


# **CORROSION AND ITS CONTROL**

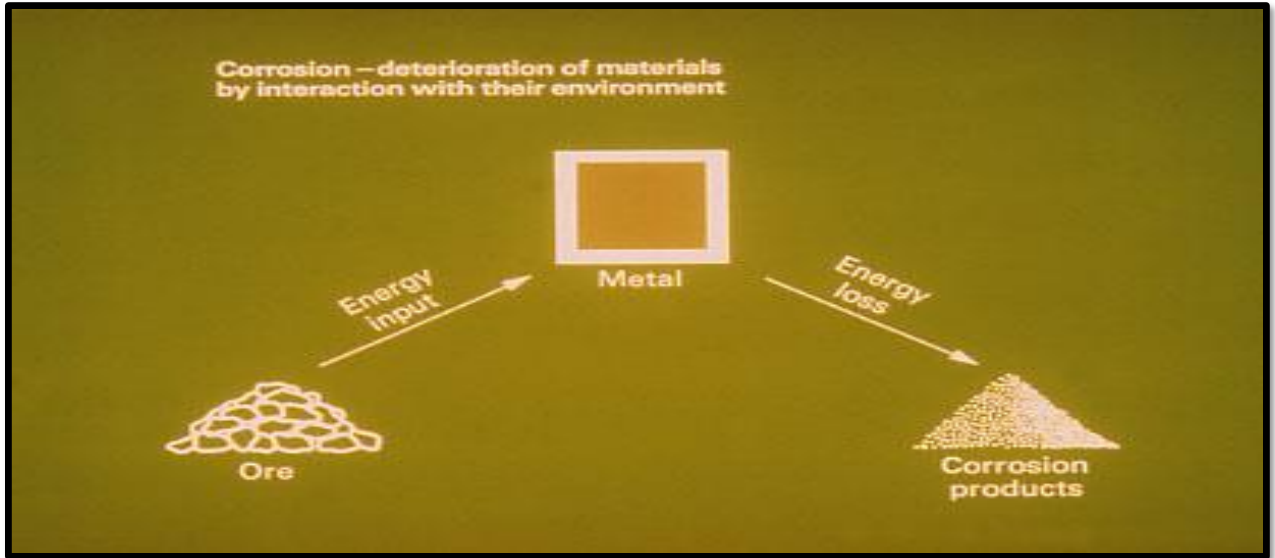
- ▣ **INTRODUCTION**
- ▣ **CAUSES OF CORROSION**
- ▣ **THEORIES OF CORROSION**
- ▣ **CORROSION REACTIONS**
- ▣ **FACTORS EFFECTING THE CORROSION**
- ▣ **TYPES OF CORROSION**
- ▣ **CORROSION CONTROL METHODS**



# INTRODUCTION

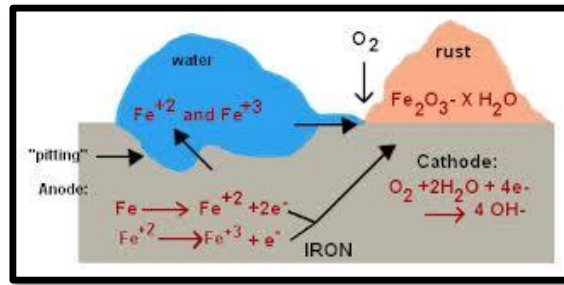
- Destruction of a metal by chemical or electrochemical reaction with its environment.
  - Physical or mechanical wearing away of a metal is not called corrosion but is called erosion
  - If corrosion and erosion take place together the destruction of the metal takes place very much faster
  - Corrosion is an unintentional attack on a material by reaction with a surrounding medium
  - The corrosion problem should be very seriously considered in all those cases where the structure or the equipment is meant to last many years say 20 years...
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# Definition of Corrosion

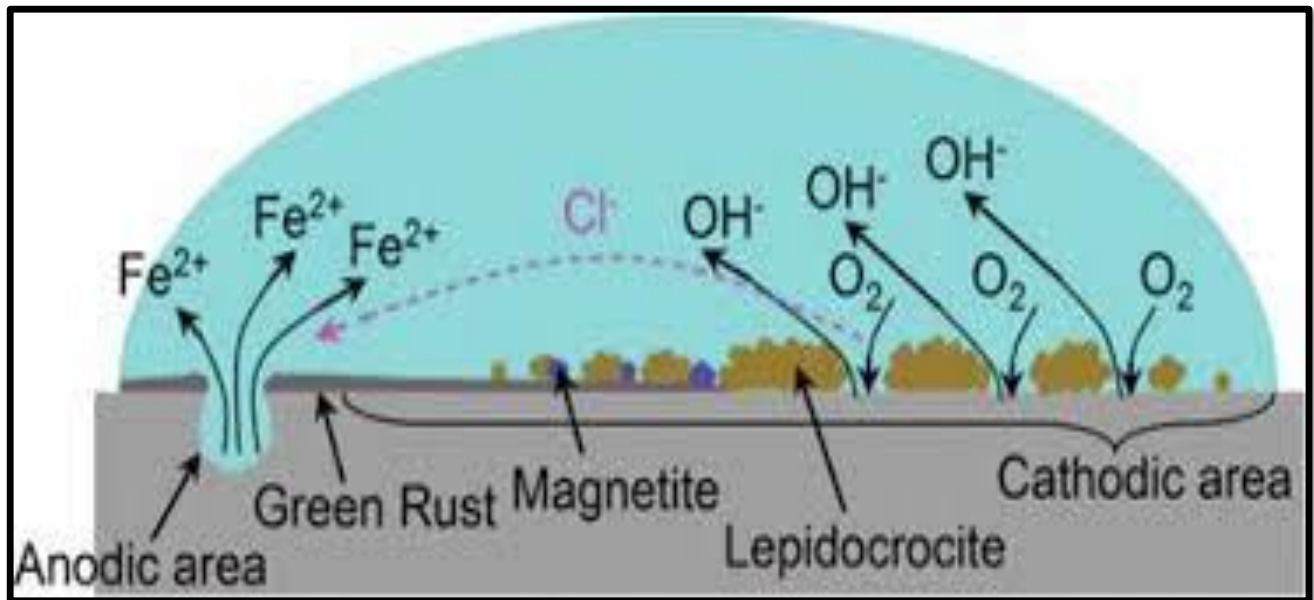


Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals.


# Rusting of iron



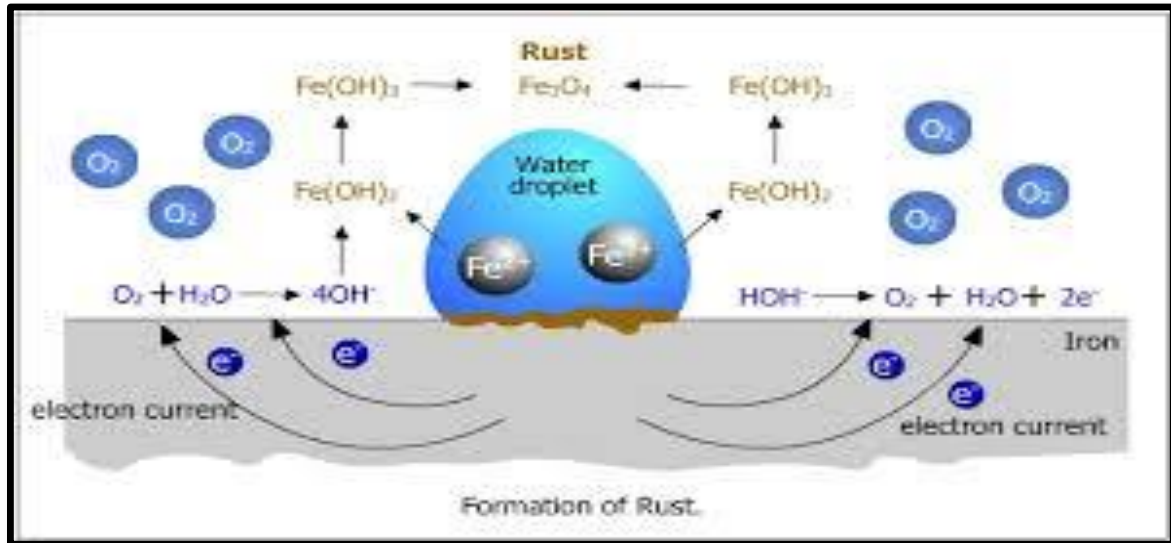
# Formation of green rust



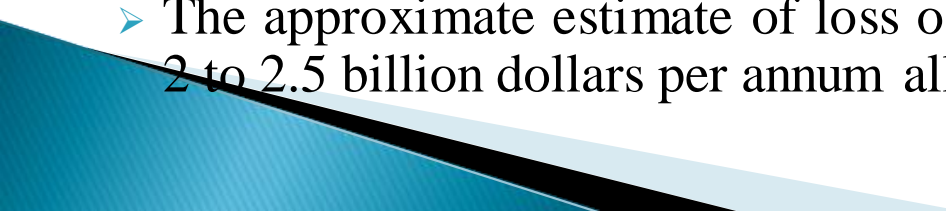
# CAUSES OF CORROSION

- The chemical combined state of the metal is known as “**ore**”
  - The ore has low energy in its thermodynamical state.
  - The extracted metal has high energy ,thermodynamically unstable .
  - Metal converts itself into stable state by reacting with the environment and undergoes corrosion.
  - The corroded metal is thermodynamically stable.
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# Formation of rust



