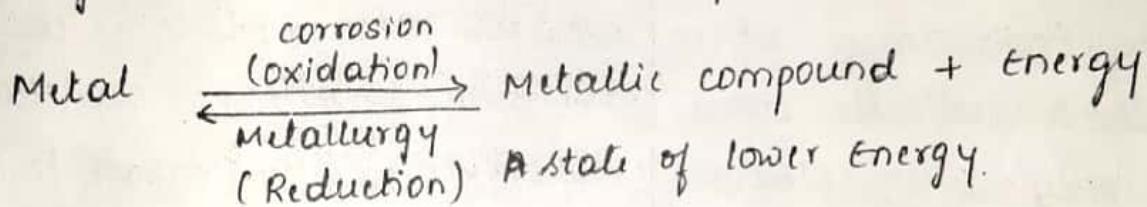


# CORROSION & ITS CONTROL

Corrosion: The process of destruction or deterioration of metals and alloys by chemical or Electrochemical attack is called corrosion.

The attack of metals by dry gases such as  $O_2$ ,  $Cl_2$ ,  $SO_2$ ,  $HCl$  and  $H_2SO_4$  fumes are the examples of direct chemical attack. The attack of metals by moist air, moist soil, water and aqueous solutions are the examples of electrochemical attack. Metals undergo corrosion mainly due to the oxidation by losing its valence electrons resulting in the formation of a corrosive product called Rust. This rust thus formed generally contains oxides or hydroxides or carbonates or sulphides of the metals.



Due to the corrosion, metals lose their valuable properties such as strength, shining, conductivity, malleability & ductility... etc.

Cause of corrosion: Corrosion is the reverse process of metallurgy. Metals have a tendency to go back to their original state such as ore form by losing or gain of  $e^-$ . In the ore form metals are more stable and less energy than the purest form of metals (less stable & more energy). This is the main cause of corrosion.

## Theories of corrosion:

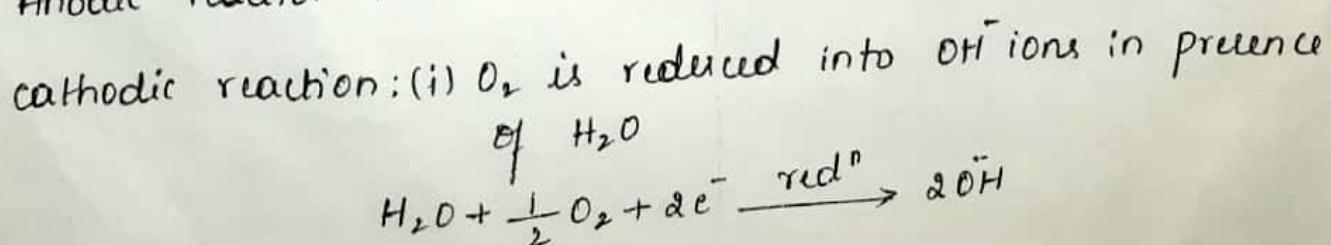
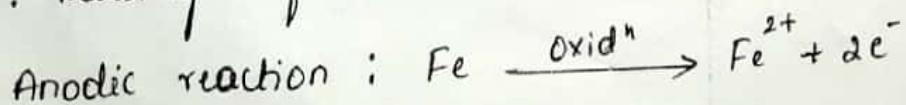
There are two important theories to explain the mechanism of corrosion.

1. Electro-chemical theory of corrosion
2. Differential Aeration theory of corrosion

## Electro-chemical theory of corrosion or wet theory

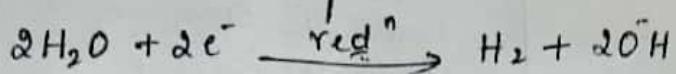
This theory explains the corrosion on the basis of galvanic cell formation in the environment. According to this theory, metal undergoes corrosion due to oxidation by losing its valence electrons. Oxidation & Reduction takes place simultaneously and hence some other substance in the environment is reduced by gaining of electrons. The metal surface where oxidation is taking place is called anode or anodic area and the surface in the environment where reduction takes place is called cathode or cathodic area. These two reactions are taking place only when electrons must flow from anode to cathode through the environment which is usually an aqueous soln. ∴ The combination of anodic area and cathodic area and the environment constitutes a small galvanic cells. Due to the formation of these galvanic cells, the metals undergo corrosion in the environment. The product formed by the electro-chemical corrosion is highly porous, dangerous than direct chemical attack.

e.g.: Rusting of iron structure in the environment.

