



# METALLIC CORROSION

# METALLIC CORROSION

**Definition:** The loss of metals/alloys or their useful properties by their chemical or electrochemical interaction with its environment is known as corrosion.

- Corrosion is the reverse process of metallurgy.

For Example:

- Rusting of iron,
- Tarnishing and blackening of silver articles and
- Dulling of brass etc.

# Cause of Corrosion:

In nature, most of the metals exist in combined state as their compounds called ores or minerals. These compounds represent their thermodynamically stable state.

The metals are extracted from these ores after expending a lot of energy. These pure metals have a natural tendency to convert back to their natural stable states, i.e. combined state. This is the basic reason for metallic corrosion.

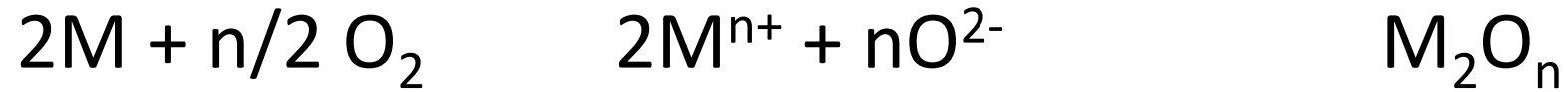
# THEORIES OF CORROSION

1. Dry Corrosion Theory
2. Wet Corrosion Theory

# TYPES OF DRY/CHEMICAL CORROSION

- Oxidation Corrosion
- Corrosion by other gases
- Liquid metal corrosion

- **Oxidation Corrosion:** When corrosion takes place by direct action of oxygen on metal in absence of aqueous medium to form an oxide layer on the metal.



The nature of oxide film can be stable, unstable, volatile or porous.

**Pilling Bedworth Rule:** The oxide layer can be protective or non-protective depending upon the ratio of volume of the metal oxide to the volume of the metal consumed. This is known as Pilling Bedworth Ratio.

Pilling Bedworth Ratio = Volume of Metal Oxide formed / Volume of metal consumed



- According to this rule,
- If Volume of Metal Oxide formed  $<$  Volume of metal, the ratio  $< 1$  i.e. the layer is non-protective and porous. Here oxygen can diffuse through these pores.

For e.g. alkali and alkaline earth metals

- If Volume of Metal Oxide formed  $>$  or  $=$  Volume of metal, the ratio  $>$  or  $= 1$  i.e. the layer is protective, non-porous and continuous. Here the further corrosion decreases.
- For e.g. Al, Cr & W.

- **Corrosion by Other gases:** Gases other than oxygen like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{F}_2$  etc. can also have corrosive effect on metals.
- For e.g.  $\text{Fe(s)} + \text{H}_2\text{S} \longrightarrow \text{FeS (ppt)} + \text{H}_2 \text{ (g)}$
- Corrosion by Liquid Metals:
- Sometimes, corrosion takes place due to the action of flowing liquid metal at high temperatures on solid metals or alloys. Liquid sodium causes corrosion in carrier tubes in nuclear reactors.

**WET THEORY OF CORROSION**  
**OR**  
**ELECTROCHEMICAL THEORY OF**  
**CORROSION**

## The necessary conditions:

- (i) The formation of anodic and cathodic areas.
- (ii) The electrical contact between cathodic and anodic areas to enable the conduction of electrons.
- (iii) An electrolyte through which the ions can diffuse or migrate. This is usually provided by moisture.

**Mechanism:** Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.



The cathodic reaction consumes these electrons with either of the following mechanisms depending upon the nature of corrosive environment:

- (a) Evolution of hydrogen or
- (b) Absorption of oxygen

## (a) Evolution of Hydrogen Gas:

- This type of corrosion occurs in **acidic medium** in absence of  $O_2$  e.g., considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions ( $Fe^{2+}$ ) with liberation of electrons.
- These electrons flow through the metal from anode to cathode, whereas  $H^+$  ions of acidic solution are eliminated as hydrogen gas.

