

# Unit 6 : Corrosion

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## Introduction:-

The (chemical or electrochemical reactions) between (metals & environment) that includes air, water, sea water, acid, alkali, gas etc leads to corrosion. These reactions occurs at different rate, at different temperature & give rise to different forms of products by consuming metal. This consumption of metal slowly leads to decay or deterioration of metals.

Corrosion is a general term that refers to the deterioration or destruction of metal.  
eg Any iron article if exposed to moist air gets rusted.

## Definition:-

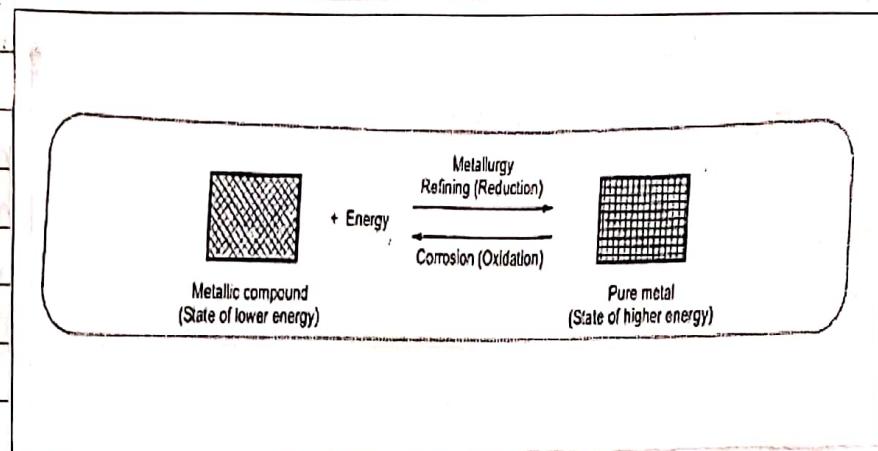
Corrosion is defined as the destruction of metal through unwanted chemical or electrochemical reaction which occurs between the surface of the metal & the environment.

## Causes of Corrosion:-

(Ores) represents thermodynamically stable state (minimum energy level of the metals). Metals are extracted from these ores through multi-step extraction process.

In all these refining steps enormous amount of energy is spent to obtain pure metal. Therefore compared to an ore, pure metal is in higher energy state. This causes pure

- metal to revert back to thermodynamically stable state.
- This natural tendency or the instability of refined or pure metal is the basic cause of corrosion.
- Nature or environment assists the pure metal to stabilize in to compound form.



### Consequences of corrosion :-

Enormous losses occur due to corrosion annually throughout the world & faced by industries that are :

- i) Loss of efficiency of the process.
- ii) Life of the equipment & machinery gets reduced.
- iii) Arrangement for preventive maintenance.
- iv) Necessity for replacing the corroded equipment.
- v) Probability of plant shut down due to machine failure.
- vi) Possibility of accidents & hazards.



### Types of Corrosion :-

On the basis of <sup>medium</sup> environment, corrosion is classified in

to two types :

### A) Dry / Direct chemical / Atmospheric corrosion —

It occurs due to chemical reaction between metal & atmospheric gases to which it is exposed.

### B) Wet / Electrochemical / or Immersed corrosion —

It occurs due to electrochemical reaction between metal & electrolyte which can be an aqueous salt soln, acids or alkali.

### A) Dry / Direct chemical / Atmospheric corrosion —

This type of corrosion occurs mainly due to direct chemical action of atmospheric gases like  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{S}$ , halogens like  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$  &  $\text{SO}_2$  etc with metal or alloy surface.

The extent of dry corrosion depends up on two factors:

- i) (Chemical affinity) between the metal & corrosive environment i.e. atmospheric gases
- ii) Ability of reaction product to form protective layer or film over the metal surface.

defn: The surface of metal or alloy when directly attacked by atmospheric gases the corrosion is called as atmospheric corrosion

There are three main types of atmospheric corrosion.

- 1) Corrosion due to oxygen
- 2) Corrosion due to Other gases
- 3) Corrosion due to liquid metals.

- 1) Corrosion due to oxygen (Oxidation corrosion)
- Oxidation corrosion is brought about by (direct action of oxygen on metal surface at low or high temperature) usually in (absence) of moisture.
- The metal oxides are formed as a product of oxidation corrosion.

### Mechanism:-

Whenever a metal is exposed to oxygen, the oxidation occurs first at the surface. The formation of metal oxide at the (metal-gas interface) occurs in four steps as:

Step I - Adsorption of atmospheric oxygen at the metal surface.

Molecules of oxygen are adsorbed rapidly by the surface of the metal. These <sup>surface</sup> metal atoms hold the oxygen molecule very firmly through their free valencies.

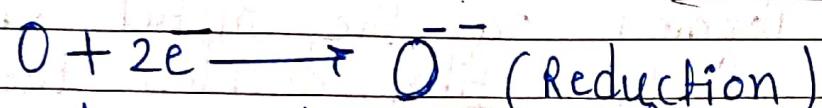
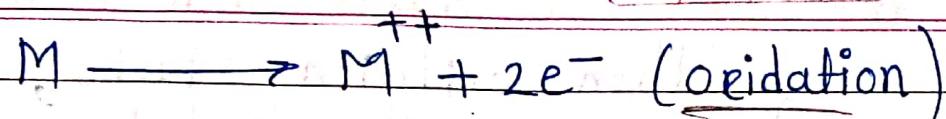
Step II - Dissociation of oxygen molecules into atoms.

Especially at increased or elevated temperature adsorbed oxygen gas molecules dissociates into atoms.



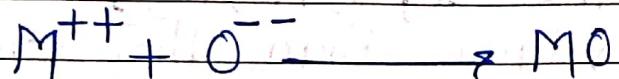
Step III -

Oxidation of metal atoms & reduction of oxygen atoms.



Metal atoms at the surface get oxidized, while oxygen atoms are reduced.

Step IV: Formation of metal oxide at the surface.



— Metal ions combine with the oxide ion & form metal oxide which may be solid or gas.

— If it is solid metal oxide ( $MO$ ), then it gets spread over the surface to produce a film or scale.