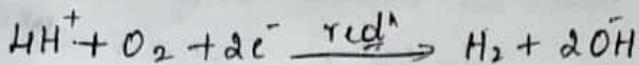


(ii) Neutral Medium without  $O_2$ :

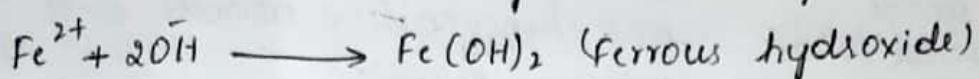
If the solution is deoxygenated, the reaction at cathode involves libration of  $H_2$  &  $OH^-$  ions



(iii) Acidic Medium:



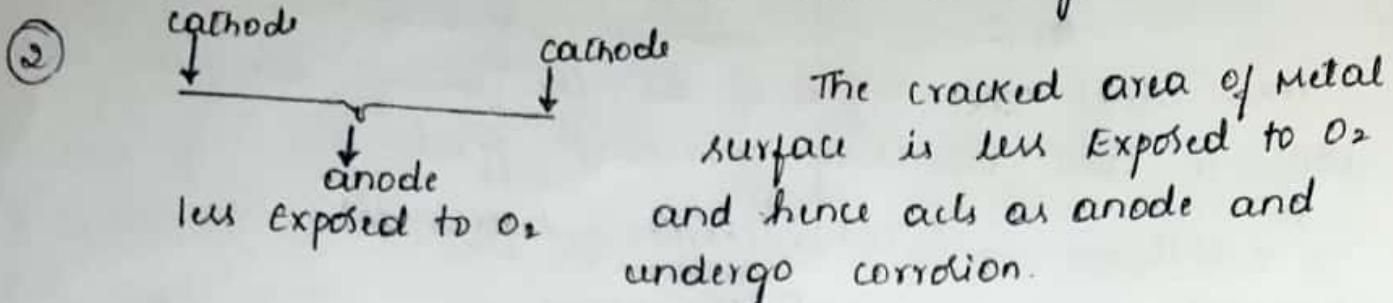
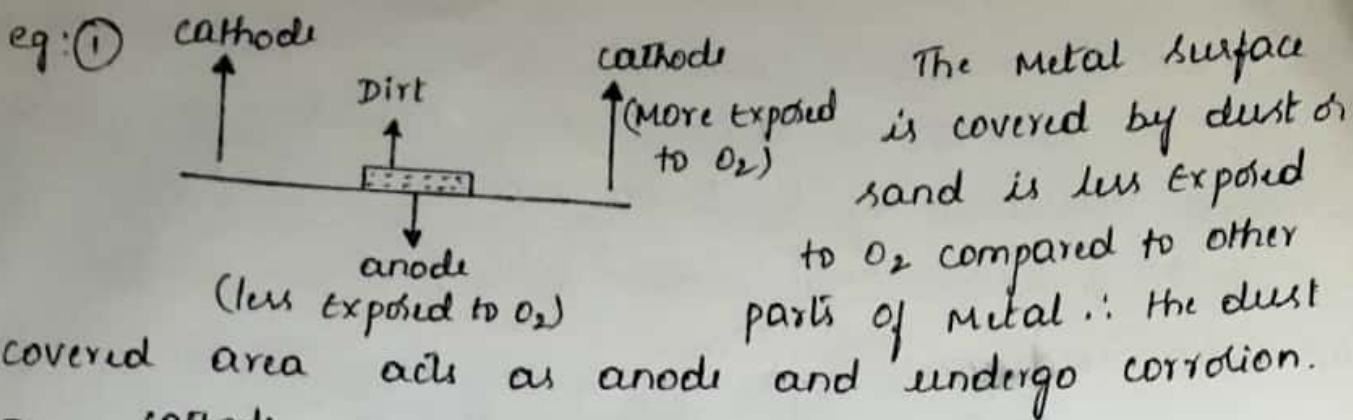
i.e. The metal ions formed at the anode combine with the  $OH^-$  ions resulting corrosion products



### Differential Aeration Theory of corrosion:

This is an extend form of electro-chemical corrosion. This theory explains corrosion on the basis of  $O_2$  conc<sup>a</sup> cell formation. According to this theory Anodic and cathodic areas are set up at different parts of the same metal surface due to the different amount of  $O_2$  or air reacting on the metal structure.