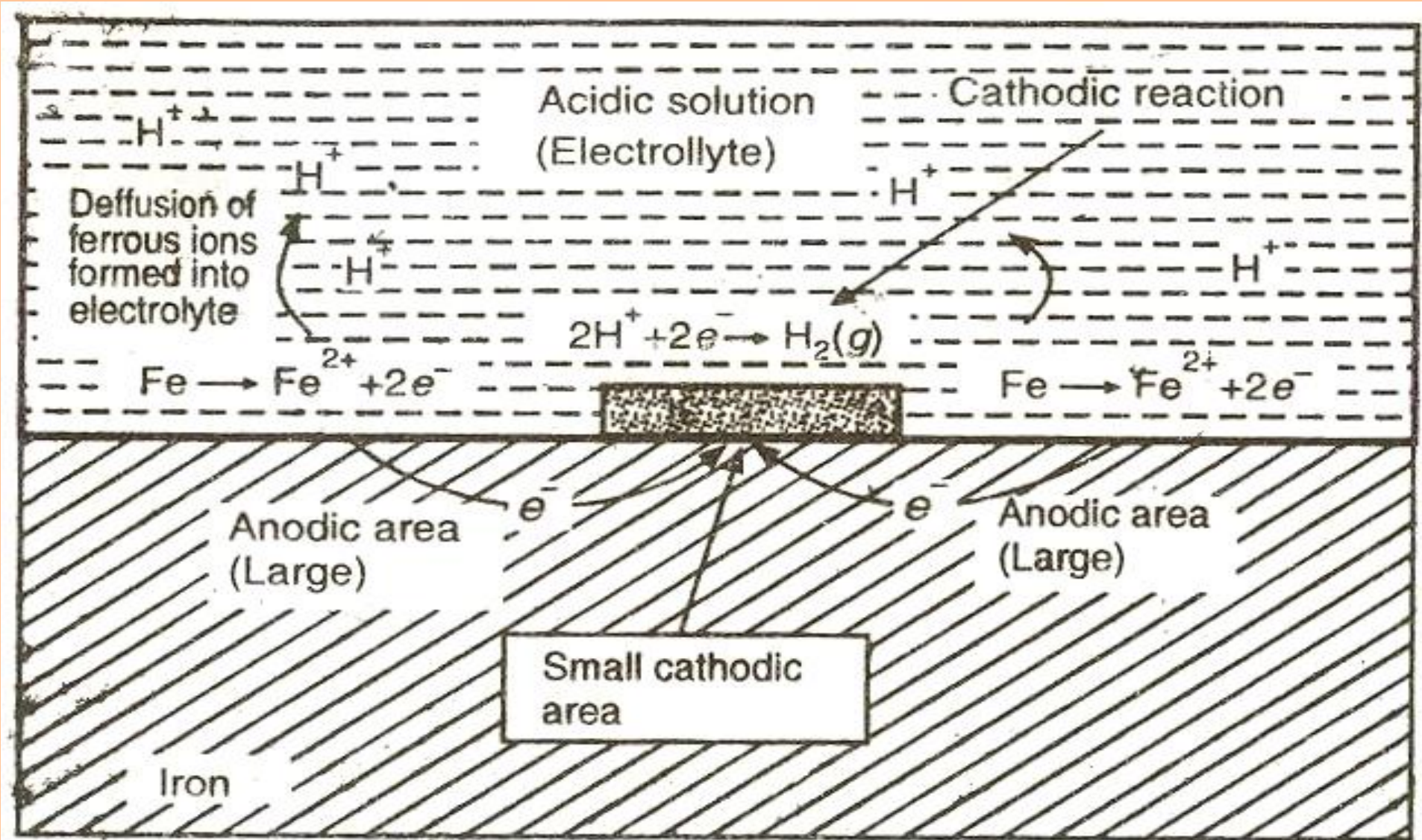


➤ This type of corrosion causes displacement of hydrogen ions from the acidic solution by metal ions.

- All the metals having lower reduction potential ( $E^0$ ) than hydrogen have a tendency to get dissolved in acidic solution with simultaneous evolution of  $H_2$  gas.
- The anodes are large areas, whereas cathodes are small areas.



# Rusting of iron by $H_2$ evolution :



## (b) Absorption of oxygen:

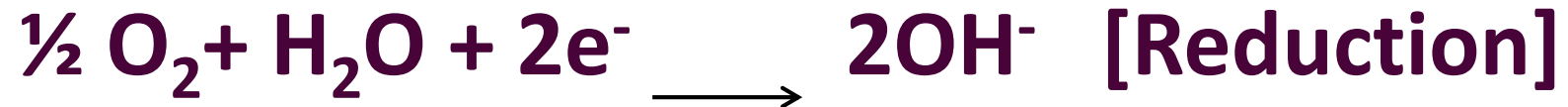
- This type of corrosion takes in presence of oxygen.
- For example, rusting of iron **in neutral aqueous solution of electrolytes** in presence of atmospheric oxygen.
- Usually the surface of iron is coated with a thin film of iron oxide.

- If the film present on the metal surface develops some cracks, anodic areas get created on the surface while the well metal parts act as cathodes.
- Here, the anodes are small areas, while the rest metallic part behaves as large cathode.

At anode:



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



(a) If oxygen is present in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.