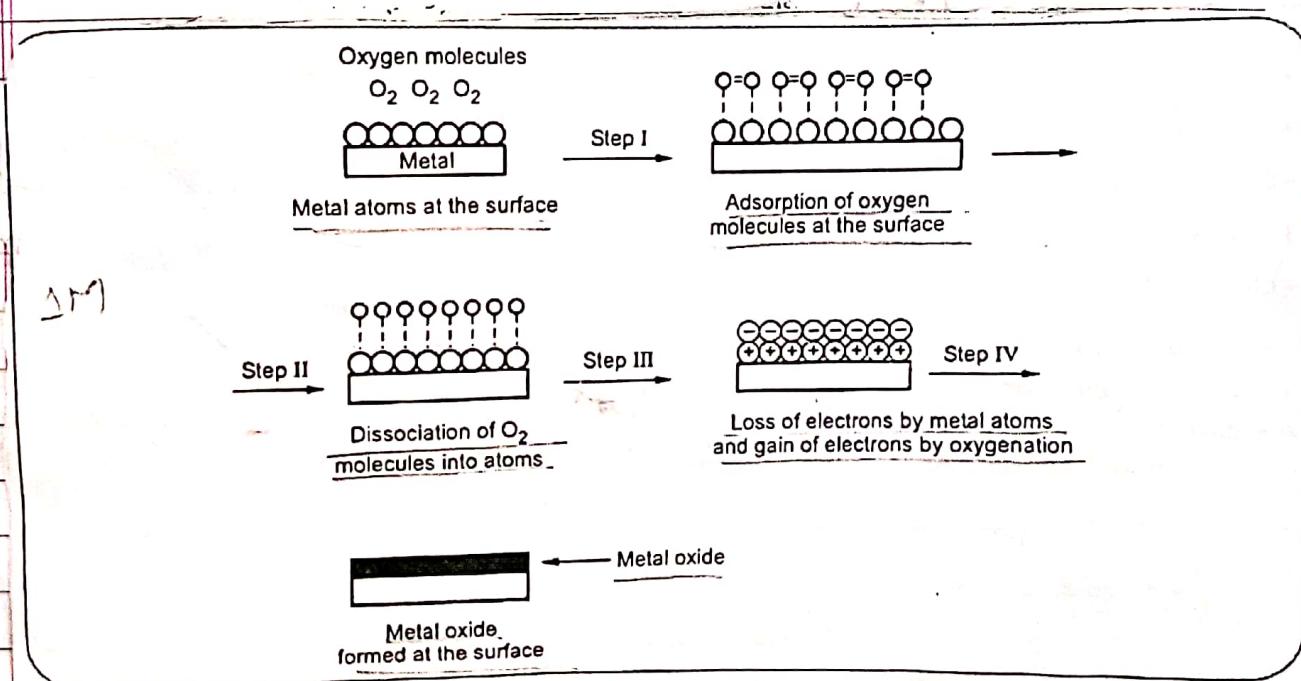


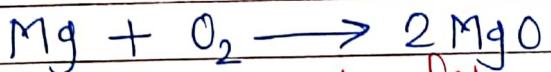
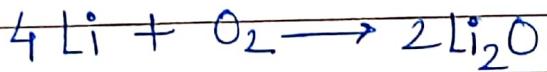
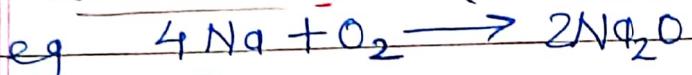
Fig. 6.2.1 Mechanism of oxidation corrosion

## \* Types of metal oxide film:

When oxidation starts, a thin layer is formed on the metal surface, the nature of this film decides the continuity of corrosion.

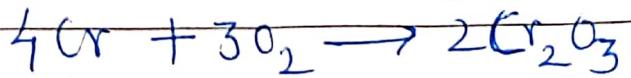
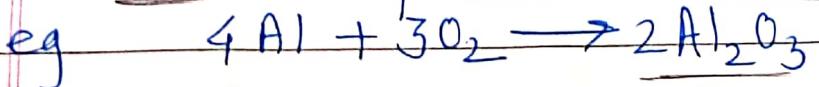
### i) Porous oxide film (Non protective)

The alkali metals & alkaline earth metals like Li, K, Na, Mg form oxide having less volume than the volume of the metal. Therefore, volume of oxide formed is insufficient to cover completely large surface area of metal. As a result oxide layer faces stress & strain so develops cracks & pores in the film through which oxygen can easily come in contact with metal & corrosion continues.



### ii) Nonporous oxide film (Protective)

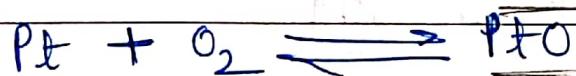
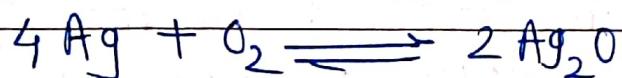
Metals like Al, Cr, Cu etc forms oxide whose volumes are greater than the volume of metal exposed. Therefore these oxide films do not have any cracks or pores & forms barrier for further attack. As a result corrosion is discontinued once oxide film is produced at the surface.



### iii) Unstable oxide film:-

When the oxide film formed is unstable i.e it decomposes back into the metal & oxygen, the net corrosion is zero.

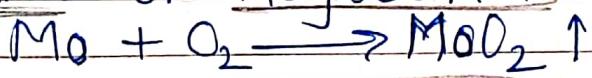
eg — Oxide of Ag, Au, Pt



### iv) Volatile oxide film:-

When the oxide film formed is volatile i.e vaporizes as soon as it is formed, the underlying metal surface is exposed for further attack of oxygen & causes continuous & excessive corrosion of the metal.

eg → Oxide of Molybdenum



### \* Pilling Bedworth's rule:-

N.B. Pilling & R.E. Bedworth in 1923 suggested that metals can be classified in to two categories based on nature of oxide which is formed after interaction with atmospheric oxygen in dry corrosion.

They classified metals as,  
Metals forming protective oxides &  
Metals forming nonprotective oxides.

In order to find out the nature of oxide formed by the metal, they gives a ratio as:

Pilling Bedworth's ratio (PBR) =  $\frac{\text{Volume of metal oxide formed}}{\text{Volume of metal consumed}}$

According to pilling Bedworth's rule,

If  $PBR < 1$ : Oxide formed is too thin & therefore it is (porous). Thus provides no protective effect.

e.g. — Na, K, Li, Mg

If  $PBR > 2$ : Oxide formed cracks thus provide no protective effect.

e.g. Fe

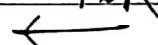
If  $1 < PBR < 2$ : (In bet<sup>n</sup> 1-2)

Oxide formed is (non porous). It provides protective effect against further corrosion.

e.g. Al, Ti, Cr.

Metal	Metal Oxide	PBR	Nature of oxide
Na	Na <sub>2</sub> O	0.541	Porous (non protective)
Li	Li <sub>2</sub> O	0.567	Porous (non protective)
Ca	CaO	0.64	Porous (non protective)
Mg	MgO	0.81	Porous (non protective)
Ba	BaO	0.67	Porous (non protective)
Al	Al <sub>2</sub> O <sub>3</sub>	1.28	Non-porous (protective)
Pb	PbO	1.28	Non-porous (protective)
Zn	ZnO	1.58	Non-porous (protective)
Ni	NiO	1.65	Non-porous (protective)
Cr	Cr <sub>2</sub> O <sub>3</sub>	2.07	Excess oxide formed which will get cracked or chips off (non protective)
Fe	Fe <sub>2</sub> O <sub>3</sub>	2.14	Excess oxide formed which will get cracked or chips off (non protective)
V	V <sub>2</sub> O <sub>5</sub>	3.25	Excess oxide formed which will get cracked or chips off (non protective)

Some important metals with P.B.R.



## ii) Corrosion by Other gases :-

**I)** Other than oxygen gas, other dry gases which cause corrosive effect on the metals are  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{S}$  &  $\text{F}_2$  etc.

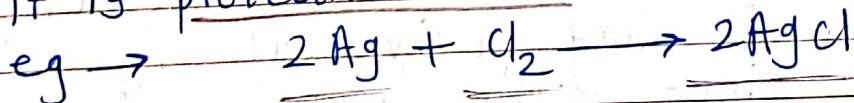
i) If the film formed is non-protective the surface of metal is gradually destroyed.

eg - When (dry chlorine gas) attacks tin Sn metal forms (volatile film) of stannic chloride ( $\text{SnCl}_4$ ) which vaporizes as soon as it is formed & leaving the metal surface exposed for further attack.



ii) If the reaction product formed is in the form of nonporous film it protects the metal from further attack.

eg Silver forms silver chloride layer when it is attacked by chlorine gas. Silver chloride film is nonporous & therefore it is protective film.



## **II) Corrosion by hydrogen -**

The action of hydrogen gas on metals occurs by two processes as

- i) Hydrogen embrittlement
- ii) Hydrogen attack

### i) Hydrogen embrittlement -

When hydrogen gas attacks the metal at ordinary temperature, it is known as hydrogen embrittlement.

e.g. presence of aqueous soln of  $H_2S$  in system evolution of atomic hydrogen at surface of metal.



This evolved atomic hydrogen diffuse readily in to the metal & collect in its void's where it recombines to form molecular hydrogen.



This process continues till the pressure becomes too high to cause blister. This affects the strength & ductility of metal & causes brittleness in metal.

### ii) Hydrogen attack —

— At high temperature, diffusion of atomic hydrogen in to the metal voids which causes hydrogen attack.

— Atomic hydrogen is formed by thermal dissociation of molecular hydrogen which is very active at high temperature & combines with elements like C, S, O or N present in metals in small quantity

e.g. →

Atomic hydrogen combines with carbon in steel at high temperature with formation of methane gas causes cracking in the metal. This reduces strength of steel & makes it brittle.



C

### c) liquid metal corrosion -

This corrosion is due to the chemical action of liquid metal on solid metal or alloy at high temperature.

The corrosion reaction involves either (dissolution) of solid metal by liquid metal or (internal penetration) of the liquid metal in to solid metals.

e.g. Such type of corrosion is found in the devices used for generating nuclear power.