$\therefore O_2$  play an important role during corrosion. Anode is the metal surface where oxidation takes place by losing  $e^-$  and the cathode is the metal surface where  $red^-$  takes place by gaining of  $e^-$ .  $\therefore O_2$  helps to gaining of  $e^-$ . Hence the metal surface which is more exposed to  $O_2$ , acts as cathode is free from corrosion. But the metal surface which is less exposed to  $O_2$  acts as anode and hence undergo corrosion.  $\therefore$  The corrosion takes place at the less oxygenated area of the metal surface. This theory satisfactorily explains pitting and waterline corrosion.



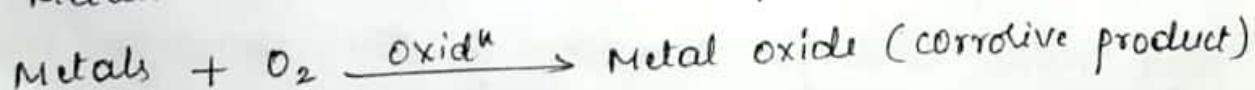
### CHEMICAL CORROSION OR DRY CORROSION

This type of corrosion takes place mainly due to the direct chemical attack by the atmospheric gases like O<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, N<sub>2</sub> and some liquids with fumes like HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> with metal surface

There are three types of chemical corrosion.

- (i) oxidation corrosion
- (ii) corrosion by the gases
- (iii) liquid metal corrosion.

(i) :- Oxidation corrosion is takes place by the direct action of O<sub>2</sub> at low or high temperature on metals in the absence of moisture. In general, the metals are slightly attacked by O<sub>2</sub> at ordinary temp. However alkali and alkali earth metals are rapidly oxidised by O<sub>2</sub> at low temperature. At high temperature almost all metals are oxidised resulting metal oxide.



(3)

(ii) corrosion by the gases such as  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  fumes on metal surface. The Extent of corrosive effect depends on the chemical affinity bet<sup>n</sup> the metal and the gas involved. The degree of attack depends on the formation of protective or non-protective films on the metal surface.

(iii) Liquid metal corrosion is due to chemical action of liquids on metal surface at high temperature. The corrosion reaction involves either dissolution of a metal by a liquid or internal penetration of the liquid into the metal surface.

#### TYPES OF CORROSION

1. Uniform or general corrosion.
2. Differential metal or galvanic corrosion.
3. pitting corrosion.
4. stress corrosion.
5. water line corrosion.
6. stray or current corrosion
7. caustic embrittlement.

#### I] UNIFORM OR GENERAL CORROSION:

The size or volume of metals decrease uniformly due to corrosion by direct chemical attack is called uniform corrosion. This type of corrosion usually takes place on the metal surface such as Zn and Aluminium are directly contact with strong acids and alkalis.

### 2) DIFFERENTIAL METAL (OR) GALVANIC CORROSION:

Metals undergo corrosion due to formation of a galvanic cell is called galvanic corrosion. Galvanic cell is formed when two dissimilar metals (e.g. Zn & Cu) are electrically connected and are dipped in solutions containing their ions. The difference in  $E^\circ$ -de potential of the two metals caused differential metal corrosion. The more active metal like Zn acts as anode and undergo corrosion by losing its valence electrons. The less active metal like copper acts as cathode by gaining electrons and is free from corrosion. ∴ The rate of corrosion increases with increasing the potential difference b/w two dissimilar metals.

e.g.: galvanic corrosion takes place when a steel pipe comes in contact with copper. Steel is anode w.r.t to Cu and hence it undergoes corrosion.

### 3) PITTING CORROSION OR LOCALISED CORROSION:

Corrosion takes place in the form of pits or cavity or holes is called pitting corrosion. This type of corrosion can be explained on the basis of differential aeration corrosion. ∴ The metal surface which is more exposed to  $O_2$  acts as cathode and hence free from corrosion. The metal surface which is less exposed to  $O_2$  acts as anode and it undergoes corrosion. ∴ The corrosion is concentrated at small anodic area than larger cathodic area of the metal surface leading in the formation of pits, cavity or holes.

Pitting corrosion is common in the following cases  
a) Metal surface is partially covered by dust or sand particles.

- (b) At riveted joints of metal surface  
(c) cracked area in the metal surface  
(d) stressed area of the metal surface... etc.

#### H] WATER LINE CORROSION

This type of corrosion usually takes place in metals or alloys which are partially immersed in water. Water line corrosion can be explained on the basis of differential aeration corrosion. i.e. the metal surface is partially immersed in water is less exposed to  $O_2$  and is acts as anode undergo corrosion due to the form of  $O_2$  concentration cell. The metal surface above the water level is more exposed to  $O_2$ . act as cathode and is free from corrosion.

e.g: Water line corrosion usually takes place in ship hulls water tank used for storage of water and metal surface is partially immersed in water or solutions.