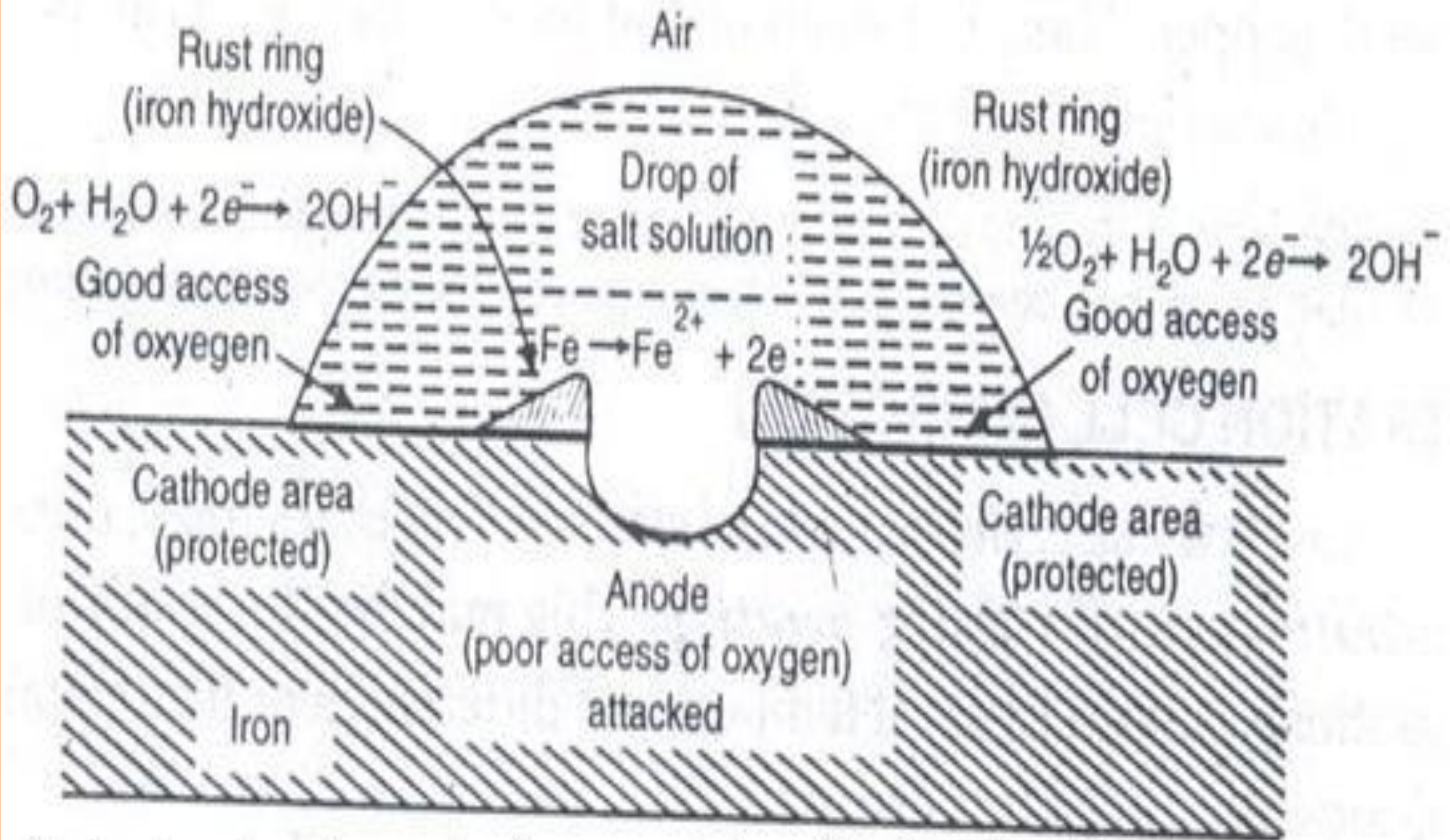


The product is called **yellow rust** and it corresponds to  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  (**Haematite**).

(b) If limited supply of oxygen is present, **black magnetite** (anhydrous ferrous ferric oxide;  $\text{Fe}_3\text{O}_4$ ) is formed.



# Rusting of iron by $O_2$ absorption :

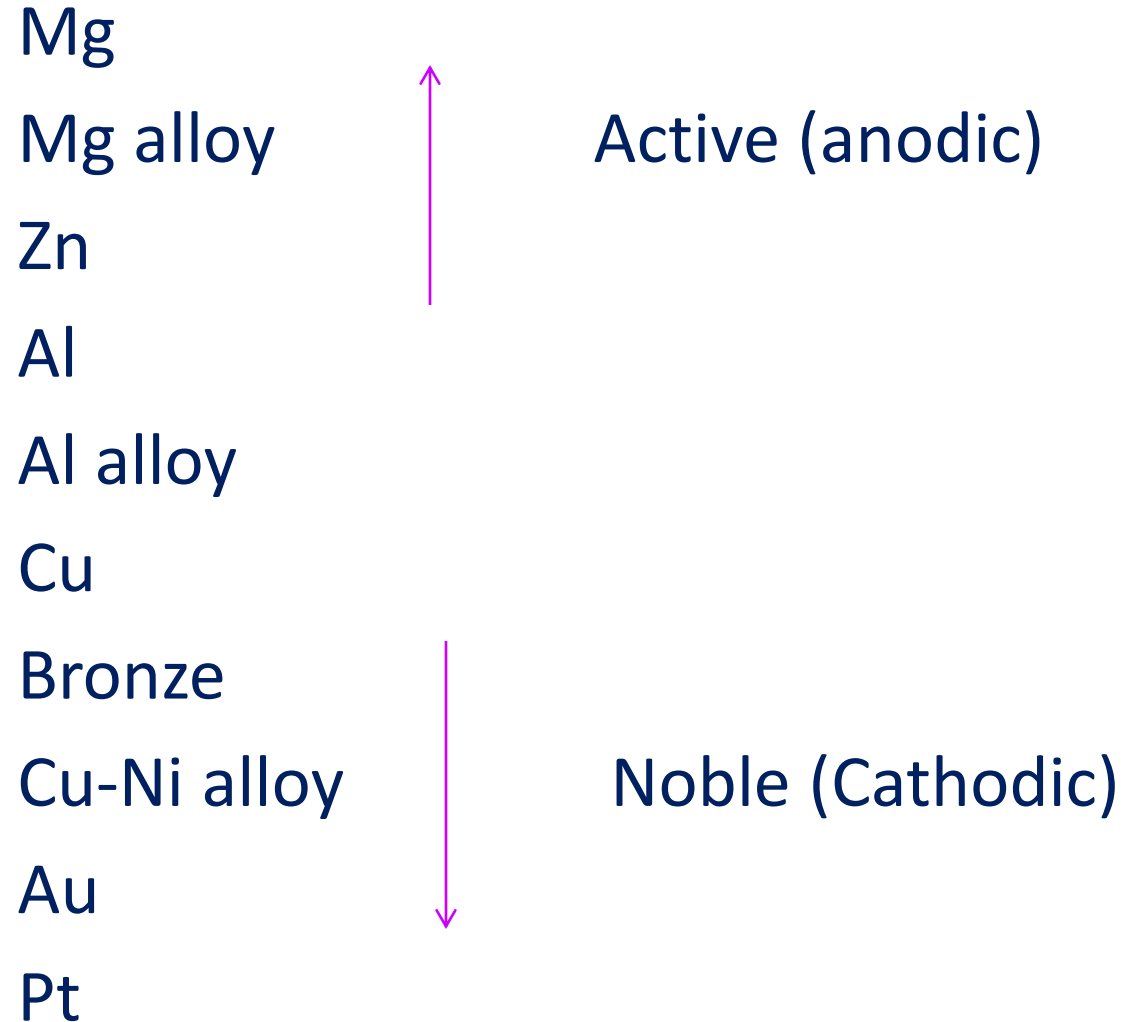


*Mechanism of wet corrosion by oxygen adsorption ( rusting of iron)*

# Galvanic Series

- Oxidation potential measurements of various metals and alloys have been made using standard calomel electrode as the reference electrode and immersing them in sea water.
- These are arranged in decreasing order of activity and this series is known as the **Galvanic series**.
- This series gives more practical information on the relative corrosion tendencies of different metals and their alloys.
- The speed and severity of corrosion depends upon the difference in potential between the anodic and cathodic metals in contact.

