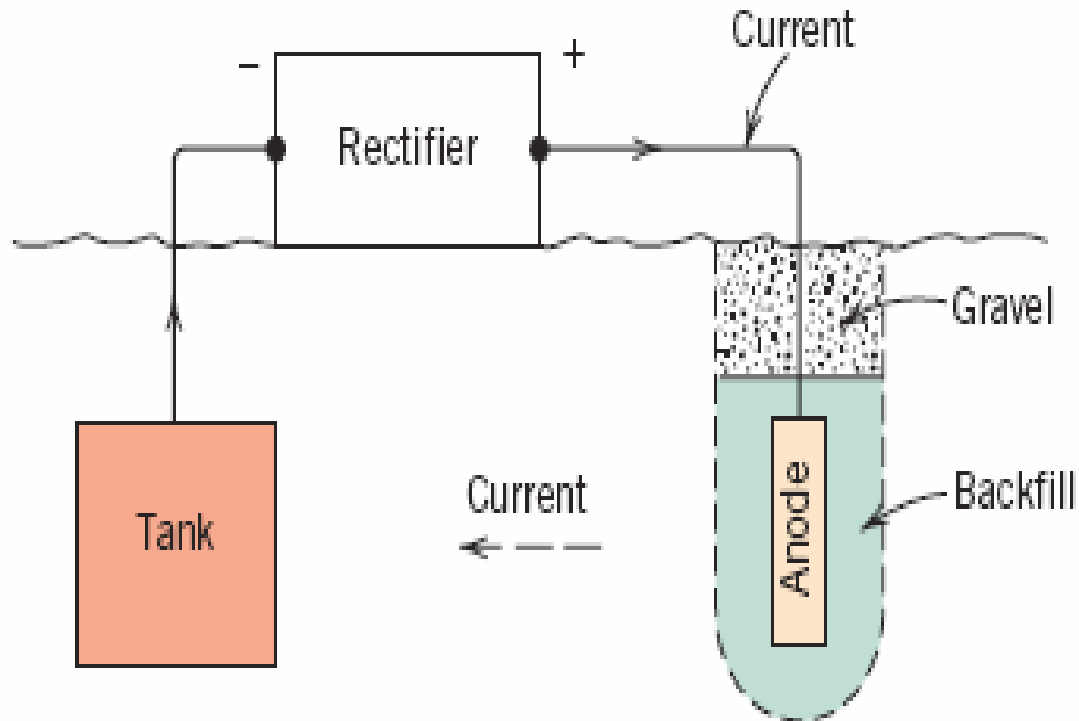
- Impressed current can be derived from a direct current source like battery.
- An inert or insoluble electrode like graphite or silica act as anode to complete the circuit.
- The surroundings of anode should be filled with salts and carbon to increased the conductivity.

Applications-

- water coolers., water tanks, buried oil & water pipes, transmission towers
1. Long term protection is needed
 2. Large structures are to be protected
 3. There is a cheap source of electrical power.



B. IMPRESSED CURRENT CATHODIC PROTECTION



METALLIC COATINGS

a. Metallic Coatings

- mostly applied on Iron and steel because these are cheap and commonly used construction materials.

Types of metallic coatings.

1. Anodic coatings

The base metal which is to be protected is coated with a more anodic metal for eg. Coatings of Zn, Al and Cd on iron are anodic because their electrode potentials are lower than that of the base metal ie. Fe.

2. Cathodic Coatings

It is obtained by coating a more inert metal having higher electrode potential, Than the base metal. Eg. Coating of Sn, Cr, Ni on Fe surface. The coating should be continuous and free from pores and cracks. These coating metals usually have higher corrosion resistance than the base metal.



METHODS OF APPLICATION OF METALLIC COATING

1. Hot Dipping

- used for producing a coating of low melting metal such as Zn, Sn, Al etc on relatively higher melting metals such as iron, steel, copper etc.
- done by immersing the base metal covered by a layer of molten flux. The flux is used to keep the base metal surface clean and also to prevent oxidation of the molten metal.

Most widely used hot dipping methods are :
(A) galvanization and (B) tinning



(A) GALVANIZATION

“coating of Zn over iron or steel sheet by immersing it in molten Zn”

The procedure involves the following stages.