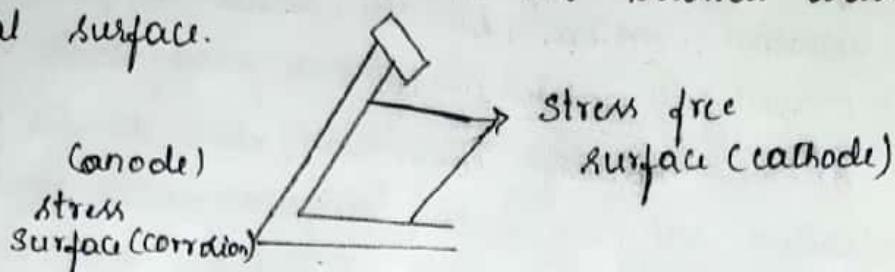
This type of corrosion can be prevented by immersing the metal surface completely in water because the concentration of  $O_2$  in water is uniform.

#### - 5) STRESS CORROSION:

Corrosion is also depends upon some physical factors such as surface conditions, internal or external stresses. The internal stress is produced during the manufacture, fabrication or heat treatment of metals or alloys. The external stress is due to service conditions of the metal surface. Stress corrosion usually takes place at riveted joints, bent portions, sharp corners of the metal structures.

The metal atoms under stress will be at a higher oxidation potential when compared with the atoms from stressed free area. ∴ The atoms in the stressed area act as anode w.r.t the stress free surface. In the corrosive environment, the stressed area undergo corrosion leading to the formation of pits, holes or cracks on the metal structure.

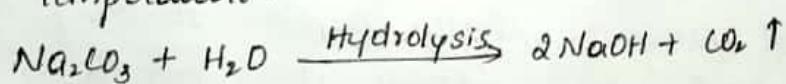
Stress corrosion can be prevented by giving proper heat treatment to the stressed area of the metal surface.



#### 6] CAUSTIC EMBRITTLEMENT:

- Metals like steel and iron become hard & brittle due to the attack of strong alkali like caustic soda ( $\text{NaOH}$ ) and hence this type of attack is known as caustic embrittlement.

This type of corrosion is due to the combined effect of stress as well as direct chemical attack. This type of corrosion is usually occurs in boilers or water heaters which are operated at high pressure and boiler feed water containing sodium carbonate which is added during the softening of water. Due to the improper circulation of water and evaporation of water in boilers the concentration of  $\text{Na}_2\text{CO}_3$  increases which undergoes hydrolysis producing sodium hydroxide ( $\text{NaOH}$ ) at high temperature.



The formed  $\text{NaOH}$  which attacks the metal surface at the stressed area such as riveted joints, bend

(5)

portions in boilers. ∵ the concentration of NaOH gradually increases at stressed area which acts as anode and undergo corrosion. The remaining parts of boilers i.e. stress free surface having dil. NaOH, acts as cathode and free from corrosion. ∵ The metal surface at stressed area becomes hard, brittle and cracks are takes place. This is one of the reason the boilers are failure.

caustic embrittlement can be prevented by adding  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , tannin, lignin, calgon to the boiler feed water.

Tannic acid  
(Complex of Fluoric acid  
Subs)  
Polymer  
Wood

### FACTORS AFFECTING THE RATE OF CORROSION:

Several factors affecting rate of corrosion because it is complicated process. Some important factors affecting rate of corrosion are,

- (i) Nature of Metal
- (ii) Nature of Environment

#### (i) Nature of Metal

- a) Nature of corrosion product.
- b) Anodic and cathodic area
- c) Electrode potential
- d) polarisation of the  $e^{-}$  de surface

#### (ii) Nature of Environment

- a)  $\text{pH}$
- b) Temperature
- c) conductance of Medium
- d) Humidity
- e) presence of impurities

### (a) NATURE OF CORROSION PRODUCT:

The corrosion product is usually the oxides of metal. The corrosion product may increase or decrease the rate of corrosion depending on the nature of corrosion product.

Eg: If the corrosive product is more passive i.e. It is highly insoluble, non porous and low ionic conductivity which prevent the rate of corrosion due to the form of protective oxide film on the surface of metal

If the nature of corrosive product is non passive, i.e. it is highly soluble, porous structure and relatively ionic conductivity which enhance the rate of corrosion.