- It is used to provide sufficient information predicting the corrosion behaviour in a particular set of environmental conditions.





# **Factors Affecting Corrosion:**

Corrosion of metal prominently depends on:

- (i) Nature of metal**
- (ii) Nature of environment**

# (i) Nature of Metal:

**(a) Relative areas of cathodic to anodic parts:** Small anodic area and large cathodic area gives rise to an intense localized corrosion. This is because the demand for electrons by large cathodic areas can be met by smaller anodic areas by undergoing corrosion more rapidly. For e.g. Steel rivets in Cu sheets

**(b) Impurities:** Impurities present in metal enhance the rate of corrosion by forming minute electrochemical cells under suitable environmental conditions and the anodic parts undergo corrosion.

**(c) Position in Galvanic Series:** The metal or alloys which are placed at higher position in the series are more reactive, thus undergoes corrosion. The greater the potential difference between the two metals coupled together, the greater is the rate of corrosion.

**(d) Nature of Oxide film:** All metals get covered by a very thin film of oxide. Greater the specific volume ratio of oxide film, lesser is the rate of corrosion. [Specific volume ratio is the ratio of volume of metal oxide layer to that of metal]

**(e) Volatility of corrosion product:** When the corrosion product is volatile, it volatilizes as soon as it is formed, thus exposing the underlying metal surface for further attack. Hence in such a case, corrosion goes on increasing with time.

**(f) Solubility of corrosion product:** If the corrosion product is soluble in corroding medium, corrosion becomes faster while if it is insoluble, it forms insoluble product which functions as a physical barrier and suppresses the rate of corrosion.

## (ii) Nature of Environment:

- (a) Effect of Temperature:** Increase in temperature increases the rate of corrosion as well as rate of diffusion.
- (b) Effect of pH:** Corrosion is more in acidic media ( $\text{pH} < 7$ ) than in alkaline media ( $\text{pH} > 7$ ) and neutral media ( $\text{pH} = 7$ ).
- (c) Effect of Corroding medium:** Higher the conductance of the corroding medium, more is the rate of corrosion.

**(d) Effect of Concentration of oxygen:** The rate of corrosion increases in presence of oxygen through differential aeration. The region where concentration of  $O_2$  is less becomes anodic and suffers corrosion.

**(e) Humidity:** It acts as a very good solvent for oxygen and form electrochemical cell. This rapidly increases the rate of corrosion.

**(f) Presence of impurities in atmospheres:** Atmosphere in the vicinity of the industrial area contains corrosive gases like  $CO_2$ ,  $SO_2$ , Fumes of  $HCl$ ,  $H_2SO_4$  etc which increases rate of corrosion due to their acidic nature.

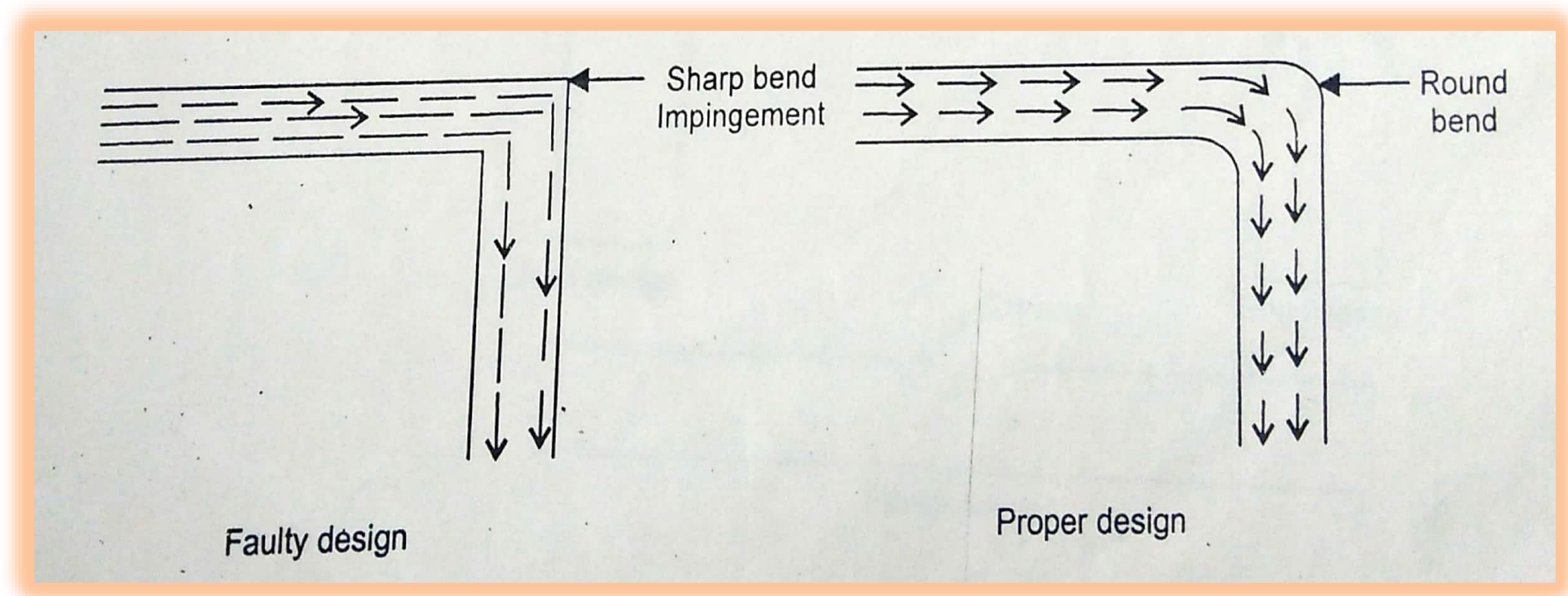
# Corrosion control methods (Prevention from Corrosion):