### \* Wet Corrosion : [Electrochemical or Immersed corrosion]

The wet corrosion occurs mostly in wet or moist conditions through electrochemical reaction.

\* Wet corrosion occurs under following conditions as :

- 1) When conducting liquid is in contact with metals.
  - 2) When two dissimilar metals are in contact in presence of conducting medium they develop anodic & cathodic area due to difference in electrode potential.
  - 3) When single metal is dipped partially in conducting medium there is anodic & cathodic area develops on metal surface due to differential aeration.
- Conducting medium can be aqueous soln of acid, base or salt.

Under above conditions, there

should be flow of electricity between anodic & cathodic area through conducting medium.

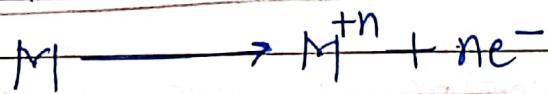
— At anodic area, there is liberation of free electrons hence it is termed as oxidation. Therefore there is tendency at anode to destroy the metal.

— At cathodic area, there is gain of electrons hence it is termed as reduction.

### ~~\* Mechanism of Wet or electrochemical or Immersed Corrosion —~~

Electrochemical corrosion involves flow of electrons bet<sup>n</sup> anodic & cathodic areas.

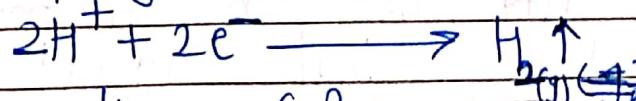
Anodic reaction: — The anodic reaction involves dissolution of metal as corresponding metal ions with liberation of electrons.



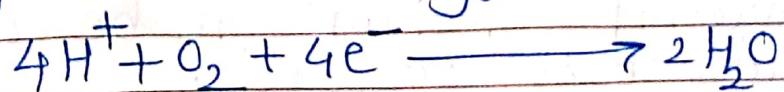
The electrons liberated flow from anode to cathode through electrolyte.

#### Cathodic reaction:

i) In acidic medium (Absence of oxygen) Hydrogen ions combine with electrons & form hydrogen gas.

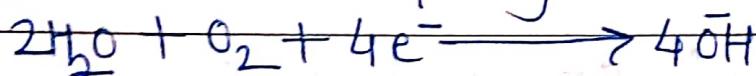


ii) In acidic medium (Presence of oxygen) Hydrogen ions combine with electrons in presence of oxygen & form water



iii) In neutral or alkaline medium (presence of oxygen)

Dissolved oxygen combines with electrons & forms Hydroxyl ions.



\* Electrochemical corrosion involves any one of the following two mechanisms depending upon the nature of environment.

I) Hydrogen evolution mechanism.

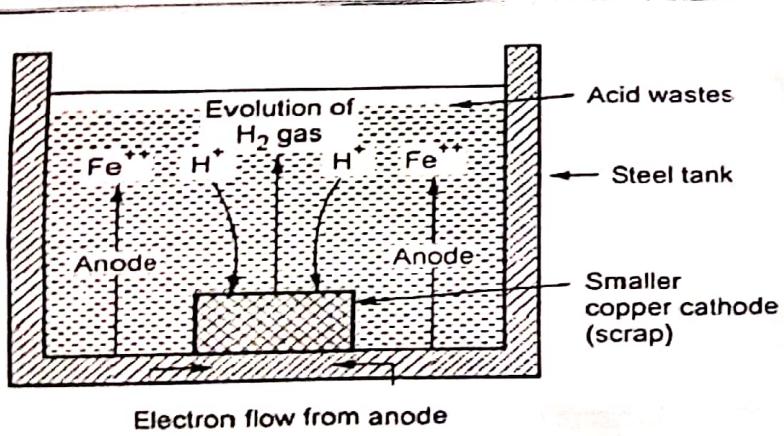
II) Oxygen absorption mechanism.

T) Hydrogen evolution mechanism :-

This type of electrochemical corrosion occurs usually in acidic environment like industrial waste soln of non-oxidizing acids.

e.g. →

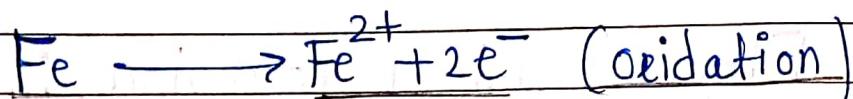
The piece of copper & steel tank in contact with each other in presence of acid electrolyte gives rise to an electrochemical cell.



Example of hydrogen evolution mechanism

In this cell, steel act as anode & copper acts as cathode. It is observed that the steel tank portion in contact with copper piece is corroded.

At Anode: At steel tank



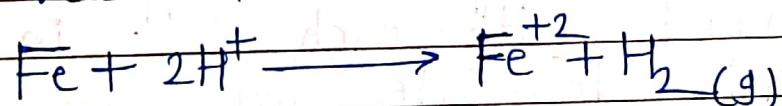
Iron passes in to the sol<sup>n</sup> as Fe<sup>+2</sup> ions & the free electrons accumulated at cathode.

At Cathode: At Copper piece

Hydrogen ions from acidic electrolyte take up the free electrons & hydrogen gas is formed is liberated in the form of bubbles at cathode.



Net cell reaction :



Corrosion by this mechanism involves displacement of Hydrogen ions from acidic electrolyte by metal ions.

Thus, all metals above hydrogen in electrochemical series will have tendency to get dissolved in acidic electrolyte with liberation of hydrogen.

In hydrogen evolution mechanism of corrosion, anodes usually have larger areas than cathode.

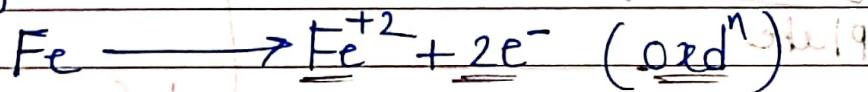
## II) Oxygen absorption mechanism:

This type of electrochemical corrosion occurs when electrolyte is (neutral aqueous sol<sup>n</sup> or alkaline) sol<sup>n</sup> containing dissolved oxygen.

e.g. → Steel plate lying on the ground & is exposed to the atmosphere, oxide layer will form on the surface of steel plate due to some atmospheric pressure cracks are generated on metal surface oxide film. & when drop of water is collected over the cracks corrosion take place as:

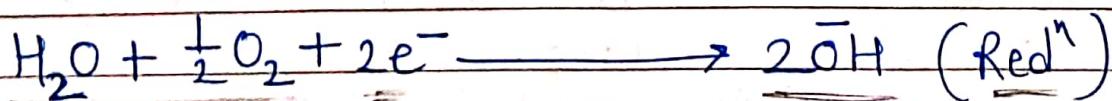
At anode:-

The steel undergo oxidation to form ferrous ( $\text{Fe}^{+2}$ ) ions.



At Cathode:-

The electrons flow from anode to cathode that from crack to oxide layer on the surface of steel plate. These electrons react with dissolved oxygen present in the electrolyte as:

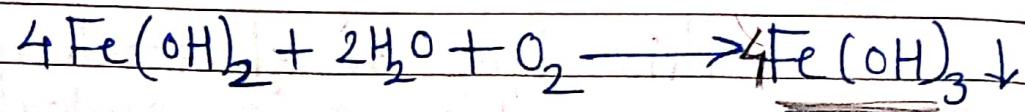


The  $\text{Fe}^{+2}$  ions at anode &  $\bar{\text{O}}\text{H}$  ions at cathode diffuse & combine to form ferrous hydroxide.



If (enough oxygen) is present in the electrolyte ferrous hydroxide is easily oxidized.

to ferric hydroxide.



If supply of oxygen is limited, the corrosion product may be black antimony  $\text{Fe}_3\text{O}_4$ .