- (1) By dipping: Iron sheet are dipped in molten zinc and then passed through hot rollers
- (2) By sherardizing: Zinc dust is heated and vapour of Zn allow to condense on the sheets

Process:

- (i) Pickling:**
- (ii) Washing:**
- (iii) Drying:**
- (iv) Hot dipping:**
- (v) Removal of excess Zn:**
- (vi) Annealing:**

Applications

- protection of Fe from atmospheric corrosion in the form of articles like roofing sheets, wires, pipes, nails, screws, tubes etc.

Pickling: Clean the article by dil H_2SO_4 for 15 – 20 min at 60 – 90⁰C in an acid bath. This treatment also removes any oxide layer present on the surface of the metal.

Washing: The article is then washed with water in a washing bath

Drying: dried in a drying chamber.

Hot dipping: It is then dipped in a bath of molten Zn kept at 425 – 435 ⁰C. The Surface of the bath is covered with NH_4Cl flux to prevent oxide formation. The article gets coated with a thin layer of Zn.

Removal of excess Zn: It is then passed through a pair of hot rollers to remove excess of Zn and to get uniform thickness for coating.

Annealing: Then it is annealed at about 650 ⁰C & cooled slowly. In the case of Zn coating even if the protecting layer has cracks on it, iron being cathodic does not get corroded.

GALVANIZING

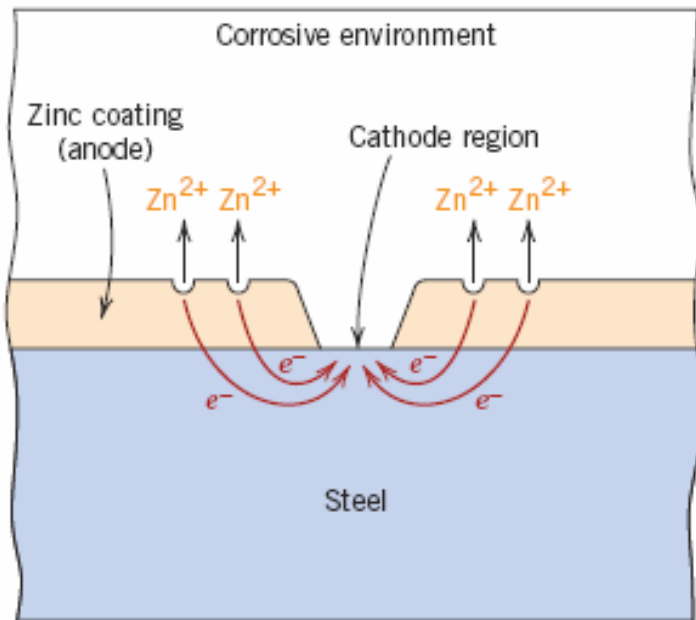


Figure 17.23 Galvanic protection of steel as provided by a coating of zinc.



3. TINNING

Tinning -----Cathodic coatings.

“coating of Sn over Fe or steel articles by immersing it in molten Sn.

Process

Step (i)-(iii) Pickling, washing, drying: Same as galvanization

(iv) Hot dipping: it is passed through a bath of $ZnCl_2$ flux which helps the molten Sn to adhere to the metal sheet. The sheet passes through **palm oil which prevents tin layer from oxidation** during solidification and keeps Tin as molten state.

(v) Removal of excess tin: The tinned metal comes out from palm oil chamber with the help of rollers.

Applications

1) Tinning is widely used for coating steel, Cu and brass sheets which are used for making containers for storing food stuffs, oils, kerosene & packing food materials.

2) Tinned Cu sheets are used for making cooking utensils & refrigeration equipments.