The corrosion control methods are as follows:

1. Proper selection and designing
2. Modification in Properties of Metal
3. Modification of Environment:
4. Protective Coatings
5. Cathodic Protection

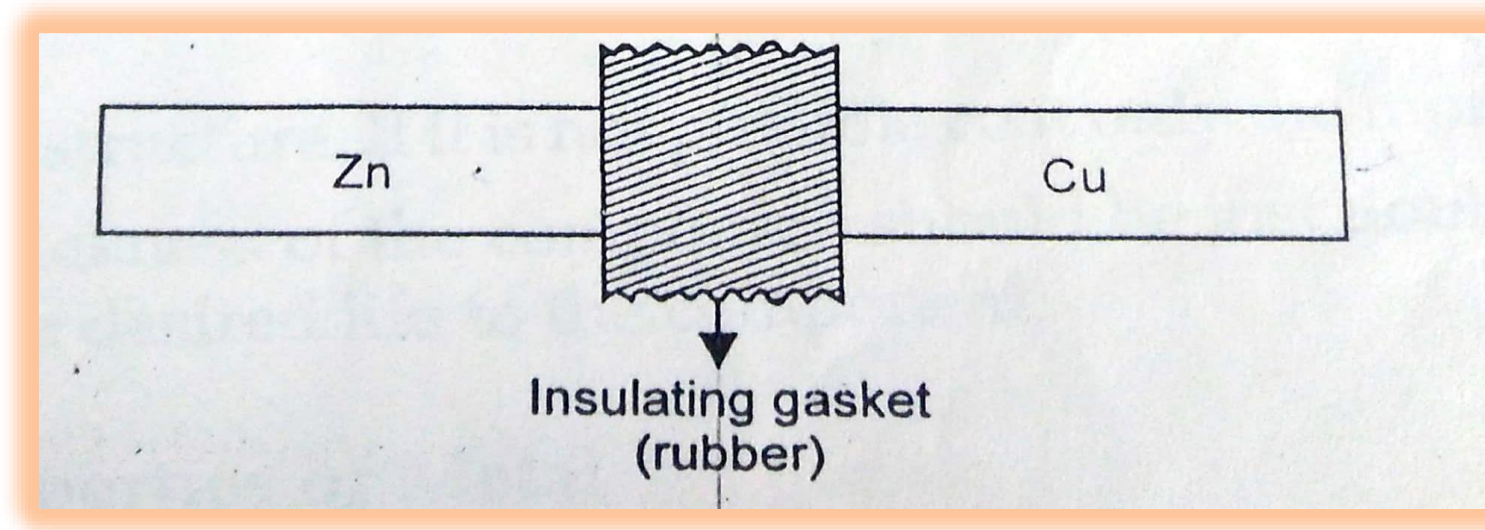
# 1. Proper selection and designing:

- Avoid sharp bends and corners in the flowing systems to reduce impingement.