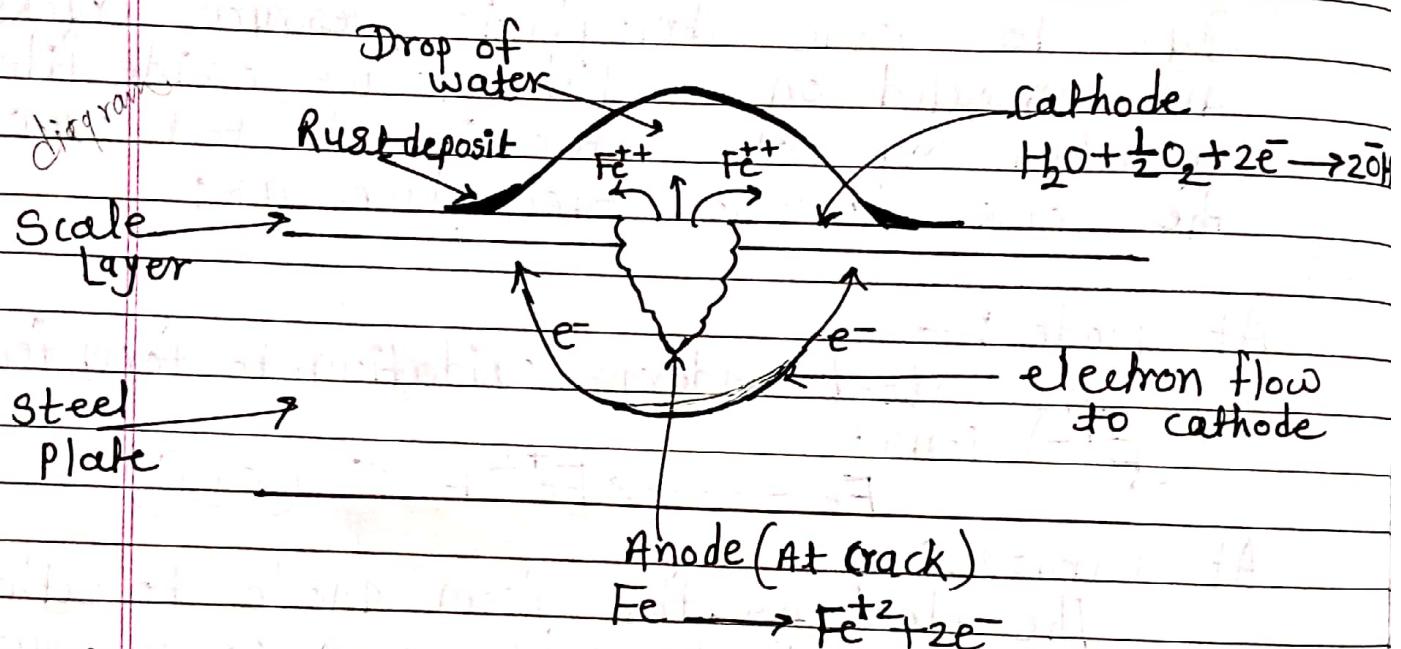


fig: Example of oxygen absorption mechanism

\* Relation between Electrode potential & corroding Tendency of metal based on electrochemical series of metals.

(All metals) do not give up electrons & pass in to solution with equal ease, they develop different electrode potential when placed in the same solution, at same temperature.

- Electrode potential of a metal depends on:

- Chemical nature of metal

- b) Nature of solution in which metal is immersed.
- c) Temperature of the solution.

$\Delta E^{\circ} \rightarrow$  Electrode potential

Electrode potential is defined as the potential difference developed (between) the metal ions in the solution & the electrons on the surface of metal at equilibrium.

\* Relation between electrode potential & corroding tendency of metal based on electrochemical series of metals:

Greater the tendency of metal to pass in to solution (dissolving tendency) greater is the number of electrons released & more negative is the value of electrode potential. As more negative value of electrode potential, greater is the tendency of metal to dissolve & has more corroding tendency.

**Electrochemical series of metals:**

**Important features:**

— Electrochemical series represents an arrangement of various metals in the order of the increasing value of their standard electrode potential.

— Metals at the top of the series, with more (negative) value of the electrode potential have (more) tendency to pass in to solution in ionic state. Whereas, metals at the bottom of the series with positive value of electrode potential have least tendency to give up their valence electrons. Thus, metals like Li, K are very active & readily pass in to solution. Whereas Au (gold), Pt has least tendency to go in to the solution.

# Galvanic Series :

Metal & alloys  
(relative positions)

	Anodic (more active)	Cathodic (more inactive)
Mg		
Mg-alloys		
Zn		
Al		
Cd		
Al alloys		
Mild steel		
Cast iron		
Lead-tin solder		
Pb		
Sn		
Ni-Mo-Fe alloys		
Brasses		
Copper		
Bronzes		
Nickel-copper alloy		
Chromium		
Stainless steels		
Silver		
Monel		
Titanium		
Graphite		
Gold		
Platinum		
	↑	↓
	Cathodic (more inactive)	

## Types of Electrochemical Cell corrosion :

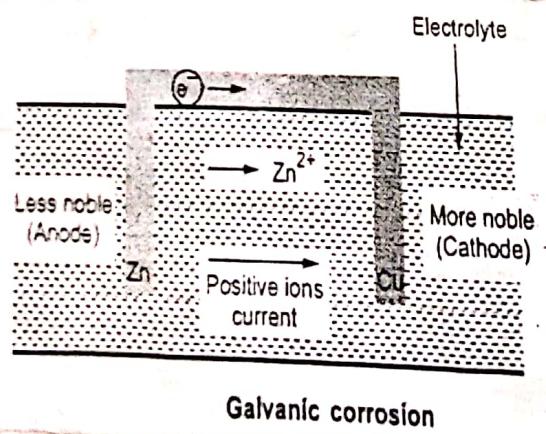
### → Galvanic corrosion:

#### Definition—

When two dissimilar metals are electrically connected & exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion.

eg → When two metals, Zinc & copper are electrically connected & exposed to an electrolyte. Zinc being less noble metal (more reactive) will dissolve & act as anode, whereas copper being more noble metal (less reactive) will act as cathode. The nature of corrosive environment decides the type of cathodic reactions.

In acidic medium, corrosion occurs by hydrogen evolution mechanism, whereas in neutral or slightly alkaline medium, it occurs by oxygen absorption mechanism. The electrons flow from anodic metal (Zn) to cathodic metal (Cu) as shown in fig.



eg → i) Copper sheets joined by iron metal.  
ii) Steel pipe connected to copper plumbing

## II) Concentration Cell corrosion:

This type of corrosion occurs when a single piece of metal is exposed to an electrolyte of varying concentration or varying aeration.

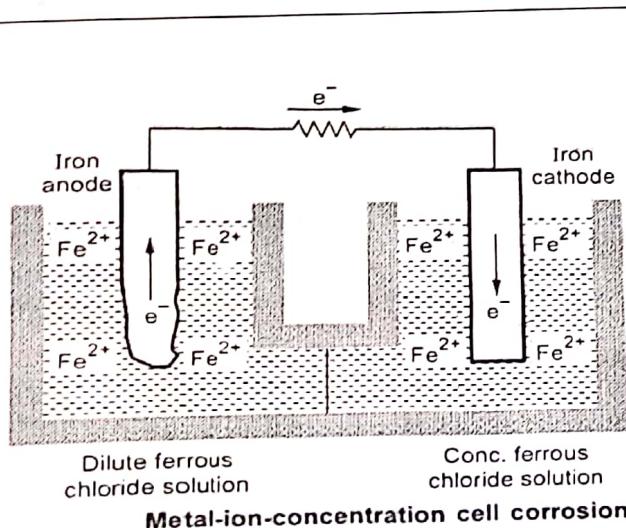
Concentration cells are of two types:

- i) Metal-ion concentration cell
- ii) Oxygen concentration cell

### i) Metal-ion concentration cell corrosion—

The electrode potential of metal depends up on the nature & concentration of solution electrolyte surrounding the electrode. Electrode potential of metal in dilute solution is more negative than in a concentrated solution.

e.g. → When two electrodes of the same metal are immersed in to two solutions of different concentration of same electrolyte are joined externally & they form a metal-ion concentration cell as shown in fig.



So that, one iron rod is dipped in dilute ferrous chloride & other in concentrated ferrous

chloride solution.