- b) ANODIC AND CATHODIC AREA: generally the rate of corrosion is more at smaller anodic area than larger cathodic area.
- c) ELECTRODE POTENTIAL: The rate of corrosion is increased with increase in the potential difference b/w two metals

- d) POLARISATION OF THE ELECTRODE SURFACE:  
The driving force of corrosion is the potential difference b/w anode and cathode but the rate of corrosion is controlled by adding some organic and inorganic substance to the corrosive environment which are corrosive inhibitors.

These substances cause some irreversible changes around the electrodes which oppose the direction of the corrosion current flow which is called polarisation of electrodes which alters the potential of anode and cathode. As a result the potential difference and current b/w anodic and cathodic areas decrease thereby the corrosion rate also decreases.

#### Nature of corrosive Environment:

- a) pH: generally the rate of corrosion is more at acidic medium than basic medium. This is because in basic medium, the protective oxide layer is formed on the surface of metal which prevent the rate of corrosion. But in acid medium, the rate of corrosion is more due to the liberation of  $H_2$  even in the absence of air at the cathode.



- b) TEMPERATURE: The rate of corrosion increases with increase in temperature, because as the temperature increases, the conductivity of the aqueous medium increases and passivity decreases, as a result of rate of corrosion increases.
- \* c) CONDUCTANCE OF MEDIUM: The rate of corrosion increases due to the presence of conductive species in the environment.  
eg: the rate of corrosion in a dry atmosphere (less conductivity in dry soil) is less than that of wet atmosphere (more conductivity in wet soil)
- \* d) HUMIDITY OF AIR: Humidity of air is the factor in atmospheric corrosion. Critical humidity is a relative humidity ∵ The rate of corrosion increases with increase in the humidity of air in the atmosphere because it increases moisture of the corrosive environment
- \* e) PRESENCE OF IMPURITIES: The rate of corrosion of metal increases due to the presence of corrosive gases such as  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  fumes etc. in the atmosphere because which increases acidity and conductivity of the metal surface.

#### PREVENTION OF CORROSION:

it is better to control rather than to prevent corrosion since it is impossible to eliminate corrosion.

The following methods are adopted to prevention of corrosion.

- 1) prevention of corrosion by protective coatings (organic & inorganic coatings)
- 2) by cathodic and anodic coatings
- 3) by corrosion inhibitors
- 4) by proper selection and design of materials

- \* 5) By modifying the corrosive environment
- \* 6) By using pH-potential diagram.
- \* 7) By Electroplating

### 1) PREVENTION OF CORROSION BY PROTECTIVE COATINGS

The process of coating of materials on metals to prevent corrosion are protective coatings. protective coatings acts as physical barrier bet" the metal surface and the corrosive environment. and hence corrosion is prevented. so protective coatings are

1. Metallic coatings
2. Inorganic coatings
3. organic coatings

#### Metal coatings : 1) GALVANISATION

The process of coating of zinc on iron or base metal to prevent corrosion of iron is called galvanisation

Zinc is anodic to iron and hence Zn undergo corrosion and protect the iron and steel structure such as wire, roofing sheets, steel pipes etc. which are exposed to the atmosphere. The popularity of galvanising is due to the low cost of Zinc, easy application & anodic protection given by Zinc. The process of galvanising is as follows.

The base metal to be coated is washed with soap or organic solvent to remove oil or grease present on the surface of metal. Then it is treated with hot dil.  $H_2SO_4$  and then rubbed with sand paper to remove scale or rust. Finally the base metal is washed with  $H_2O$  and dried. The cleaned iron sheet is passed through a bath of molten Zinc which is maintained about  $450^\circ C$ . Finally it is passed under the rollers to

(7)

remove excess of zinc and to adjust thickness of Zn layer. A thin and uniform layer of Zinc is coated on the outer surface of metal (Iron)

### Applications:-

- 1) Galvanising Iron articles are used for making wire mesh, wire fence, roofing Iron sheets, steel pipes etc
- 2) Galvanising Iron articles can not be used for storage of food stuffs because Zinc reacts with food acids forming Zinc complex, which is highly toxic and poisonous.

### 2) TINNING:-

The process of coating of Tin on Iron or steel articles to prevent the corrosion is called Tinning. Tin is cathodic to Iron and hence corrosion of Iron is prevented. The process of Hot dipping of tinning is as follows.