# Effects or disadvantages of corrosion

- The valuable metallic properties like conductivity, malleability, ductility etc are lost due to corrosion.
  - Life span of the metallic parts of the machineries is reduced.
  - The process of corrosion is very harmful and is responsible for the enormous wastage of metal in the form of its compound.
  - The failure of the machinery takes place due to loss of useful properties of metals.
  - The approximate estimate of loss of metal due to corrosion is 2 to 2.5 billion dollars per annum all over the world.
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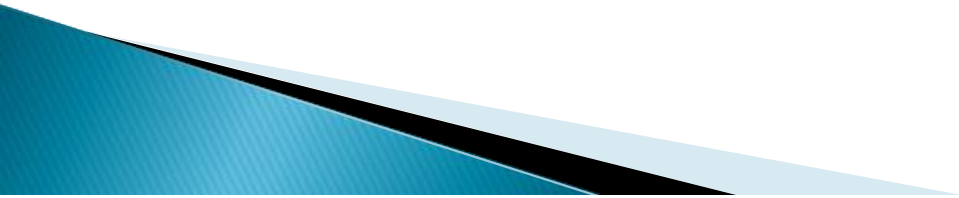




# TYPES OF CORROSION

Different types of electrochemical corrosions are

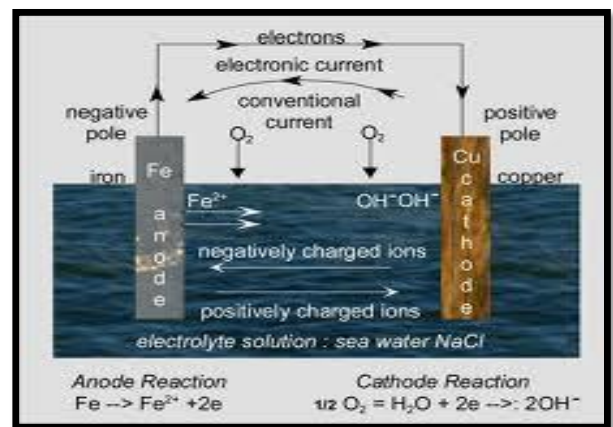
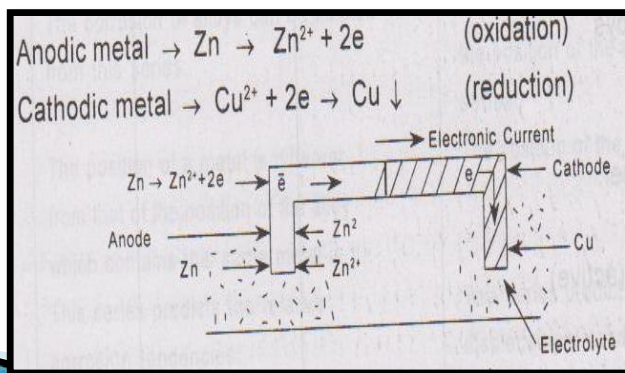
- Galvanic corrosion
- Pitting corrosion
- Intergrannular corrosion
- Water line corrosion

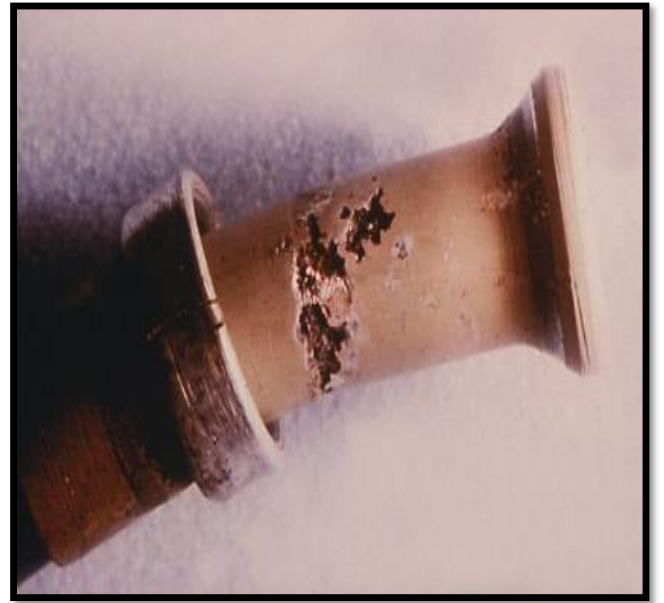
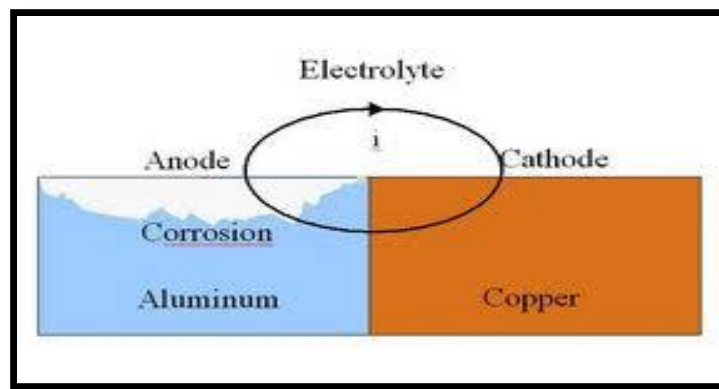




# Galvanic corrosion

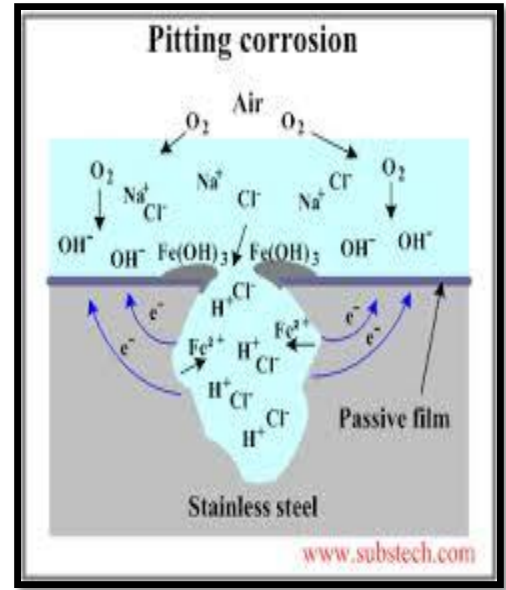
- ▣ This corrosion occurs when different metals are in contact and exposed to corrosive atmosphere.
- ▣ The metal which has higher electrode potential value will form anode and undergoes corrosion. Example: Zn-Cu galvanic cell zinc behaves as anode and corrosion occurs, copper behaves as cathode and protected.