It is observed that iron electrode dipped in low concentration of  $\text{Fe}^{+2}$  ions becomes anode & undergoes corrosion. The electrons flow from anode to cathode. The electrode dipped in concentrated solution of ferrous ions ( $\text{Fe}^{+2}$ ) becomes cathode & is protected.

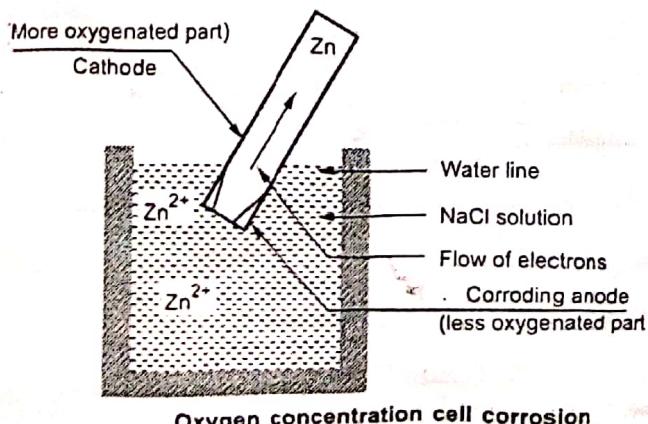
### i) Oxygen concentration cell corrosion :-

When (two parts) of the (same metal) are exposed to (different aeration), the potential difference is developed due to differential aeration.

- Electrode potential of less aerated part of metal is (more negative) than that of more aerated part of metal. Thus less aerated part of metal behaves as anode & more aerated part behaves as cathode. At anode metal dissolves forming metal ions & liberated electrons as,



The electrons released flow from anode to cathode through electrolyte.



Oxygen concentration cell corrosion.

## \* Factors influencing rate of corrosion

The rate & extent of corrosion depends up on the (two main) factors as:

- A) Nature of metal
- B) Nature of environment

### A) Nature of metal —

#### i) Electrode potential (oxidation potential)

The rate, extent of corrosion depends up on the potential difference of the two metals. More the two metals are apart in the galvanic series, the greater will be the difference in their oxidation potential & hence, the faster will be the corrosion of anodic metal.

When two dissimilar metals are in contact, the metal placed higher in galvanic series undergoes corrosion whereas the other metal is protected.

#### ii) Over-voltage —

This factor affects rate of corrosion only in acidic medium.

In acidic medium electrochemical corrosion occurs by hydrogen evolution mechanism in which anode gets dissolved & hydrogen gas is liberated from cathode.

The voltage or potential at which hydrogen gas is liberated at cathode is known as decomposition potential.

At this potential, hydrogen gas is in equilibrium with hydrogen ions. This potential can be theoretically calculated. But experimentally it is observed that the actual

evolution of hydrogen gas at cathode does not occur at this theoretical calculated voltage or potential (but requires a higher potential or voltage).

The difference between the theoretical decomposition potential & the actual potential at which hydrogen gas is liberated at cathode is known as over-voltage.

The value of over-voltage depends up on the nature of metal, nature of electrolyte & current density.

The rate of corrosion depends up on the nature of metal value of over-voltage. Higher the over-voltages lower or lesser is the corrosion.

e.g. Metals like Pb, Sn, Cd are not corroded in aerated dilute hydrochloric acid, because of high value of over-voltage.

### iii) Relative areas of anode & cathode:

When two dissimilar metals are in contact, the corrosion of anodic part is directly proportional to the ratio of less areas of cathodic part & the anodic part.

If the ratio of the cathodic area to anodic area is greater, then the rate of corrosion is greater.

Corrosion is more rapid, & localized if anodic area is smaller because the great demand of electrons from larger cathodic area can be provided by the smaller anode only by undergoing more corrosion.

Thus small areas of anodic metal cause highly localized & rapid destruction of anodic metal.

#### iv) Purity of metal :-

Purity of metal is very important factor in corrosion. As pure metal have high resistance for corrosion as compared to impure metal. The impurities present in metal form minute galvanic cells with the metal under appropriate environment & the anodic part gets corroded.

e.g. - Impurities such as Pb, Fe in Zinc, I.e.

#### v) Physical state of metal -

The rate of corrosion is influenced by the physical state of metal such as grain size, crystals, stressed part etc.

The smaller the grain size of the metal or alloy, the greater will be its solubility & hence greater will be its corrosion. Also, areas under stress, even in a pure metal tend to be anodic & corrosion takes place at these areas.

#### vi) Nature of oxide film :-

Metals like Al, Cr, Ni & other heavy metals form (nonporous oxide) film (protective) therefore once this film is formed there is no effective corrosion take place.

(Volatile oxide) formed by the metal corrosion rate is very high. If porous (nonprotective) oxide film is formed by metal corrosion rate is moderate. But if nonporous (protective) oxide film is

formed, leads to initial corrosion of surface exposed but further corrosion stops after formation of oxide film.

### vii) Nature of corrosion product :-

In electrochemical corrosion if the corrosion product is soluble in corroding medium, corrosion proceeds at faster rate. Whereas, if it is insoluble in the medium, forms a (barrier) & suppress further corrosion & if it is volatile it causes rapid & continuous corrosion.

## B) Nature of Environment :-

### i) Temperature:-

The rate of chemical reactions & the rate of diffusion increases with temperature. Thus, corrosion enhances with rise environmental temperature.

### ii) Humidity:-

The corrosion of metal is very fast in humid atmosphere than in dry atmosphere. Because moisture act as solvent for atmospheric gases like  $O_2$ ,  $CO_2$  etc & forms salts. This produces electrolyte which is essential for corrosion.

### iii) pH of the medium:-

- Acidic medium is more corrosive than alkaline & neutral medium.

- The corrosion of iron is slow above pH 5 in absence of oxygen. The presence of oxygen increases the rate of corrosion.

#### iv) Nature of ions present -

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

Whereas (chlorine ions), if present in medium destroy the protective surface film & exposing the metal surface for fresh corrosion leading to rapid corrosion.

#### v) Conductance of the corroding medium :-

Conductance of the medium plays an important role in corrosion. Mineralized soil is more conductive than sandy soil.

Thus the rate of corrosion is high in highly conducting medium.

#### vi) Formation of Oxygen concentration cell :-

If two different portions of the same metal are exposed to different aeration & receive different amount of oxygen, then oxygen concentration cell is formed.

Such differential aeration leads to corrosion of less oxygenated part, as it act as anode. Highly oxygenated metal surface is less reactive to corrosion.



### Methods of corrosion control & prevention

Corrosion of metal can be controlled by following ways as:

- i) Proper designing & material selection.
- ii) Modification of environment.

- iii) Applications of inhibitors
- iv) Cathodic & anodic protection
- v) Application of protective coatings.

## 1) Cathodic protection:-

Principle:

In electrochemical corrosion, anode undergoes corrosion & cathode remains protected from corrosion. In cathodic protection the metal to be protected is forced to behave like cathode.

Cathodic protection is of two types:

- a) Sacrificial anodic or galvanic protection.
- b) Impressed current cathodic protection.

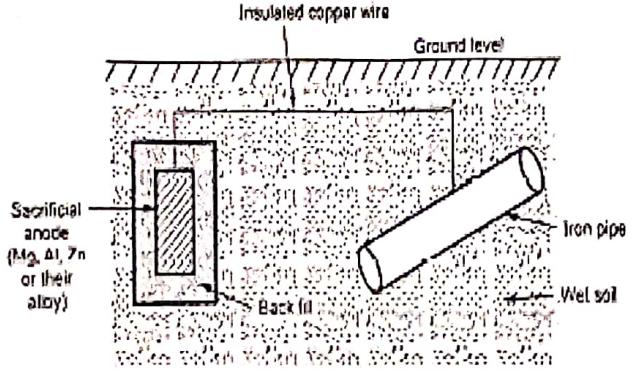
### a) Sacrificial anodic or galvanic protection:

In this method the structure to be protected is connected to a piece of more active/anodic metal. The more active metal works as anode.

The corrosion attack is concentrated at this more active metal & it slowly undergoes corrosion. The main structure act as cathode & remains protected from corrosion.