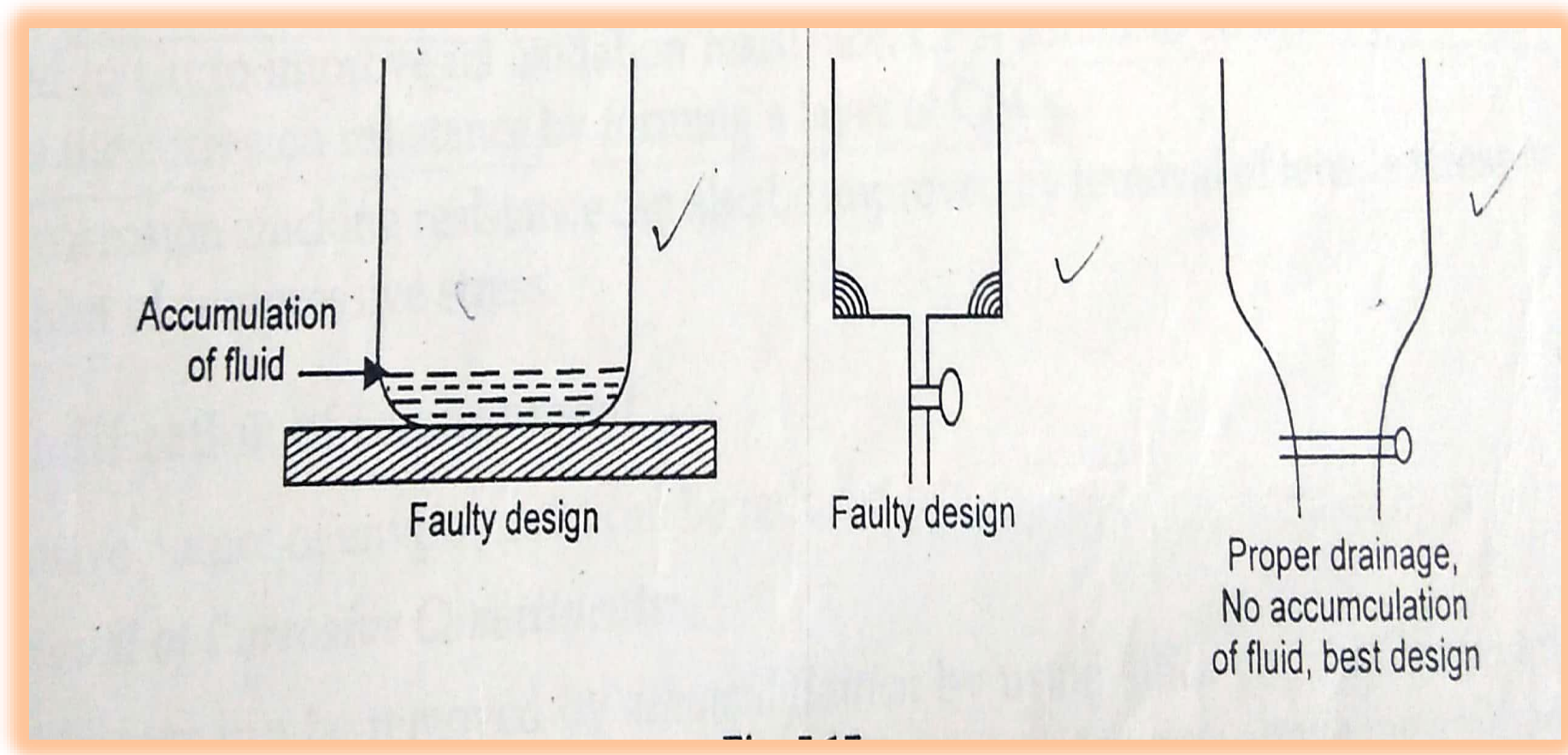




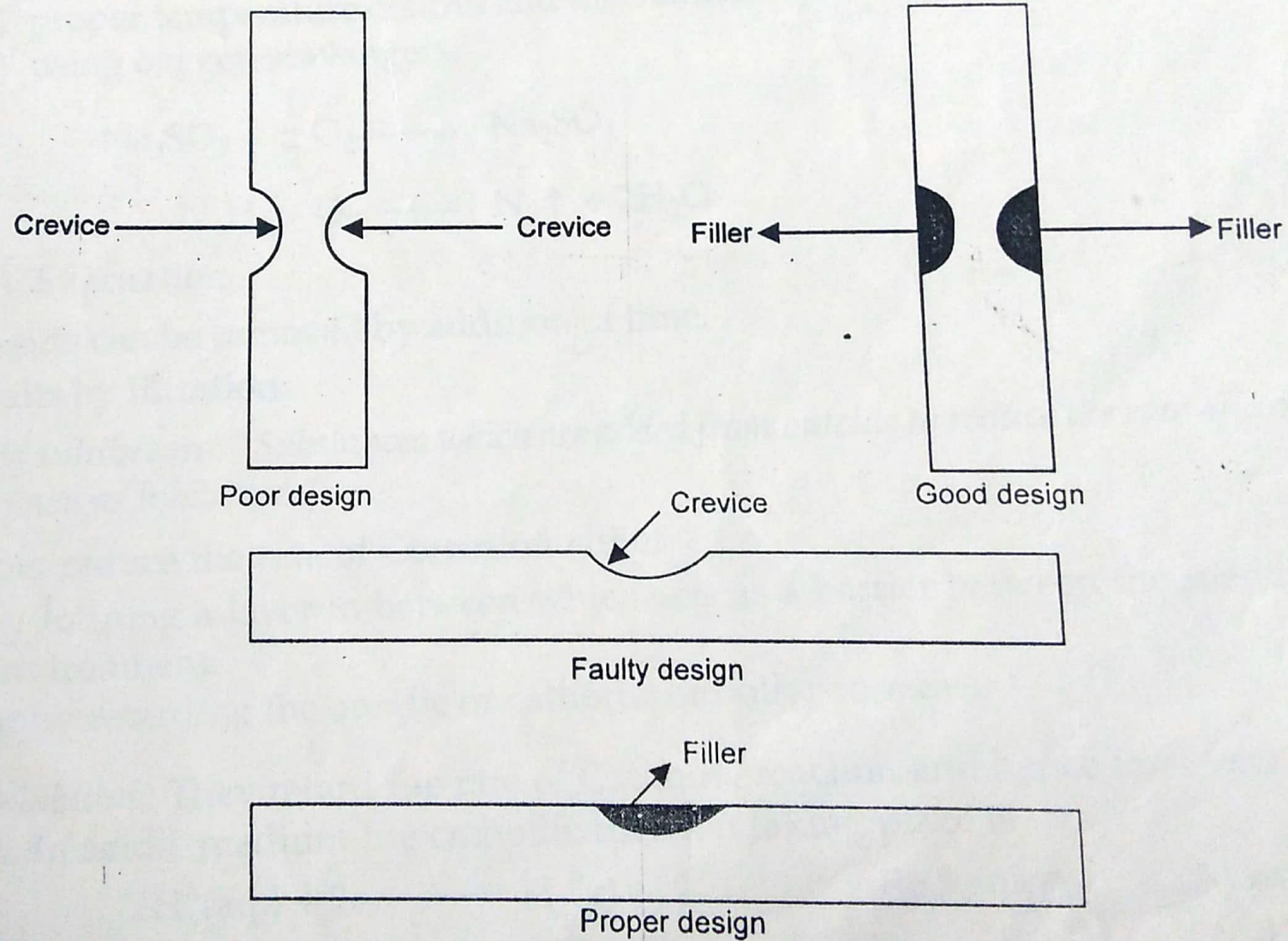
- Avoid galvanic coupling either by using **insulating gasket** between them or by selecting pair of metals which are **closer to each other in galvanic series**.



## ➤ Proper drainage of fluid



## ➤ Avoid crevices in structures



- Avoid small anodic area and large cathodic area.
- Coat the entire structure.
- Increase the wall thickness of the structure.