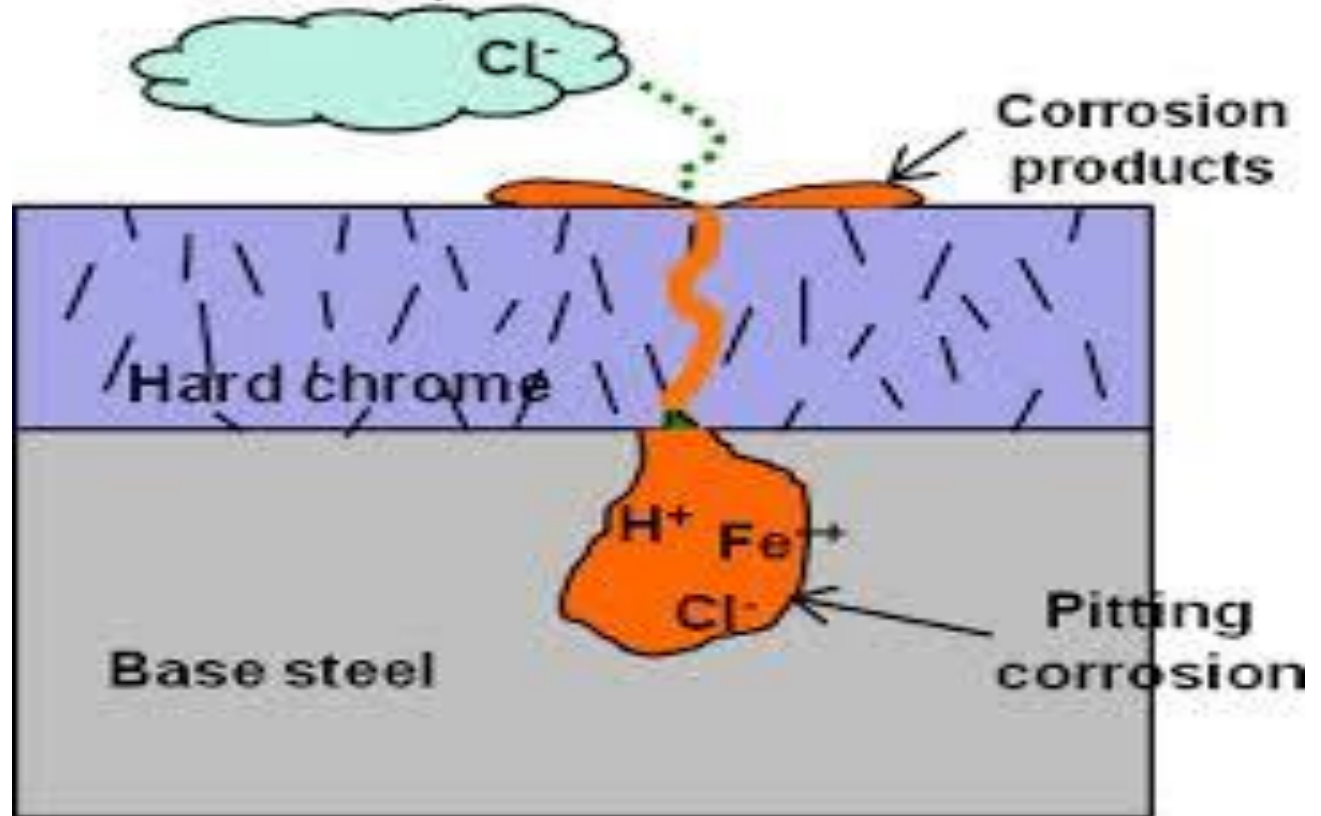


# Pitting corrosion

- When corrosion starts on a metal surface at certain spots they become less open to oxygen with the result that corrosion proceeds faster at those very spots making deeper and deeper cavities.
- Pitting corrosion can be explained on the basis of differential aeration.
- The pit created becomes deeper, its bottom becomes less open to oxygen which makes it more anodic.
- The part which has higher oxygen concentration is cathodic.



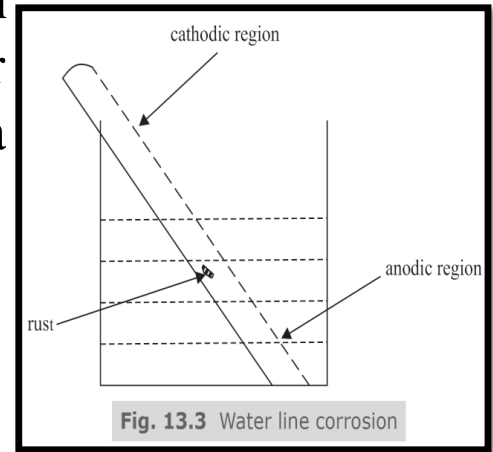
Corrosive atmosphere





# Water line corrosion

- The concentration of oxygen dissolved in water is greater at the surface than deeper down. This causes formation of a concentration cell.
- Anode is the lower portion .
- Cathode is at the water level.
- Due to the poor conductivity of water the ions just below the water level are available for reaction, the metal corrodes just below the water level.








# Theories of corrosion



# THEORIES OF CORROSION

- In atmospheric corrosion the metals tend to revert to the states in which they occur in nature.
  - Several theories of corrosion have been proposed from time to time..
  - The three theories are
    - i) ACID THEORY
    - ii) CHEMICAL CORROSION (**DRY CORROSION**)
    - iii) ELECTROCHEMICAL CORROSION (**WET CORROSION**)
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# ACID THEORY


Acid theory of corrosion considers acid to be the main cause.

Rusting takes place faster in acid solutions than in neutral or basic solutions.

Oxygen and water are necessary for rusting of iron.

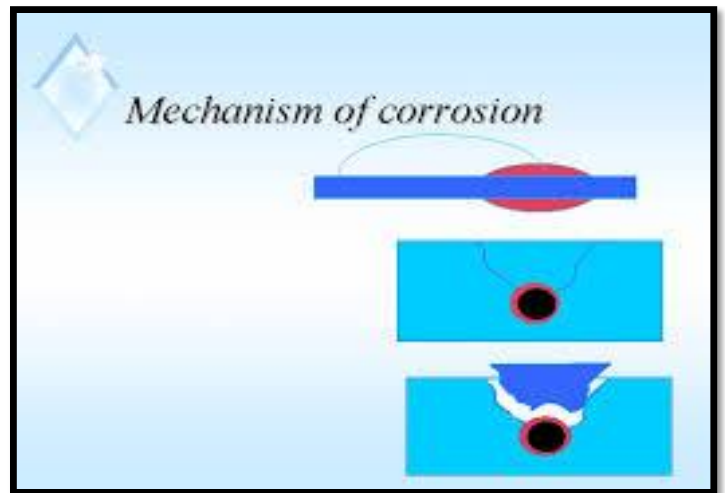
This is not true for all the metals like Zn etc..

Rate of corrosion in absence of Carbon di oxide is also seen.



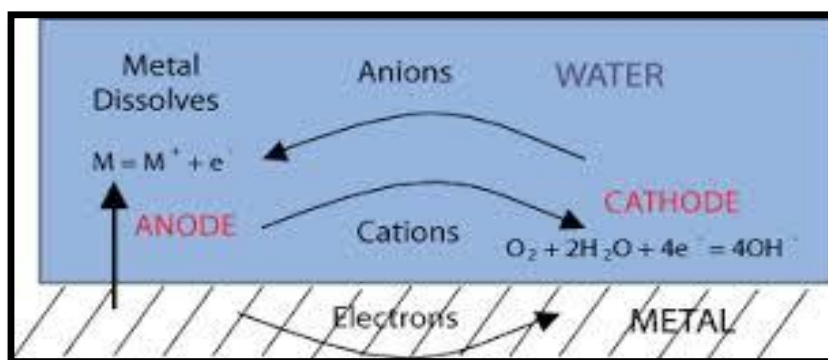
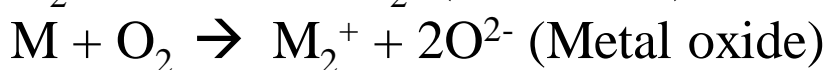
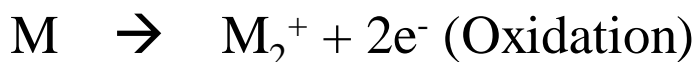
# Dry corrosion or chemical corrosion

- The direct chemical reaction of environment/atmospheric gases or inorganic liquids with metal surfaces .
- There are three types of chemical corrosion
  - i) Oxidation corrosion
  - ii) Corrosion by other gases
  - iii) Liquid metal corrosion



**(1.) Oxidation Corrosion:** This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture.

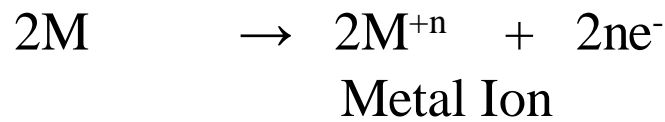
Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).