The more active metal is called "Sacrificial anode". The corroded sacrificial anode block is replaced by fresh one, when consumed completely. To increase electrical contact, sacrificial anodic metal is placed in black till (coke or gypsum).

Metals commonly used as sacrificial anodes are Mg, Zn, Al & their alloys.



Sacrificial anodic protection of underground pipelines

### Advantages of Sacrificial anodic protection:-

- i) No external power is required.
- ii) It is easy to install.
- iii) Installation can be inexpensive if installed at the time of construction.
- iv) Anodes can be easily replaced.
- v) Minimum maintenance is required.

### Limitations:-

- vi) Limited driving potential.
- vii) Limited current output.
- viii) Poorly coated structures may require many anodes.
- ix) Installation can be expensive if installed after construction.

### Applications:-

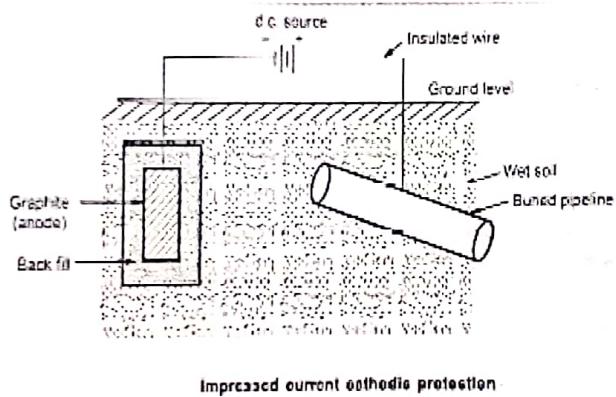
This method can be applied for the protection of -

- i) Buried pipelines
- ii) Underground cables

- iii) Marine structures
- iv) Water tanks.

### b) Impressed Current Cathodic protection —

In impressed current method of cathodic protection, an impressed external current is applied in the opposite direction to the metal to nullify the corrosion current. So, the metal is converted from anode to cathode thus get protected.



Usually the impressed current is derived from direct current source like battery or rectifier. It is connected with an insoluble anode like graphite, stainless steel buried in soil & to the metallic structure to be protected.

The anode is usually in black fill to increase electrical contact with surrounding soil.

## Advantages —

- i) large structures can be protected for long term operations.
- ii) It can be designed for a wide range of voltage & current.
- iii) It can be applied in high resistivity environment.
- iv) Effective in protecting uncoated & poorly coated structures.

## Limitations —

- i) It requires periodic maintenance.
- ii) Requires external power, resulting in monthly power costs.
- iii) Over protection can cause coating damage.

## Applications —

- i) Box coolers
- ii) Water tanks
- iii) Buried oil & water pipes
- iv) Condensers
- v) Marine pipes.

## Anodic Protection :-

- The metal/alloy which get readily passivated are protected by the growth of protective oxide surface film by application of anodic current on metal/alloy.
- 'Passivity' is the phenomenon in which a metal or an alloy exhibit higher corrosion resistance than expected by forming highly protective, thin, nonporous oxide film on the surface. 'Passivity' is quite common for metals like Al, Cr, Ni, Ti etc.

### Principle :-

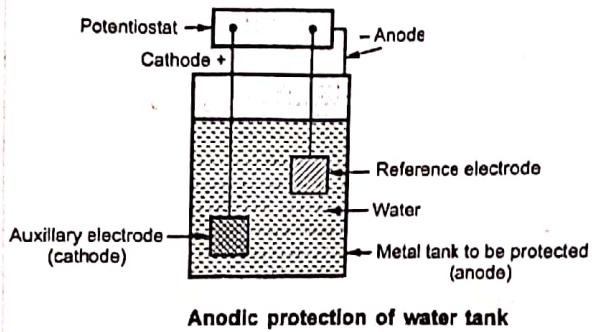
- In anodic protection method, the part of metal to be protected is made more anodic by applying external impressed direct current in the same direction of corrosion current. As a result a thin, <sup>nonporous</sup> oxide film is formed which protects the surface from further corrosion.

### e.g Anodic Protection of water tank.

(Metallic tank) which is to be protected from corrosion is connected to potentiostat. Potentiostat maintains a constant potential & has a reference electrode attached to it.

- An auxiliary electrode (cathode) does not suffer much corrosion in oxidizing environment. The metal tank to be protected act as anode.
- The potentiostat is adjusted for particular current & potential so that anodic metal tank get oxidized & get passivated. There is formation of thin corrosion resistant Oxide layer which protects the metal from corrosion.
- Once the metal become (passive)

the potential changes to high positive value. Then very small current is sufficient to maintain passivity of metal, to prevent its corrosion.



### Advantages:-

- (Anodic protection) has greater throwing power (i.e to give uniform deposition) than cathodic protection, hence complex structures can be protected.
- Method can be applied to highly corroding medium like concentrated acids.
- It requires low current density, hence its operation cost is low.

### Limitations:-

- This method is applicable only to those metals & alloys which exhibit passivity.
- During anodic protection method, corrosion take place at very slow rate but it is not reduced to zero.

### Applications:-

This method is applied for corrosion protection of:

- i) stainless steel containers used for transporting corrosive chemicals like concentrated acids
- ii) Chemical reactors, tanks.
- iii) Pipes carrying corrosive liquids.

## \* Comparison between Cathodic & Anodic protection

### Cathodic Protection

### Anodic protection

- |  |  |
|--|--|
| i) Applicable to all metals  | j) Applicable to only those metal which shows active-passive behaviour |
| ii) The metal to be protected forced to behave as cathode.                       | ii) The metal to be protected is made more anodic.                     |
| iii) Can be used where there is no source of power                               | iii) Requires a source of power  |
| iv) Installation cost is low   | iv) Installation cost is <del>high</del> but operating cost is low.    |
| v) Throwing power is less so used for protecting structures with standard shape. | v) Throwing power is better hence complex structures can be protected. |

## \* Applications of Protective Coating.

Metals can also be protected by coating their surface with some protective material. The metal to be coated is called base metal while the protective material is called coating. Protective coatings can be metallic or nonmetallic.

### Metallic coating:-

Metallic coatings can be of two types as:

- i) Anodic coating / sacrificial coating
- ii) Cathodic coating / noble coating.

### A) Types of metallic coating —

#### 1) Anodic coating / Sacrificial coating :-

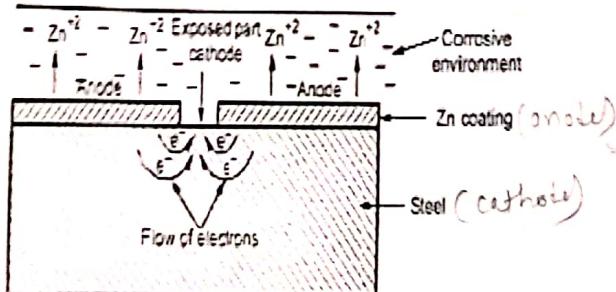
## I) Anodic coating / sacrificial coatings:

i) Anodic coatings are produced from coating metal which are anodic to base metal i.e. which have higher position in the electrochemical series or galvanic than the base metal.

e.g. → Coating of Zn, Al, & Cd on steel are anodic. In case any pores, breaks or discontinuity occurs in such anodic coating, a galvanic cell is formed between coating metal & exposed part of base metal.

ii) e.g. → In case of galvanized steel (steel coated with Zn), the coated metal Zn is more anodic to iron (from steel) therefore it will undergo corrosion, protecting the base metal (iron). There will be no corrosion attack on iron, until all zinc get corroded.

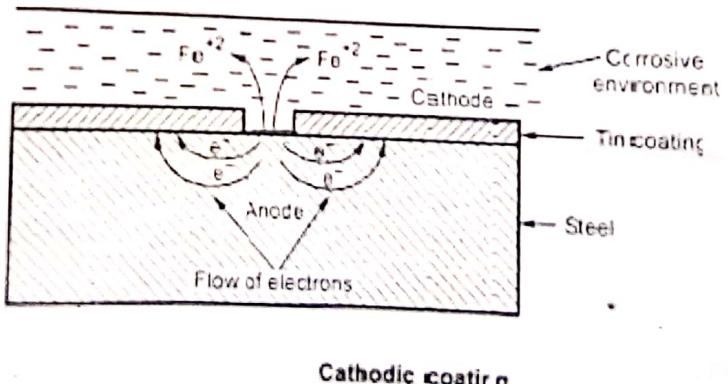
Thus Zn coating protects iron sacrificially, hence it is also known as sacrificial coating.