## 2. Modification in Properties of Metal:

The resistance of a metallic material can be improved by changing its composition by any of these three methods:

**(a) Refining**

**(b) Alloying**

**(c) Annealing**

**(a) Refining:** Means decreasing the concentration of impurities. For e.g. lowering of sulphur, phosphorus, and carbon in steel increases the corrosion resistance of steel.

**(b) Alloying:** Alloying is often used to improve the corrosion resistance of the metals. For e.g. Al, Mg, Be etc. are added to Cu for the improvement of its corrosion resistance. Cr is added to stainless steel. It forms a layer of  $\text{Cr}_2\text{O}_3$ .

**(c) Annealing:** It is a heat treatment given to metals to remove the residual stresses.

### 3. Modification of Environment:

The corrosive nature of environment can be reduced by:

- (a) Removal of Corrosive Constituents**
- (b) Use of Inhibitors**

### **(a) Removal of Corrosive Constituents:**

(i) Moisture: can be removed by dehumidification by using silica gel etc. or by increasing the temperature to 5-6 °C of the storing area above the ambient temperature.

(ii) Oxygen: can be removed by deaeration by mechanical agitation or by using oxygen scavengers like  $\text{Na}_2\text{SO}_3$  etc.

(iii) Acids: can be removed by addition of lime.

(iv) Salts: can be removed by filtration.



## **(b) Use of Inhibitors:**

Substances which are added from outside to reduce the rate of corrosion are known as inhibitors. The inhibitors reduce the rate of corrosion either:

- By retarding the rate of anodic or cathodic processes or
- By forming a layer in between the metal and environment which acts as a barrier.

The inhibitors can be of following types: Cathodic Inhibitors, Anodic Inhibitors and Vapour phase inhibitors

**Cathodic Inhibitors:** They retard the rate of cathodic reaction and hence, the overall rate of corrosion is reduced. **In acidic medium** the cathodic reaction take place as:



Organic cathodic inhibitors like amines, mercaptans, substituted ureas and thioureas having lone pairs of electrons reduce the rate of cathodic reaction by reacting with  $\text{H}^+$ .

**In neutral electrolytic solution;**



(i) The formation of  $\text{OH}^-$  ions can be stopped by adding reducing agent like  $\text{Na}_2\text{SO}_3$  or by deaeration. By these ways diffusion of  $\text{O}_2$  is stopped towards cathode.

(ii) Another way is by adding Zn, Ni, or Mg salts which react with  $\text{OH}^-$  at cathode to form impermeable barrier over cathode, thus they retard diffusion of  $\text{O}_2$  to cathode.

- **Anodic Inhibitors:** Inhibitors which retard the rate of anodic reaction by reacting with the ions present at anode, are known as Anodic Inhibitors. They form a layer in between metal and the environment.
- e.g. alkalis, chromates, phosphates, tungstates, are generally used as anodic inhibitors.
- Vapour phase Inhibitors: These are organic inhibitors which readily sublime and form a protective layer on the surface of metal.
- For e.g. dicyclohexylammonium nitrite is used for the protection of machineries and sophisticated equipments.

## 4. Protective Coatings:

An important method for protecting a metal from corrosion is to apply a protective coating. The protective coatings may be metallic, inorganic or organic. The coated surface isolates the metal from the corroding medium. The coating applied must be chemically inert towards the environment. Coating can be of three types:

- (a) Metallic Coatings
- (b) Organic Coating
- (c) Inorganic Coating

## (a) Metallic Coatings

Metallic coatings are applied on iron and steel. It is done by Electrolysis in an electrolytic cell using direct current. The electrolytic solution of metal ion whose coating is to be provided is electrolyzed and the metal which is to be coated is made cathode.

The anode may be inert material or the coating metal itself. On electrolysis the cathode will be coated up. Metallic coating may be of two types:

## S.No. Sacrificial Coating

1. Base Metal is coated with a metal which is more reactive than the base metal.
2. Protects the underlying base metal sacrificially.
3. Known as Anodic Coating as the reduction potential of coating metal is less than that of the base metal.
4. If pores or breaks develop in such a coating, the base metal remains protected till all the coating metal is consumed.
5. Zn, Cd, Al are generally used as sacrificial coating.
6. e.g. Coating of Zn on iron i.e. Galvanized iron

## Noble Coating

Base Metal is coated with a metal which is nobler than the base metal.

Protects the underlying base metal. It has noble character and higher corrosion resistance..

Known as Cathodic Coating as the reduction potential of coating metal is more than that of the base metal.

If pores or breaks develop in such a coating, localized intense corrosion takes place because of small anodic area and large cathodic area therefore, multiple layers of coating is preferred.

Ni, Ag, Cr, Pb, Au are generally used as noble coating.

e.g. Coating of Sn on Fe

## Galvanization

Galvanization is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc. It is an example of anodic coatings

## Tinning

It is the process of coating Sn over Fe or steel articles by immersing it in molten Sn. The process of coating tin over the iron or steel articles to protect it from corrosion is known as **tinning**. It is an example of cathodic coatings.



## **(b) Organic Coatings:**

These are inert organic barriers like paints, varnishes and plastics etc. applied on metallic surface and constructional materials for corrosion prevention and decoration both. For e.g.

Paint = Pigment (particles of metal oxides) + Vehicle (liquid containing drier, thinner, binder)

**(c) Inorganic Coating:** These are also known as chemical conversion coating and are inorganic surface barriers, produced by chemical or electrochemical reaction at the surface of base metal. Many of these coatings are particularly useful to serve as excellent bases for the application of paints, enamels and other protective coatings.