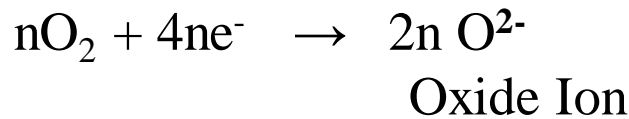


## Mechanism:-

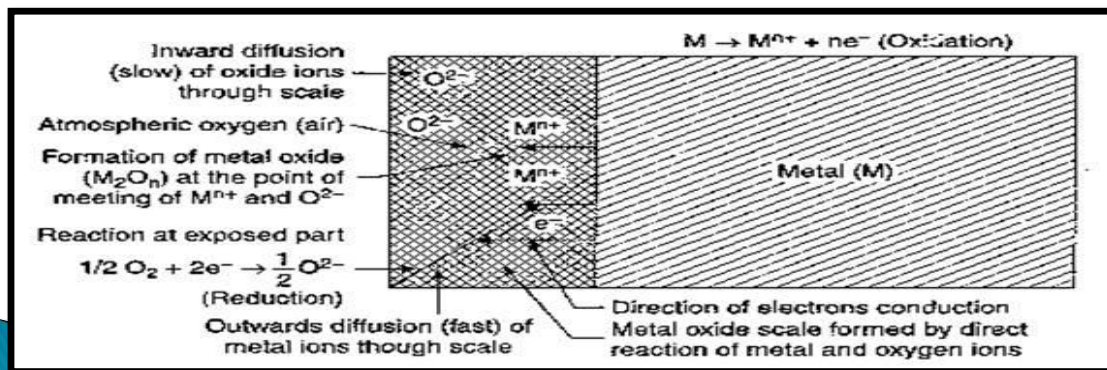
1. When temp increases the metal undergoes oxidation and losses  $e^-$



2. Electron are gained by the oxygen molecules forms oxide ions



3. Scale of metal oxide formed  $2M + nO_2 \rightarrow 2M + 2n O^2$   
Metal Oxide



**2.) Corrosion due to other gases:** This type of corrosion is due to gases like  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{F}_2$  etc. In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous does not allow the penetration of corrosive gases.



(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.


Ex. In petroleum industry,  $\text{H}_2\text{S}$  gas at high temperature reacts with steel forming a FeS scale.  $\text{Fe (steel)} + \text{H}_2\text{S} \rightarrow \text{FeS (porous)}$

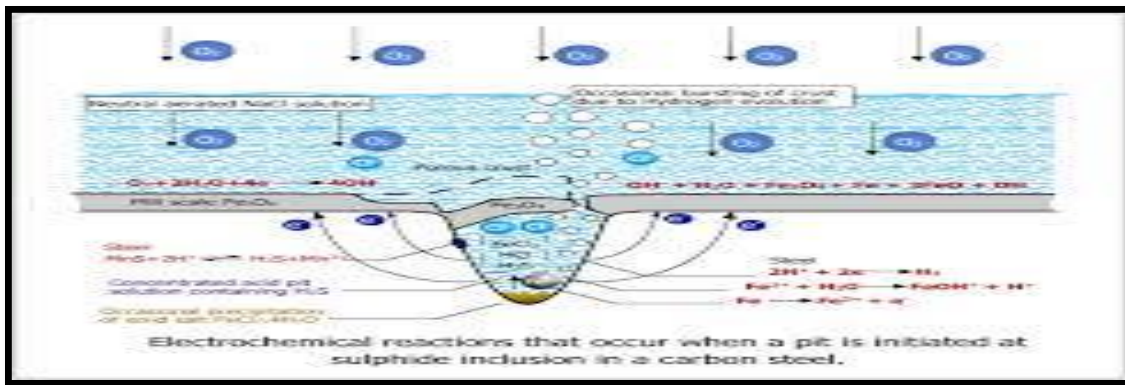
3.) **Liquid metal corrosion:** This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.



# Wet or Electrochemical corrosion

- The electrochemical corrosion occurs when
    - i) a conducting liquid is in contact with a metal.
    - ii) when two dissimilar metals or alloys are immersed partially in the solution.
  - Corrosion occurs due to the presence of anodic and cathodic areas.
  - At anode oxidation reactions takes place
  - At cathode reduction reactions takes place
- 



- Occurs when aqueous solution or liquid electrolytes are present
- Wet corrosion takes place in environments where the relative humidity exceeds 60 %.
- Wet corrosion is most efficient in waters containing salts, such as NaCl (e.g. marine conditions), due to the high conductivity of the solution.

# Mechanism Of Electrochemical Corrosion

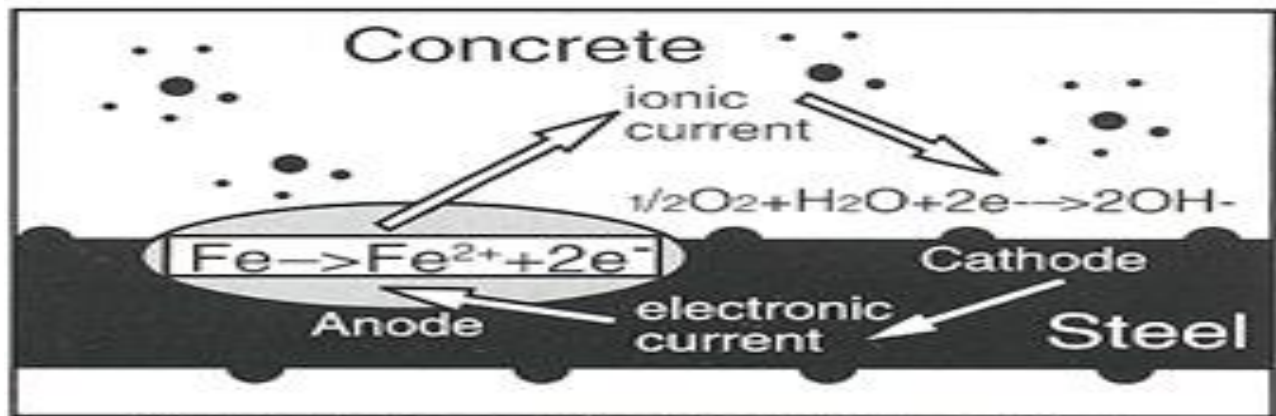


Figure 1: The anodic and cathodic reactions

## Mechanism Of Electrochemical Corrosion

### Anodic Reaction:

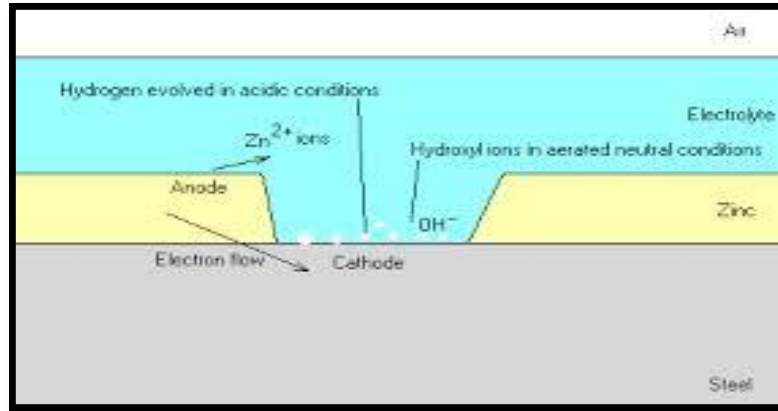
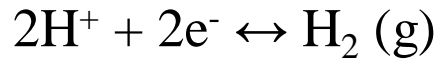
Dissolution of metal takes place.

As result metal ions are formed with the liberation of free electrons.



## Cathodic Reaction

- (i) Hydrogen Evolution :- Occurs usually in acidic medium



- (ii) Oxygen Absorption :- occurs when solution is aerated sufficiently.



# Wet corrosion takes by the following ways.

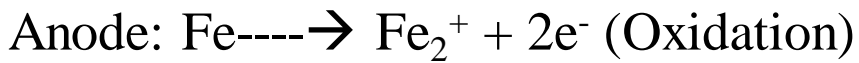
- Hydrogen gas evolution
- Oxygen gas absorption



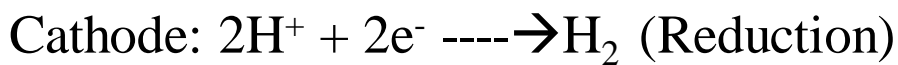


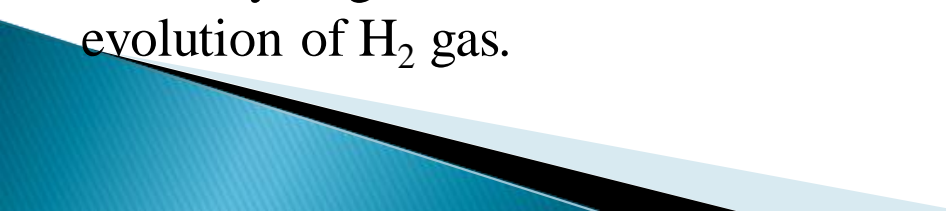
This type of corrosion occurs in acidic medium.