Functioning of anodic coating

## Cathodic coating / Noble coating:-

- i) Cathodic coatings are obtained when the coated metal is cathodic to the base metal. Coating metal has lower position in the electrochemical Series than the base metal.
- ii) Coating metal being more noble than base metal & protect base metal because it offers higher corrosion resistance than base metal.
- iii) e.g. If iron is the base metal, then coating of tin (Sn) will be cathodic coating. Tin plated steel can be used for food storage. Cathodic coating provides effective protection to the base metal only when coatings are completely continuous & free from pores, breaks or discontinuities.
- iv) If coating is broken, a galvanic cell is formed between the coating & the exposed part of base metal in moist environment. Tin is cathodic to iron therefore, tin forms cathode & exposed iron part form anode undergoes corrosion.
- v) Thus the base metal iron get corroded. Here the anodic area is smaller than cathodic area. So the corrosion taking place will be very much localized & intense.
- vi) Therefore (anodic coatings) are always preferred over cathodic coating.



## \* Comparison between anodic & cathodic coating

### Anodic coating

- i) It protect the base metal by sacrificing itself.
- ii) Coating metal has higher oxidation potential than base metal.
- iii) In case of any cracks or pores in the coating, the base metal not corroded till the coating metal is consumed.
- iv) eg - Coating of Zinc on iron (galvanized steel)

### Cathodic coating

- i) It protect the base metal due to its noble character i.e. higher corrosion resistance.
- ii) Coating metal has lower oxidation potential than base metal.
- iii) In case of cracks or pores in the coating there will be faster corrosion of base metal.
- iv) eg - Coating of (Sn) tin on iron (tinning of steel).

## \* B) Surface preparation before metallic coating

Long life of any protective coating on metal surface can be achieved when the metallic surface is well cleaned & properly treated before application of coating material.

\* Surface treatment involves 3 steps -

- 1) Removal of grease & other contaminations.
- 2) Removal of oxide scale, rust & corrosion product.
- 3) Etching treatment for better adhesion of coat.

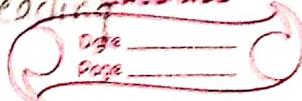
### Step I - Removal of grease & other contaminations

This method used for removal of grease & other contaminations like paints it involve the cleaning procedure as :

#### 1) Solvent cleaning -

- i) It is used to remove oil, greases, fatty substances.

wetting agents — The substances which reduce surface tension of water & increases the spreading <sup>desire</sup> ability of liquid.



- i) Organic solvents like  $\text{CCl}_4$ , toluene, xylene, acetone etc can be used for cleaning
- ii) It is followed by cleaning with steam & hot water containing wetting agents.
- 2) Alkali cleaning :-
  - i) It is used for removing old paints coating from metal surface.
  - ii) Alkali cleaning agent like trisodium phosphate along with soaps & wetting agent like caustic soda are used.
  - iii) Alkali treatment is followed by mild rinsing with water & further treatment with slightly acidic solution to neutralize the traces of alkali.

## Step 2: Removal of oxide scale, rust & corrosion products.

- 1) Mechanical cleaning —  
It removes loose rust & impurities from the surface. It can be done by using scrapers, wire brushes etc.
- 2) Flame cleaning —  
Metal surface is heated with a hot flame to remove moisture & loosely adhering scales, followed by wire brushing.
- 3) Sand blasting —  
It is used for removing oxide scales & for getting slightly roughed surface. The process consists of introducing the sand into an air stream under a pressure of 25 to 100 atmosphere is blasted on metal surface. It removes the last traces of scales.

## Step 3: Etching treatment for better adhesion of coat.

- i) In order to achieve better adhesion of metallic coating (pickling) method is widely used.
- ii) It involves immersing the metal in acidic or alkaline solution to provide clean, smooth surface.
- iii) Acid pickling (pickling) is more convenient to remove scales as compared to mechanical cleaning & sand blasting.  
eg Metals can be dipped in dil  $HCl$ , dil  $H_2SO_4$ , dil  $HNO_3$  solutions.

C)

### Methods of applying metallic coating —

Following methods are widely used

to apply metallic coatings.

- 1) Hot dipping
- 2) Metal cladding
- 3) Cementation
- 4) Electroplating.

#### 1) Hot dipping —

Hot dipping is used for producing a coating of low melting metals such as Zn ( $m.p = 419^\circ C$ ), Sn ( $m.p = 232^\circ C$ ), Pb, Al etc on iron, steel, copper which have comparatively higher melting points.

The process is carried out by immersing (clean base metal) in the bath of molten coating. eg - Coating of Zn on iron (Galvanizing)  
Coating of Sn on iron (Tinning)

#### 1) Galvanizing —

Def<sup>n</sup> - The process of coating iron or steel (base metal) with a thin coat of zinc by hot dipping to prevent base metal from

Date \_\_\_\_\_  
Page \_\_\_\_\_

classmate

6

Fe

Zn more active

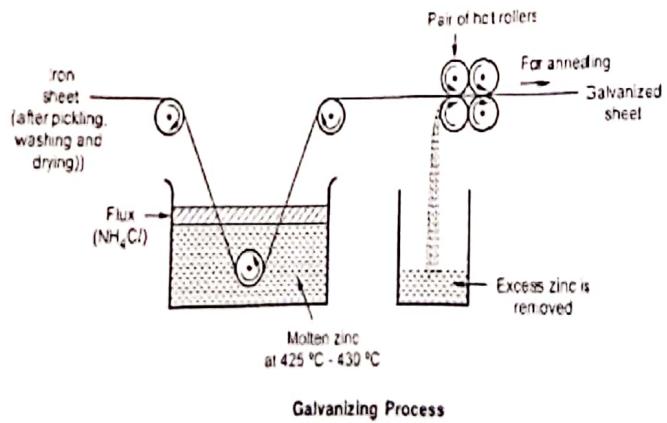
Sn Pb Cu less active

Corrosion is called galvanizing.

Zinc is anodic with respect to base metal (iron) when exposed to corrosive medium, only Zinc undergoes corrosion, protecting base metal.

Process -

- i) The metal article is cleaned & degreased by using organic solvents.
- ii) It is treated with dil  $H_2SO_4$  for 15-20 min at  $70-90^\circ C$  to remove any rust or scale.
- iii) It is then washed with water & dried.
- iv) The metal article is then dipped in bath of molten zinc, maintained at  $425-430^\circ C$ . The surface of bath is covered with flux ( $NH_4Cl$ ). Flux cleans the metal surface before coating for better adhesion & prevents the oxidation of molten coating metal after coating.
- v) It is then passed through pair of hot rollers to remove excess of zinc & produce thin uniform coating.
- vi) It is then annealed at  $650^\circ C$  <sup>To give uniform texture</sup> & cooled to room temperature slowly.



Uses -

Galvanized sheets are used for roofing sheets, wires, pipes, screws, tubes, buckets etc. Zn gets dissolved in dilute acids to form toxic compounds, therefore galvanized utensils are not used for storing acidic food.

2) Tinning -

Defn — The process of coating iron or steel (base metal) with a thin coat of tin by hot dipping to prevent base metal from corrosion is called tinning.

Tin being more cathodic, gives better corrosion resistance, protecting base metal.

Process:

- i) The clean surface of metal article is treated with dil  $H_2SO_4$  (pickling) to remove any oxide film, washed with water & dried
- ii) It is then immersed in a flue of  $ZnCl_2$  &  $NH_4Cl$  which will facilitate better adhesion of coating
- iii) The metal article is then passed through a tank of molten tin maintained at about  $240^\circ C$ .
- iv) Finally it is passed through a series of rollers in the palm oil. Palm oil protects the hot tin coated surface from oxidation.