4. ELECTROPLATING

Electroplating -----electrolysis process

Process

- Coating metal is deposited on the base metal by passing direct current through an electrolyte containing the soluble salt of the coating metal.
- Base metal to be electroplated is made the cathode of the electrolytic cell whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity like graphite.
- The article has to be cleaned thoroughly before electroplating by
 - solvent cleaning alkali cleaning.
 - Acid washing to remove surface oxide film

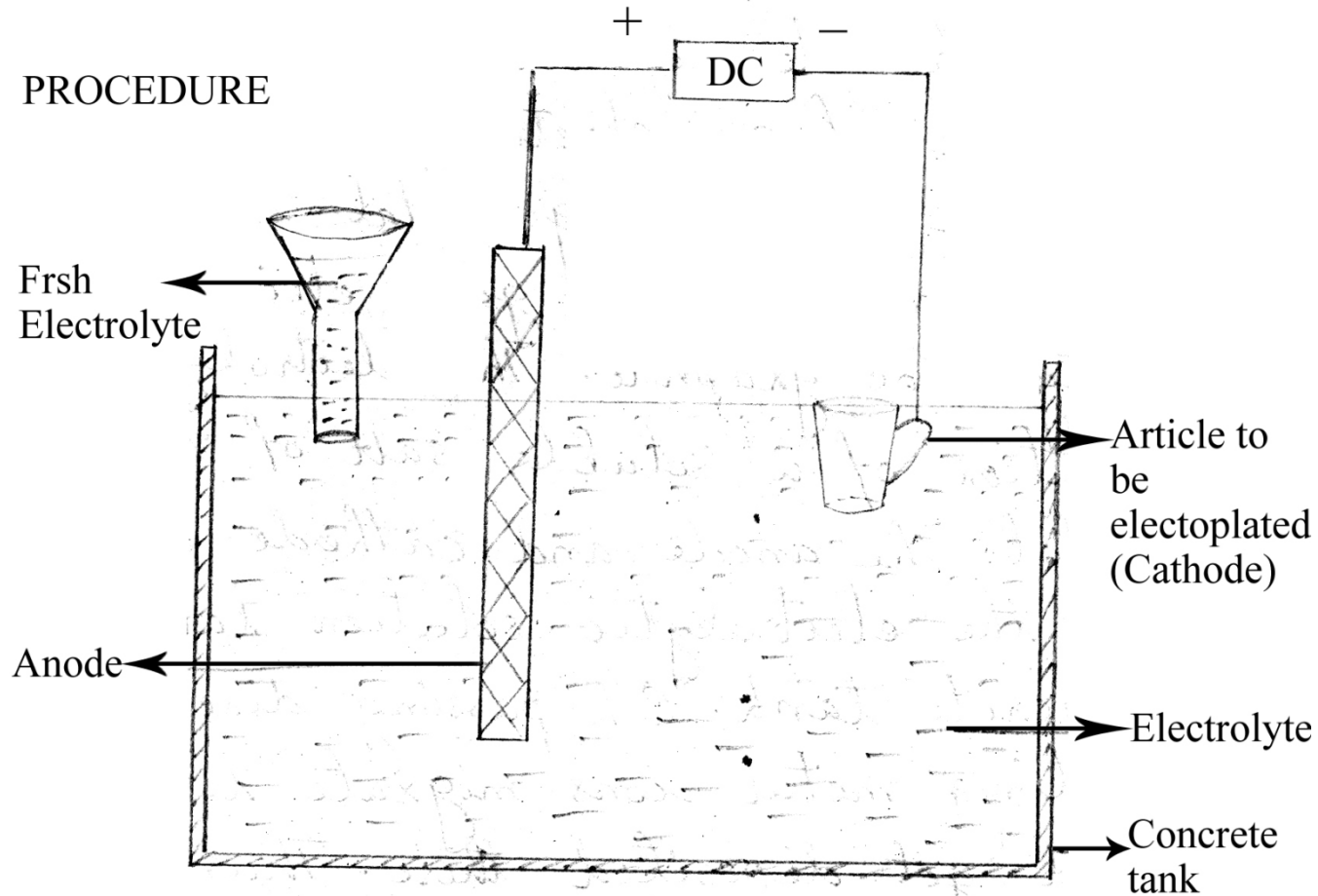
Objectives

1. To increase the resistance to corrosion
2. To increase resistance to chemical attack
3. To increase physical appearance and hardness
4. To improve the surface properties
5. To increase the decorative and commercial values of the metal



ELECTROPLATING

PROCEDURE



The cleaned article is then made cathode of an electrolytic cell. The anode is either the coating metal itself or an inert material of good electrical conductivity like graphite. The electrolyte is a solution of a soluble salt of the coating metal.