E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

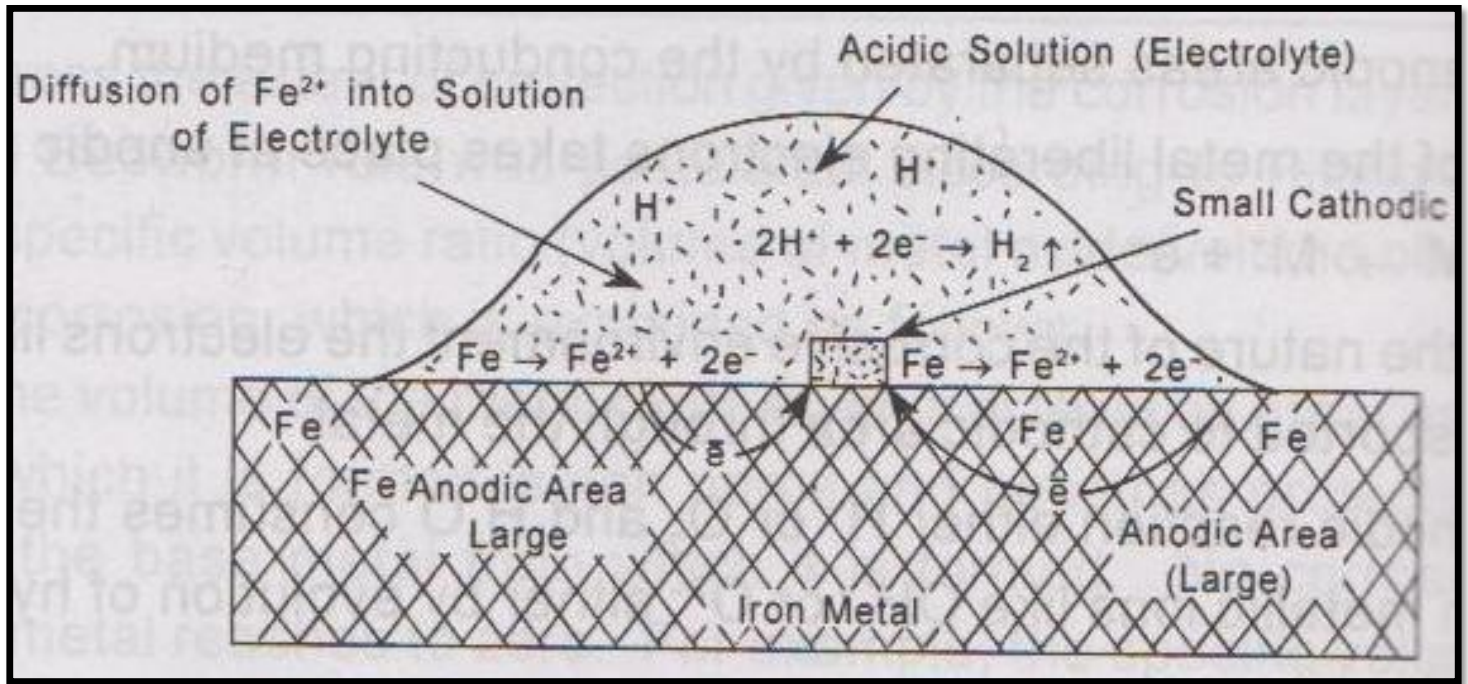


- The electrons released flow through the metal from anode to cathode, whereas  $\text{H}^+$  ions of acidic solution are eliminated as hydrogen gas.



- The overall reaction is:  $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}_2^+ + \text{H}_2$
  - All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of  $\text{H}_2$  gas.
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# Mechanism of wet corrosion by hydrogen evolution



# Absorption of oxygen

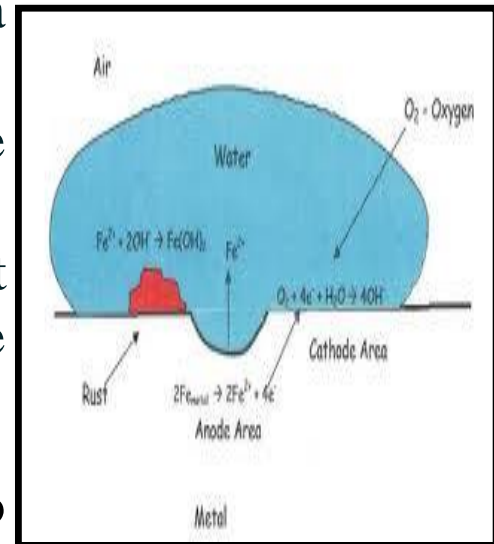
**Absorption of oxygen:** For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen.

➤ Usually the surface of iron is coated with a thin film of iron oxide.

➤ If the film develops cracks, anodic areas are created on the surface.

➤ While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes.

The released electrons flow from anode to cathode through iron metal.

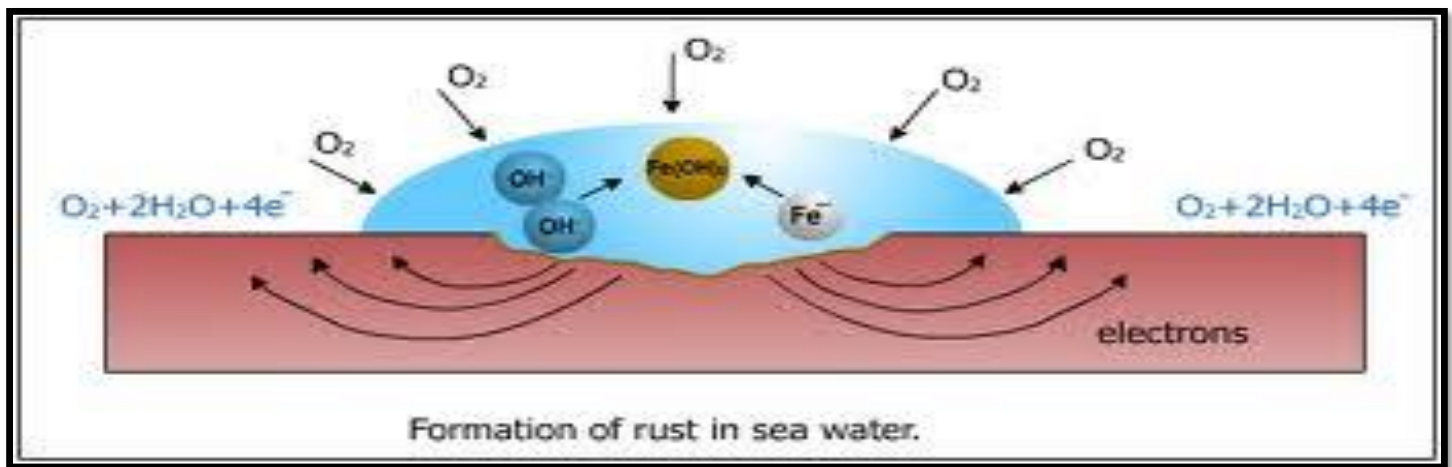


At anode:  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$  (Oxidation)

At cathode:  $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$  (Reduction)

Overall reaction:  $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$

The product called yellow rust corresponds to  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$



# FACTORS EFFECTING THE CORROSION

□ The factors that effect corrosion are

*i)* Nature of the metal

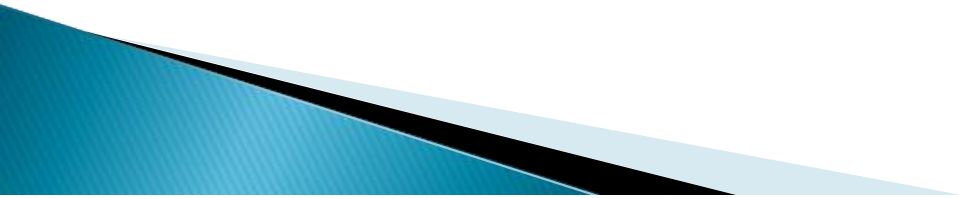
*ii)* Nature of the environment




# *Nature of the metal*

□ The rate and the extent of corrosion depends on the following factors

- A ) Purity of a metal
- B ) Position in galvanic series
- C ) Over voltage
- D ) Nature of oxide film
- E ) Nature of corrosion product



# *Nature of the metal*


- 1. *Purity of the metal:*** Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.
  - 2. *Electrode potentials:*** metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. Whereas the metals with lower reduction potentials readily undergo corrosion (e.g.. Zn, Mg, Al etc.).
  - 3. *Position of metal in Galvanic series:*** Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.
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When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.

The rate of corrosion depends on the difference in their position in Galvanic series. Greater the difference more will be the extent of corrosion at anode.