The most commonly used surface conversion coatings are chromate coatings, phosphate coatings and chemical oxide (e.g. coating obtained by treating of base metal with alk.  $K_2Cr_2O_7$ ) coatings applied on the surface of metals

## 5. Cathodic Protection:

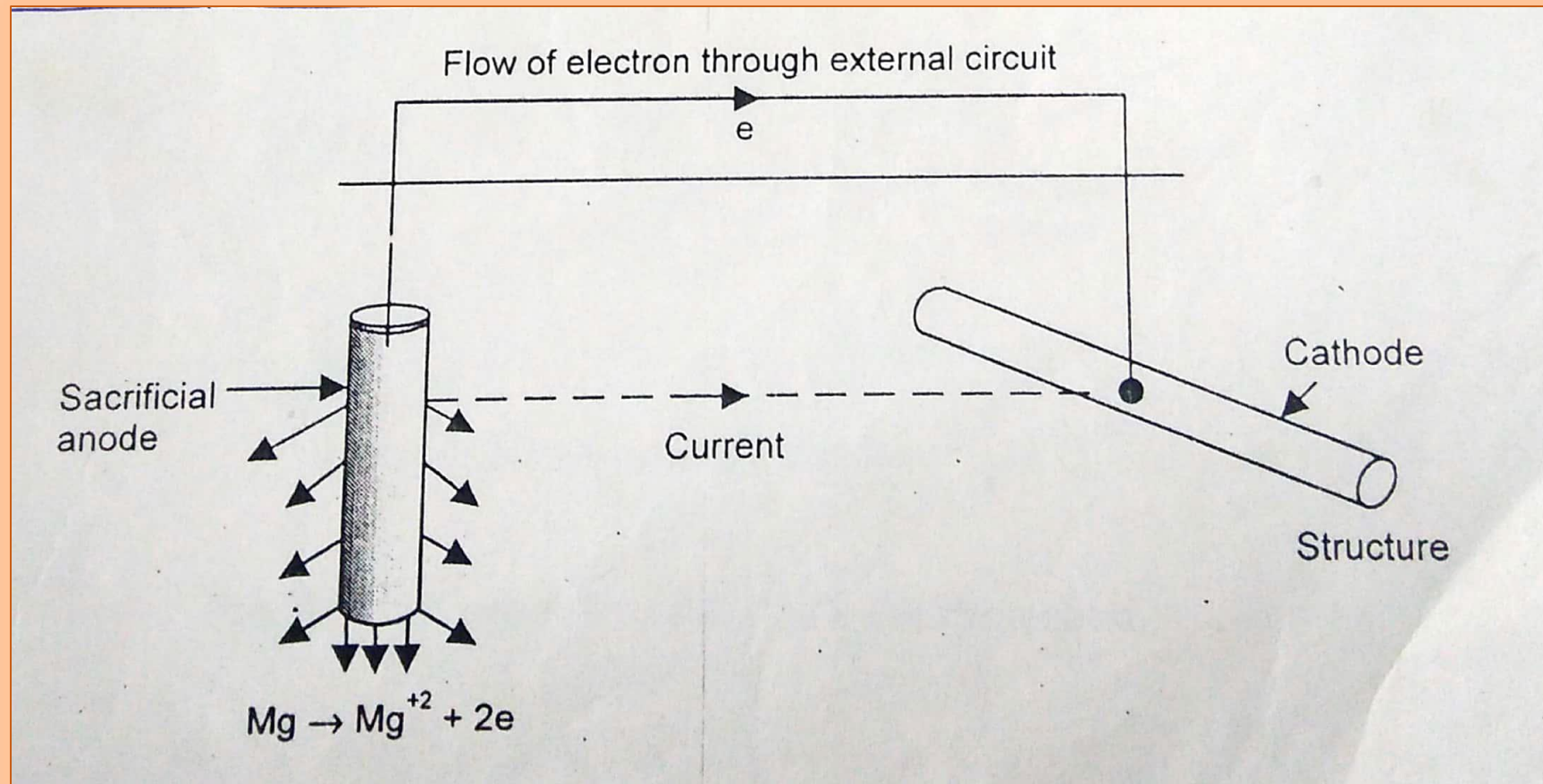
In this method, the corroding metal is forced to behave like a cathode. There are two types of cathodic protection methods:

- (a) Sacrificial Anodic Protection  
(By Appropriate Galvanic Coupling)**
- (b) Impressed current cathodic protection:**

## **(a) Sacrificial Anodic Protection (By Appropriate Galvanic Coupling)**

In this method, the 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. The more active metal loses electrons and gets corroded and this metal is called sacrificial anode.

**Thus, the structure remains protected as it acts as a cathode. Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys. For e.g.  $E^0$  for Mg = -2.36 V, while for Al = -1.66 V. Therefore Mg acts as sacrificial anode for Al.**



# Applications of Sacrificial Anodic Protection :

- Protection of buried pipe lines and underground cables from soil corrosion.
- Protection of ships and boats hulls from marine corrosion.
- Prevention of rusting water tanks by inserting Mg sheets or rods into domestic water boilers or tanks.

## (b) Impressed current cathodic protection:

An impressed current is applied to convert the corroding metal from anode to cathode. The applied current is in opposite direction to nullify the corrosion current. Usually the Impressed current cathodic protection requires impressed current derived from a DC source (like battery or rectifier) and an insoluble anode (like graphite, high silica iron, stainless steel or platinum).

The anode is buried in the soil or placed in a backfill (composed of graphite or gypsum etc.) so as to increase the electrical contact with the surrounding soil.

In impressed current cathodic protection, electrons are supplied from an external source, so that the object itself becomes cathodic and not oxidized.

**Applications:** This type of cathodic protection has been applied to water coolers, water tanks, buried oil pipes and water pipes, transmission towers etc. This type of protection is employed when

- **long term protection is needed.**
- **Large structures are to be protected.**
- **There is a cheap source of electrical power.**

This method has advantage over sacrificial anodic protection as (i) It can be controlled from outside. (ii) No anode has to be replaced.



# Impressed current cathodic protection