Procedure- The anode and cathode are dipped in the electrolytic solution taken in a concrete tank. On passing direct current, coating metal ions migrate to the cathode and get deposited there. Thus a thin layer of coating metal is obtained on the article which acts as the cathode.

If the anode is made of coating metal itself, the concentration of electrolytic solution remains unaltered, since the metal ions deposited from the electrolyte are compensated by the reaction of free anions with the anode metal. However, if the anode is made of some inert material, fresh electrolyte has to be added whenever required.

Example-1) For electroplating of Ni, NiSO_4 and NiCl_2 are used as the electrolyte. 2) For electroplating of Cr, chromic acid is used as the electrolyte.

3) For Au plating, AuCl_3 solution is taken as the electrolyte. For Cu plating CuSO_4 solution is used as the electrolyte.

4) In silver plating, AgNO_3 solution is used as the Electrolyte.



METAL SPRAYING

In this process, the coating metal in the molten state is sprayed on the previously cleaned base metal with the help of a sprayer. **The sprayer coatings are continuous but somewhat porous \ a sealer – oil is applied on such a coating to provide a smooth surface.** However, adhesion strength of metallic spraying is usually lesser than obtained by hot dipping or electroplating. It is therefore essential to have a cleaned metal surface. Spraying can be applied by the following two techniques.

- 1) Wire – gun method
- 2) Powder – metal method



Applications

1. Coating can be applied to fabricated structure
2. Coating can be applied to large & irregular shaped articles.
3. Coating can be applied even on to non – metallic bases made of glass, wood, plastic etc.



4. METAL CLADDING

In this process, a thick homogeneous layer of coating metal is bonded firmly & permanently to the base metal on one or both the sides. This method enhance corrosion resistance.

The choice of cladding material depends on the corrosion resistance required for any particular environment. Nearly all existing corrosion resisting metals like Ni, Cu, Al, Ag, Pt and alloys like stainless steel, Ni alloys, Cu alloys can be used as cladding materials. Cladding can be done by different means.

- a. Fusing cladding material over the base metal
- b. Welding
- c. Rolling sheets of cladding material over base metal.



USE OF CORROSION INHIBITORS

“Chemicals which are added in small quantities to the corroding medium in order to reduce the corrosion rate are called corrosion inhibitors”

They reduce corrosion by forming a protective film either at the cathode or anode.

there are two types of corrosion inhibitors –

1. anodic inhibitors and
2. cathodic inhibitors



ANODIC INHIBITORS

Chromates (CrO_4^{2-}), phosphate (PO_4^{3-}) and Tungstates (WO_4^{2-}) of transition metals are used as anodic inhibitors.

They react with the newly produced metal ions at the anode forming a protective film or barrier there by preventing further corrosion.

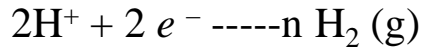


CATHODIC INHIBITORS

Slow down the corrosion reaction by diffusion of H^+ ions to the cathode .

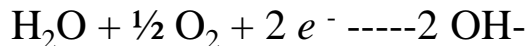
Cathodic reaction takes place with either evolution of H_2 or absorption of O_2 depending on the nature of the corroding medium.

1. Evolution of H_2 in acid medium

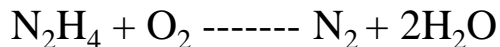
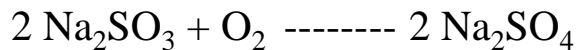


Evolution of H_2 can be prevented by slowing down the diffusion of H^+ ions to the cathode or by increasing H_2 over voltage. Diffusion of H^+ ions can be prevented by adding organic inhibitors such as amines, urea, thiourea etc. These are adsorbed at the surface as a film. Arsenic oxide or antimony oxide is added to increase the H_2 over voltage. These oxides form adherent film of metallic arsenic or antimony at the cathodic areas.

b. Absorption of O_2 in metal or alkaline medium



The formation of OH^- ions can be prevented either by removing O_2 from the medium or by decreasing the diffusion of O_2 in to the cathode. O_2 is removed either by adding reducing agents like Na_2SO_3 , N_2H_4 etc or by mechanical deaeration.



Salts of Zn, Mg or Ni are added to the corroding medium to reduce the diffusion of O_2 towards cathode. These salts react with OH^- ions at the cathode forming insoluble hydroxides which are adsorbed at the cathode.