**4. *Relative areas of anodic and cathodic cells:*** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. *i.e.*, the relative areas of corrosion is influenced by cathodic to anodic cells.


**5. *Physical state of metal:*** Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.






6. ***Hydrogen over voltage:*** when a cathode reaction is hydrogen evolution type, the metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, since the liberation of hydrogen gas is easy at this condition. Hence the cathodic reaction is very fast which in turn makes anodic reaction fast. Hence the rate of corrosion increases. Higher the over voltage, lesser is the corrosion.

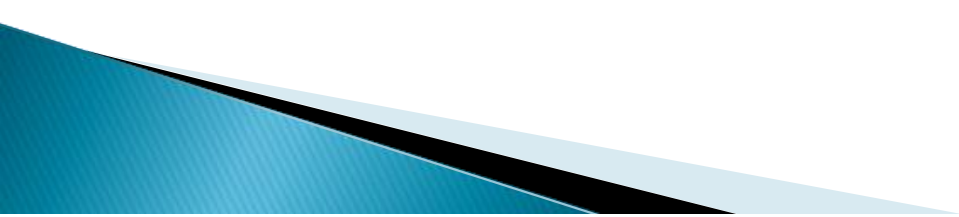
7. ***Nature of surface film:*** If the corrosion product formed is more stable, insoluble and non porous, it acts as protective layer and prevents further corrosion (E.g.. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).



# Nature of the environment

1. Temperature: the rate of corrosion reactions increases with increase in temperature.
  2. Humidity in air: the moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.
  3. Presence of impurities: Atmosphere is contaminated with gases like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ; fumes of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion.
- 

4. pH value: pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.
5. Amount of oxygen in atmosphere: As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.
6. Velocity of ions which flow in the medium: As the velocity of the diffusion of the ions in the medium increases, the rate of corrosion increases .



# CORROSION CONTROL METHODS

The various measures taken for corrosion protection are

I) CATHODIC PROTECTION

II) SURFACE COATINGS



# CATHODIC PROTECTION

- The method of protecting metals and alloys from corrosion making them completely cathode.
- To achieve this auxiliary anode is provided in the corroding medium which is connected to the structure.
- Cathodic protection is of two types
  - i) Sacrificial anodic method
  - ii) Impressed current cathodic method



# Cathodic Protection

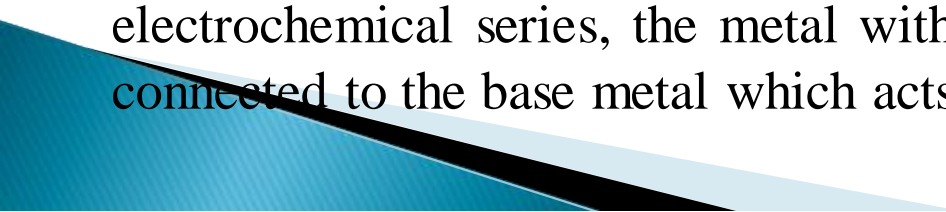
Force the metal to be protected to behave like cathode.

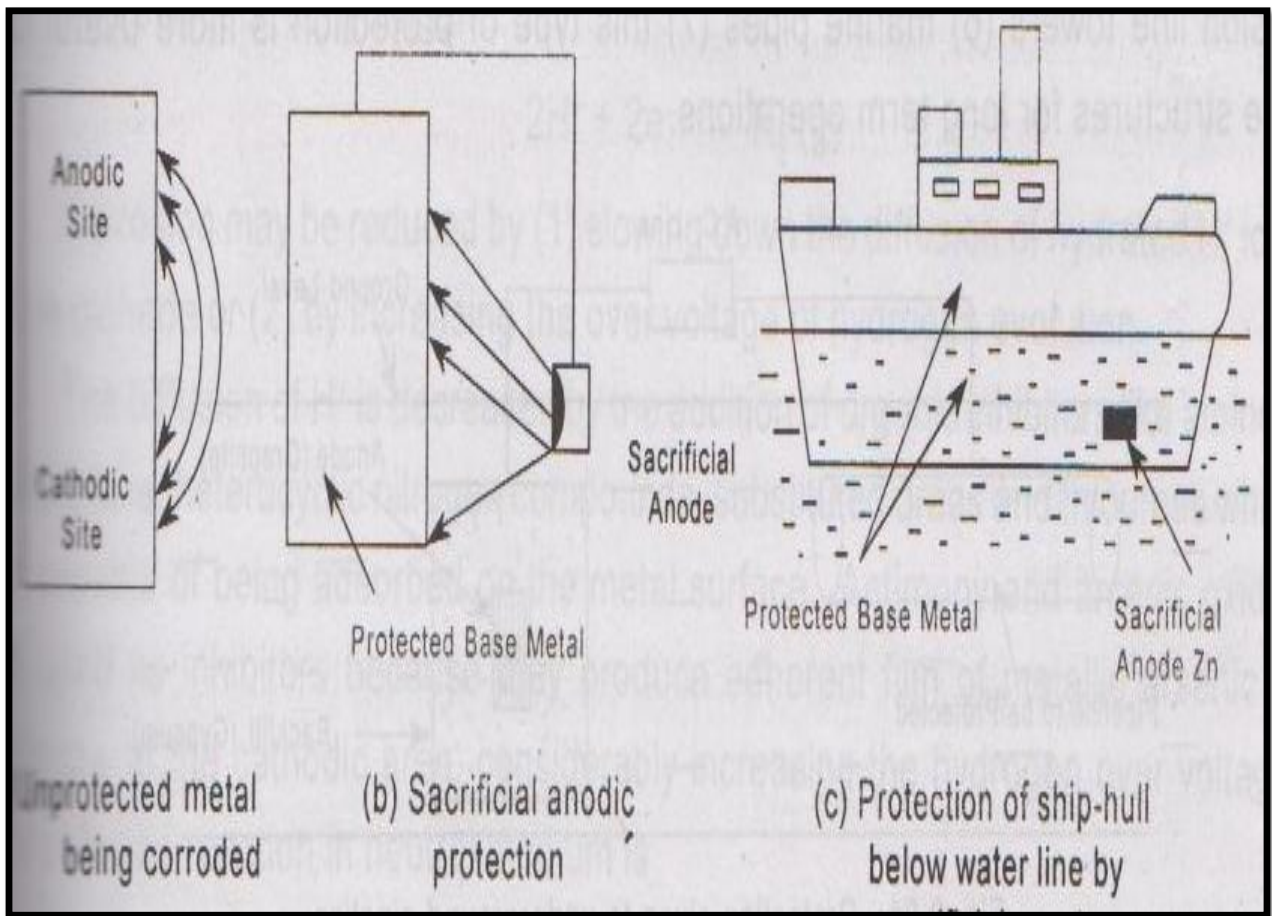
(i) **Sacrificial anodic protection:**

- Metal to be protected from corrosion connected to more anodic metal
- Commonly used metals Mg, Zn, Al and their alloys

Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

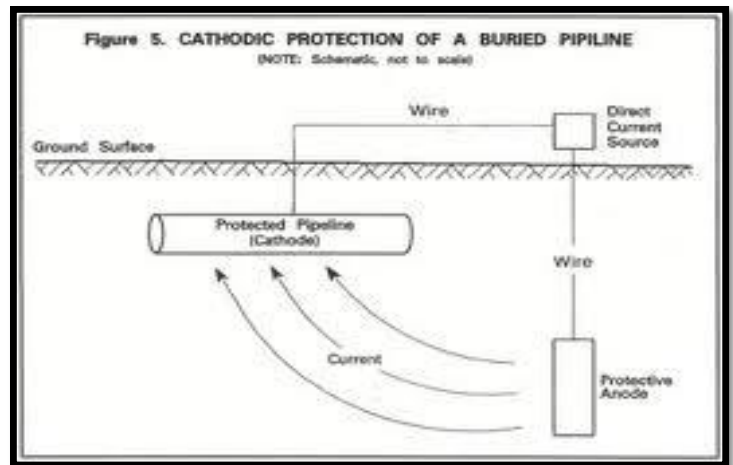
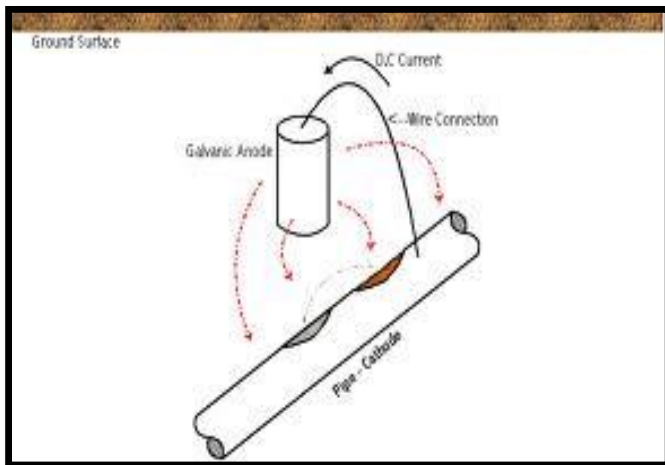
Eg. The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