The Iron sheet to be coated is washed with organic solvents to remove oils or grease and it is treated with dil.  $H_2SO_4$  to remove oxide film on the structure. Then the sheet is rubbed with sand paper to remove scale or rust the surface. and it is dipped in a bath of  $ZnCl_2$  flux which helps to adhere the molten tin on the surface of iron sheet. The cleaned Iron sheet is passed through a bath of molten tin which is maintained about  $250^\circ C$ . Then the sheet is finally passed under the rollers to remove excess of Tin and to adjust the thickness of tin layer. After this the Iron sheet is again dipped in palm oil which protect the tin coated surface against the corrosion.  $\therefore$  a thin & uniform tin layer is coated on the outer surface.

of the Iron structure which prevents corrosion.

### APPLICATIONS:

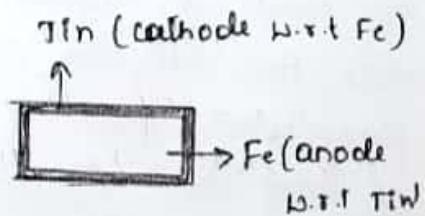
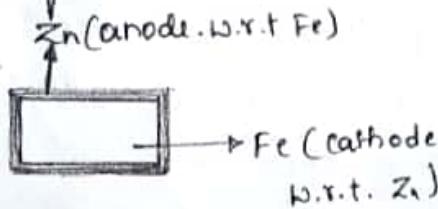
- i) Tin coated articles are used for storage of food stuffs, ghee, oils, kerosene, packing materials because it avoids food poisoning
- ii) Tin coated copper articles are used for making cooking utensils and refrigerating equipments.. etc.

Why galvanising is referred than Tinning?

Galvanising is the process of coating of Zn on Iron article. If there are some small cracks or scratches are developed on the galvanising article, Zn undergo corrosion and protect the iron structure from corrosion. because zinc is anodic to Iron.

But Tinning is the process of coating of Tin on Iron article. If there are some small cracks or scratches are developed on the tinning article, Iron undergo corrosion at the faster rate than without tinning article because Tin is cathodic to Iron.

This is Because galvanising is referred than Tinning.



## INORGANIC COATINGS: Anodized coatings:

The process of coating of oxide film on the metal surface using suitable electrolyte to prevent corrosion is called oxidized coatings.

The process of oxidized coating is produced by the anodic oxidation of metals like Al, Zn, Mg...etc. in which the bare metal to be anodized made as anode in presence of suitable electrolyte.

e.g. Anodized coating of Aluminium

It is carried out by passing Electric current (D.C) to the bath solution containing  $H_2SO_4$ , chromic acid or boric acid etc. in which the bare metal of Al is made as anode at  $40^\circ C$ . During electrolysis, protective oxide layer is deposited on the metal surface of Al which is highly porous and softer than bare metal. Hence the porous structure of Al is treated with boiling water (d) dilute sodium dichromate sol<sup>n</sup> which sealed the porous structure of Al due to the formation of alumina ( $Al_2O_3 \cdot H_2O$ ) which prevent corrosion of the Al.

## phosphate coatings:

The process of coating of the aqueous sol<sup>n</sup> of phosphoric acid and phosphate on the metal surface to prevent corrosion is called phosphate coating.

phosphate coating is produced by the chemical reaction of bare metal with aqueous sol<sup>n</sup> of phosphoric acid a phosphate. phosphates like Iron, Mn or Zn are used for phosphate coating along with accelerator like Ce salts which Enhance the rate of reaction

phosphate coating is usually done by either immersion of base metal in the soln or spraying of phosphate soln on the metal surface. The chemical reaction between base metal and phosphating soln forming a thin and uniform phosphate layer on the metal surface which prevent corrosion.

phosphate coating is generally applied for the metals like Zn, Al, Cd, Cu, Tin etc.

### ORGANIC COATINGS

The base metal to be protected from corrosion using organic coatings such as paints, varnish, tar, oil, grease and polymers. These organic coatings applied on the metal surface to prevent corrosion and also they give decorative effect to the metal surface.

Enamels: These are pigmented varnish. Enamel gives harder, smoother, glossier and durable finish to the metal surface. Enamelled cast iron and steel are used in refrigerators, water taps and sanitary wares etc.

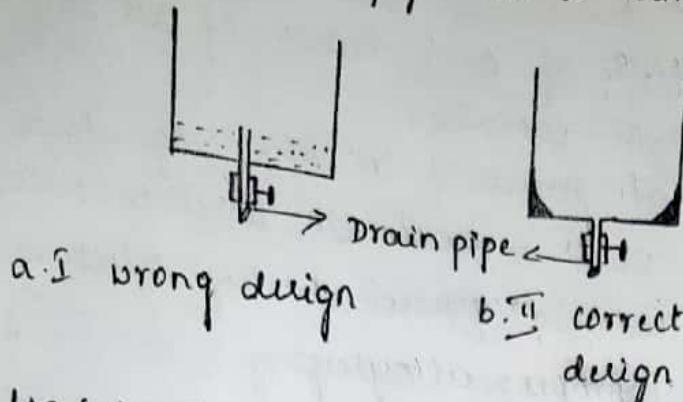
### Preventing corrosion by design and proper selection of Materials

Corrosion can be prevented by proper selection, proper use of materials and proper design of the materials eg: (1) Materials like wood, paper, cloth, asbestos, lead washers etc. are absorb moisture. Hence such materials should not be used in contact with metals because they lead to corrosion due to water and entirely on the metal surface. To prevent the corrosion of metals, better to use rubber or plastic washers because they do not absorb moisture & moreover they insulate the metals.

- ② Metals under internal stress undergo corrosion due to stress. Hence before using such metals, the stress has to be released by a proper heat treatment.
- ③ Some times, the presence of even traces of an impurity in metals & alloys undergo corrosion.  
 eg: The presence of Iron as impurity in Al or Mg which undergo corrosion because Iron is cathodic to these metals. In such case, corrosion can be prevented by selecting metals of high purity or by proper alloying.  
 eg: Corrosion of Al due to the presence of Iron can be controlled by adding a little Mn or Cr. The resultant alloys ( $\text{Al}, \text{MnFe}$ ) ( $\text{AlMnFe}$ ) have potentials very close to that of Al and hence corrosion is prevented.
- ④ Some times use of more than one metal in the same sys or equipment becomes unavoidable. The rate of corrosion depends upon the potential difference bet' the two metals and relative sizes of anodic and cathodic area. In such cases corrosion can be prevented by selecting metals having little potential difference and by making smaller part of the equipment using noble metals.  
 eg: A steel belt in copper equipment is undesirable. This is because steel is anodic to copper and anodic area of steel belt is very small compared to the cathodic area of copper. Hence corrosion is concentrated in the steel belt resulting in pitting corrosion

Q. 6) Prevention of corrosion by proper design; corrosion can be prevented by proper design of the equipments.

eg. ① A drain pipe in a tank for chemicals.



The fig (a) illustrates a wrong design because some vol<sup>n</sup> will be left after draining and this will corrode the drain pipes and tanks.

Fig (b) shows a very slight modification in the design. In this case the vol<sup>n</sup> can be completely drained. The leakage of drainpipes, tanks, taps fittings can be prevented by slightly changing the design of the equipments like fig ③

eg. ②

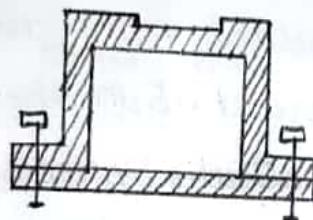


fig (a)  
wrong design

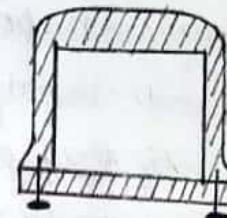


Fig (b)  
correct design.

The fig (a) illustrates wrong design because rain water may collect at the top and also pass in to the space bet<sup>n</sup> the belt and Head. corrosion takes place at this points due to the capillary action.

Fig (b) illustrates correct design because a slight change in the design is made to avoid the above defects.