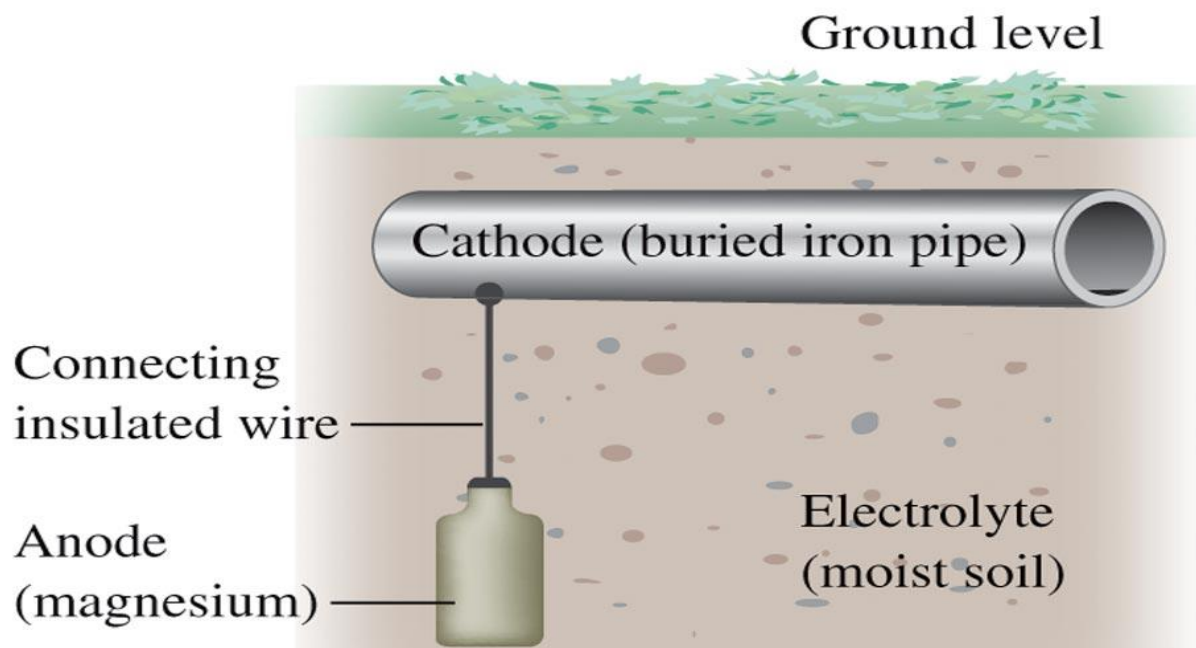


# Impressed current method:

- Direct current is applied in opposite direction to nullify the corrosion current
- Converts the corroding metal from anode to cathode.

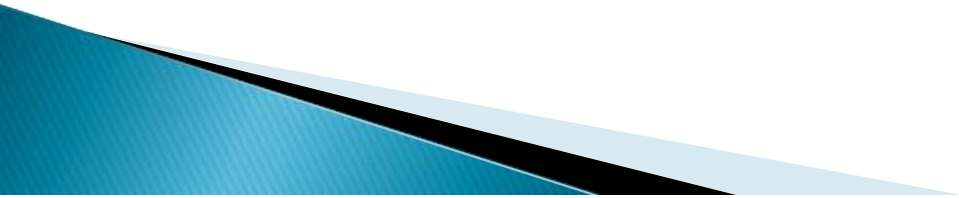






# SURFACE COATINGS

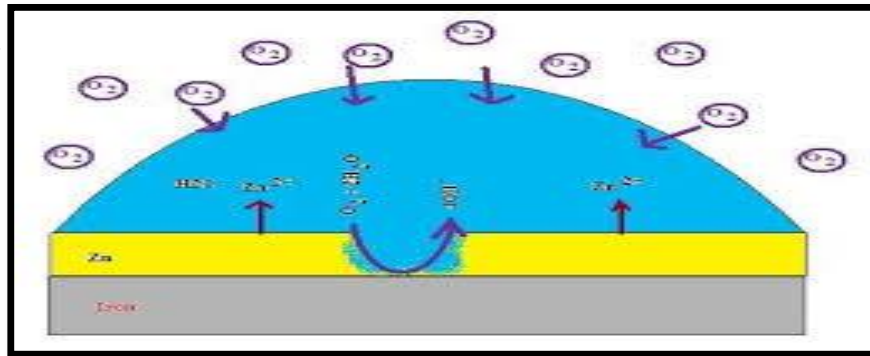
- ▶ The metal surface is covered with a coating to protect it from corrosion.
- ▶ These may be
  - i) Metallic**
  - ii) Organic**



# METALLIC COATINGS


The metals used for coatings may be placed under two categories

i) metals which are anodic to the metal i.e., metals above it in galvanic series.




ii) metals which are cathodic to the metal i.e., metals below it in galvanic series.

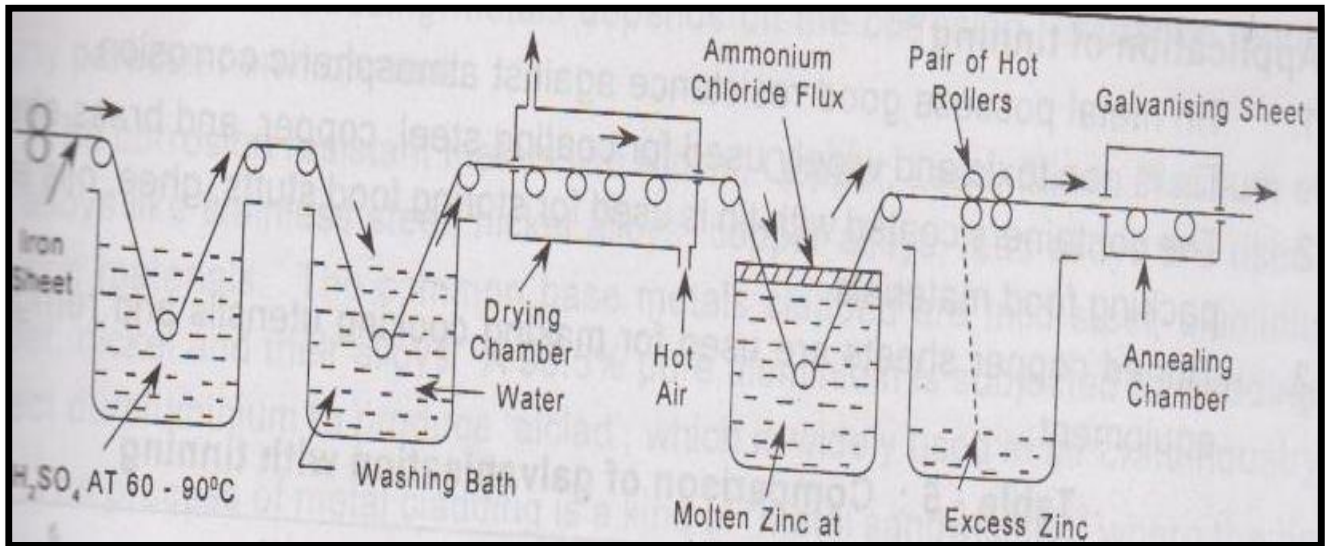
# Methods of applications of metal coatings:

- Hot dipping: This technique is most widely used to control corrosion. Hot dipping is used for producing a coating for low melting metals such as Zn, Sn, pb ,Al.
  - on Iron, steel, copper which are having high melting point usually underwent into corrosion due to their oxidising property.
  - The process in general consisting of immersed a metal in a bath of its molten coating& covered by a molten layer.
  - The flux cleans the base metal& prevent oxidation of metal coating with molten solution.
  - Hot dipping is widely applied either by  
(1)GALVANIZING (2)TINNING
- 

# Galvanizing

- It is the process in which iron or steel is protected from corrosion by coating with a thin layer of zinc.
  - Iron or steel is first cleaned by pickling with dil.  $\text{H}_2\text{SO}_4$  solution for 15-20 mts at  $60^\circ\text{C}$ - $90^\circ\text{C}$ . The steel is then washed well and dried .
  - Then the metal sheet is dipped in bath of molten Zinc maintained at  $425^\circ\text{C}$ - $430^\circ\text{C}$ .  
The surface of bath is kept covered with a  $\text{ZnCl}_2$  flux to prevent oxide formation.
  - Then the metal sheet is passed through a pair of hot rollers which removes excess of Zinc and maintain uniform thickness of Zinc on metal sheet.
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➤The sheet is subjected to annealing process at 650c and cooled slowly.



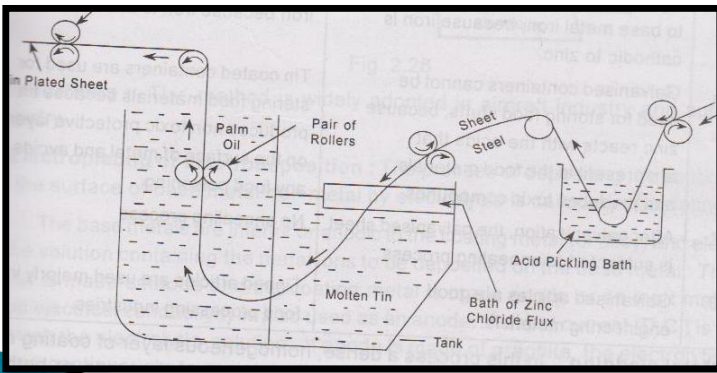
**Uses of Galvanization:** It is used to protect Iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets, and tubes.

**Defects :** Galvanised utensils are not used for cooking because of solubility of Zn.

# TINNING

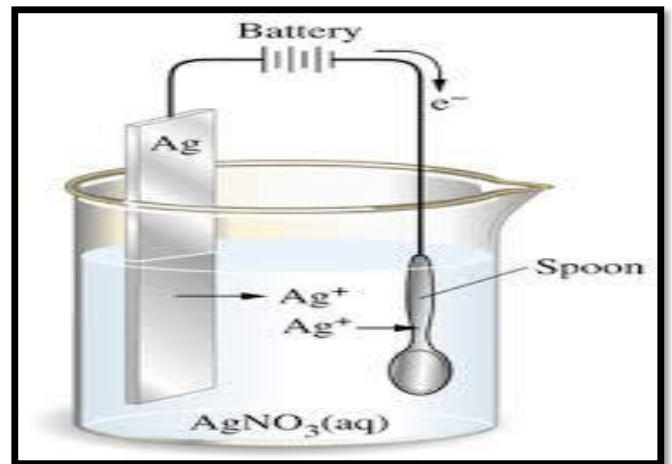
- Tinning is the process of coating of tin over the Iron sheet or steel articles
- A cleaned iron sheet is passed through a bath of molten flux, then passes through a tank of molten tin and finally through a layer of palm oil which protect hot tin coated surface against oxidation.

Uses: (1) It is widely used for coating of steel, copper, brass & bronze etc . It is used to store food stuff, ghee oils, kerosene & pickles and used for refrigerators equipment.




# ELECTROPLATING

- Deposition of coating metal on the base metal by passing direct current through an electrolytic solution which contain the soluble salts of the coating material.
- Pure metal is made as cathode and base metal as anode.
- Electrochemically coat metal is deposited on base metal.
- This metal gives smooth, fine and uniform coating
- It depends on
  - (i) Temperature
  - (ii) Current density
  - (iii) Electrolyte Concentration
  - (iv) Nature of base metal
  - (v) Time






# Applications of Electroplating

- It is most important & frequently used technique in industries to produce metallic coating
  - Both metals & non metals can be electroplated.
  - In metals the electroplating increases resistance to corrosion, chemical attack, hardness, wear resistance and surface properties.
  - In non metals electroplating increases strength and decorates the surface of non metal like plastics, wood, glass.
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# Electroless Ni plating:

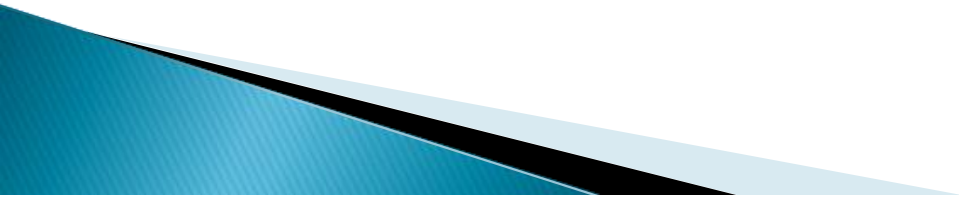
- ❑ Pre treatment of surface:
  - ❑ (1) CO, Ni, steel and Al can be directly plated.
  - ❑ (2) Pb, Cd and Sn are first electroplated with Ni prior to electroless plating.
  - ❑ (3) Non conductors are activated in  $\text{SnCl}_2$  &  $\text{HCl}$  followed by dipping in  $\text{PdCl}_2, \text{HCl}$ . on drying thin pd layer is formed.
- 

# Organic paints



# ORGANIC COATINGS

- ❑ Organic coatings protect the surface as they act as physical barriers between the metal to be protected and the corroding environment and are decorative.
- ❑ The extent of protection given by the organic coatings depends on
  - A) Impermeability to gases ,salts and water
  - B) Chemical inertness to the corrosive environment
  - C) Good surface adhesion



The Organic & Natural  
paint co.



# PAINTS


- ▶ Paints form a protective layer over the surface of the metal to prevent corrosion.

The main constituents of the paints are


- ▶ Pigment
- ▶ Vehicle
- ▶ Thinner
- ▶ Driers
- ▶ Fillers
- ▶ Plasticizers
- ▶ Anti skinning agents



# Pigment

- It is a solid constituent that obscures the surface and provides a decorative color.
  - A liquid binds the pigment to the surface and protects it from decay.
  - It usually comprises of 60 to 80% of the weight of the paint film.
  - Increases the life of paint film since it prevents the entry of ultra violet rays.
  - E.g.; lead oxide, red lead, lead chromate etc.,
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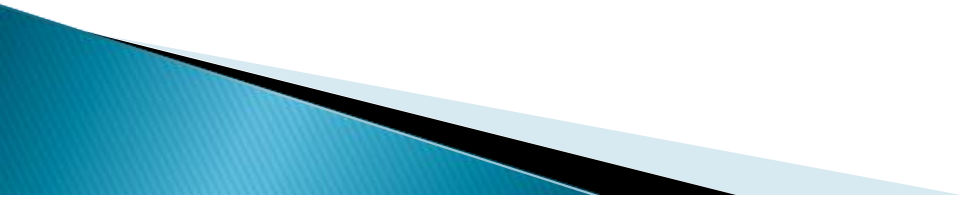
# Vehicle

- Film forming constituent of the paint.
  - They hold the pigment on the metal surface.
  - They give metal adhesion to the metal surface.
  - They impart durability and toughness to the film.
  - They isomerize , polymerize and condense to form characteristic tough, elastic ,coherent, highly cross linked structured macromolecular film.
  - E.g.: mustard and sunflower oil etc.,
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# Thinners


- ❑ Viscosity is reduced by the addition of thinners.
- ❑ It is a volatile solvent helps to adjust the consistency of the paint.
- ❑ Thinner being volatile evaporates.
- ❑ They remain permanently in paints and varnishes.
- ❑ They improve elasticity of the film.
- ❑ They suspend the pigments in the paints.  
E.g. Turpentine, mineral spirits, xylol, kerosene.



# Fillers

- ❑ They are inert materials.
  - ❑ They are used to improve the properties of the paints.
  - ❑ They reduce the cost of paints.
  - ❑ They serve to fill the voids in the film.
  - ❑ Increases the random arrangement of pigment particles.
  - ❑ Improves the durability of the film.
  - ❑ E.g.: talc, chalk, silica etc.,
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# Driers

- ▣ Drying of the oil film is accelerated or catalyzed by driers.
  - ▣ To reduce the drying time a drier is added.
  - ▣ They are oxygen carrier catalyst.
  - ▣ To improve the drying quality of oil film.
  - ▣ This is done by condensation , oxidation and polymerization.  
E.g. linoleates , borates, resinates etc.,
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# Plasticizers & Anti skinning agents

- ▣ They remain permanently in paints and varnishes.
- ▣ They improve elasticity of the film.
- ▣ To prevent cracking of the film.
- ▣ Anti skinning agents prevent the gelling and skinning of the paint film.

E.g.: tricresyl phosphate, tri phenyl phosphate,  
di butyl tartarate etc.,