### Eg. (3) Roofing Iron sheets (Zinc sheets)

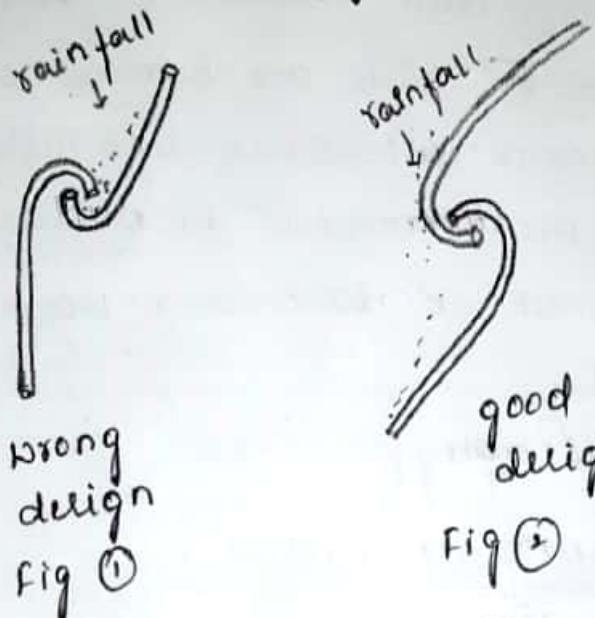


Fig ② correct joining because of a

slight change in the type of joining is made to avoid the above defect

\* Prevention of corrosion by Anodic protection:  
In this method, the metal to be protected is made as more anodic by connecting +ve terminals of the battery while the -ve terminal is connected to the cathode in presence of electrolyte. When an electric current is applied the metal surface becomes more passive and hence a protective film is formed around the surface of metal which prevents the rate of corrosion.

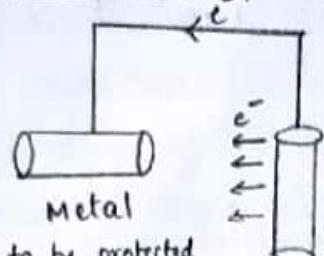
This technique is applicable to the metals like Ni, Fe, Cr, Ti and their alloys. The major drawback of this method is required very high current. Anodic protection of steel pipes are used in industry.

## Cathodic protection:

It is one of the important method to protect metals & alloys from corrosion which are buried pipelines underground cables, marine structures, ship hulls, water-tanks and the metals are immersed in conducting solution. Cathodic protection can be done in 2 ways.

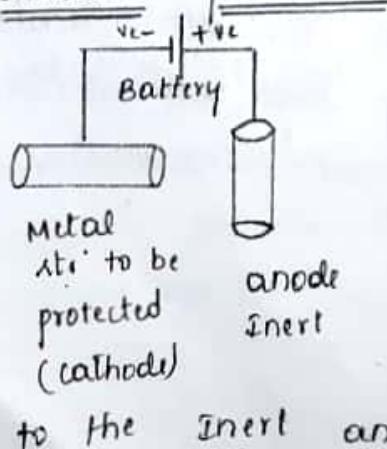
- i) By using sacrificial metal
- ii) by the Expense of electrical energy.

### i) cathodic protection by sacrificial method:



In this method the metal str<sup>n</sup> to be protected from corrosion is connected by a metal wire to a more anodic metal like Mg, Zn or Al which are called sacrificial metals. The sacrificial metal acts as anode and undergo corrosion. The metal structure acts as cathode and hence free from corrosion. The anodic metal is replaced by a fresh one after completely corroded. This is very important method to prevent corrosion in boilers, ships, iron tanks, buried pipe lines, marine str<sup>n</sup> ... etc.

### ii) cathodic protection by using Electrical Energy:



In this method, the metal surface to be protected from corrosion is made the cathode by connecting it to the -ve terminal of the battery while the +ve terminal is connected to the inert anode.

when the electric energy is applied. the metal surface becomes cathodic and hence free from corrosion.

This type of cathodic protection is applied to water coolers, water tanks, buried oil pipes, water pipes, marine structures, condensers, transmission line towers etc

### Prevention of corrosion by corrosion inhibitors:

The substances are added to the corrosive environment to prevent or decrease the rate of corrosion are called inhibitors. These are added to control either anodic or cathodic reaction and hence corrosion is prevented.

Type of Inhibitors: Anodic and cathodic inhibitors.

Anodic Inhibitors: substances such as  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_3\text{PO}_4$ , Nitrites, Sodium silicate...etc are added to the corrosive environment to control or decrease the anodic reaction and Hence they are called anodic inhibitors.

These are react with metal surface and deposited as protective oxide film on the metal surface. This film acts as a barrier bet<sup>n</sup> the Metal and corrosive Environment. Hence the anodic reaction is inhibited.

Cathodic Inhibitors: substances such as Ca, Mg, Zn & Ni salts are added to the corrosive environment to control cathodic reaction and Hence are called cathodic inhibitors. The functions of cathodic inhibitors either absorbing the dissolved  $\text{O}_2$  or eliminating  $\text{OH}^-$  ions in the corrosive environment and Hence corrosion is prevented.

The above mentioned inorganic inhibitors are not effective in presence of acids, reducing agents and

and bacteria. In such cases organic inhibitors such as organic bases, polar compounds and colloid substances are added to control corrosion

### passivity:

Metals or alloys exhibit a much higher corrosion resistance than expected due to the formation of highly protective oxide layer on the metal surface is known as passivity.