Uses -

Because of (nontoxic nature of tin), tinning is used for coating iron, steel, copper, brass. Used for manufacturing containers to store food stuff, oils, ghee, kerosene etc. Tinned copper

Sheets are used for making cooking utensils & refrigeration equipment.

### Comparison of galvanizing & tinning

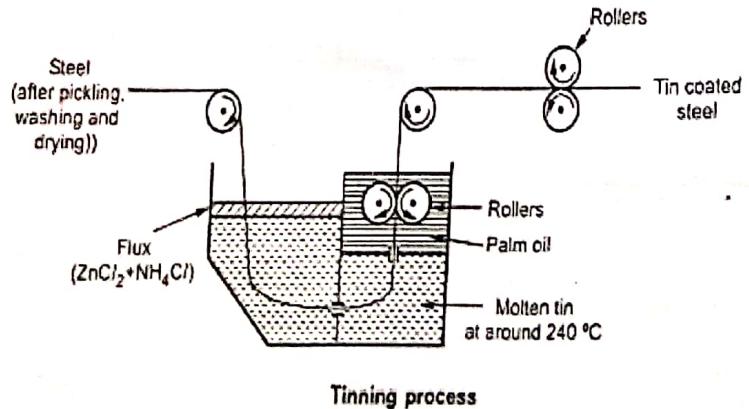
#### Galvanizing

- It is the process of covering iron/steel with thin coat of Zinc by hot dipping to prevent corrosion.
- Zinc protects the base metal sacrificially.
- In galvanized article, even if the coating is ruptured, still Zinc continues to protect the base metal sacrificially by forming galvanic cell.
- Galvanized containers can not be used for storing food stuff because zinc reacts with food acids forming toxic compounds.

#### Tinning

- It is the process of covering iron/steel with thin coat of tin by hot dipping to prevent corrosion.
- Tin protects the base metal due to its noble nature & higher corrosion resistance.
- In tin coated article, tin protects the base metal till the coating is perfect. If coating is ruptured, then it causes rapid corrosion of base metal.
- Tin coated containers & utensils can be used for storing any food stuff because tin is non toxic.

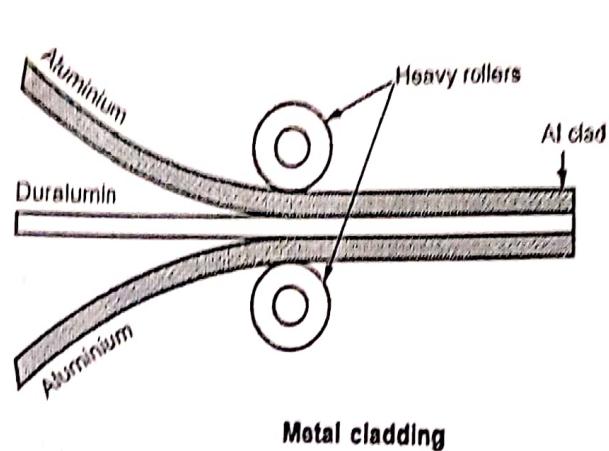
Tinning  
Tip



Tinning process

## 2) Metal cladding:

Defn → Metal cladding is the process by which coating metal is bonded firmly & permanently to base metal on one or both sides.



— This coating metal is called cladding metal. Cladding metal can be selected depending upon the corrosion resistance required for environment. Metals like nickel, copper, lead, silver, platinum & alloys like stainless steel, nickel alloy, copper alloy, lead alloy etc are used as cladding material.

— Base metals on which cladding can be done are mild steel, aluminium, copper, nickel & their alloys.

— Cladding is done by forming a sandwich of protective layer & the base metal, which are passed through rollers & bonded under the action of heat & pressure.

e.g. → Al cladded sheets are used in aircraft industry which are made by sandwiching duralumin between the two layers of 99.5% pure aluminium.

Applications of this process is limited only to simple shaped articles.

### 3) Cementation / Diffusion coating

- Cementation / diffusion coating is obtained by heating base metal in a revolving drum containing a powder of the coating metal.
- The powdered coating metal diffuses in to the surface of the base metal. It results in the formation of an (alloy) of the coating metal & the base metal on the surface of the base metal.
- The process is suitable for coating small articles of uneven surfaces like bolts, screws, valves etc.
- Coating metals like Zn, Cr, & Al can be coated on iron.

#### a) Sherardizing:

- It is the process of cementation, using zinc powder as coating metal.
- In the process, iron article is cleaned & packed with zinc dust in a drum. The drum is sealed tightly so that oxidation of zinc is minimum. The drum is rotated for 2-3 hours & heated at 350-370°C. During the process, zinc get diffused in to iron forming Fe-Zn alloy on the surface.

- This method is used for coating small articles like bolts, screw, nuts, valves etc.
- An advantage of this process is coating is (uniform) even in case of crevices or depression.
- There will be practically no change in the dimension of article after coating.

#### b) Colorizing:

- It is carried out by heating metal

N powder  
aluminium  
oxide

840-930°C

4-6 hr.

objects with (rough) surface in a tightly packed drum with a mixture of aluminium powder & aluminium oxide together with trace of  $\text{NH}_4\text{Cl}$  flux.

The process is carried out at 840-930°C for 4 to 6 hrs. Air is excluded from the drum.

This method is applied for the protection of furnace parts, valves, condensers in oil refineries & in general appliances where resistance to attack by sulphur at high temperature are required.

### c) Chromizing:

This process is carried out by heating the base metal with mixture of chromium powder & alumina at 1300°C to 1400°C for 3-4 hours.

It is extensively used or applied for the protection of gas turbine blades. Chromized steel is also used in appliances where resistance to corrosion by salt or dil  $\text{HNO}_3$  is required.

### 4) Electroplating:

Defn

Electroplating or electrodeposition is the process by which the coating metal is deposited on the base metal by passing a direct current through the solution of an electrolyte, containing the soluble salt of coating metal.

- The base metal to be plated is usually made cathode of electrolytic cell, whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity like graphite.

### Objectives of electroplating -

#### I] Electroplating on metals -

- i) Increases the resistance to corrosion.
- ii) Increases the resistance to chemical attack.
- iii) Improves physical appearance.
- iv) Improves decorative & commercial values of metal.

#### II] Electroplating on nonmetals

- i) Increases strength.
- ii) Preserves & decorates the surface of non metal.
- iii) Makes the surface conductive.

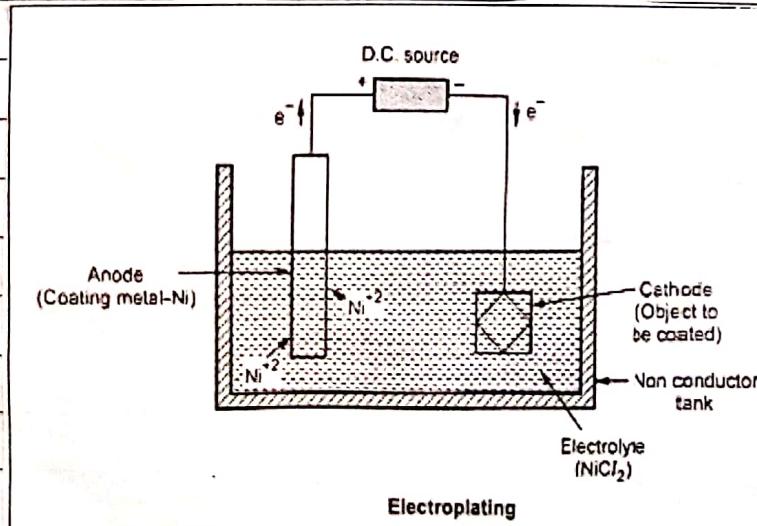
### Process -

- i) The base metal article to be coated is cleaned to remove oils, greases, oxides, scales etc.
- ii) Electroplating is carried out in electroplating bath.
- iii) The (metal article) to be plated is made (cathode).
- iv) (Coating metal) is made anode.
- v) Series of cathodes & anodes can be suspended alternatively for getting uniform deposition.
- vi) Cathode & anode are dipped in the electrolyte containing suitable concentration of mineral acid.

- vii) (PH of electrolyte) is adjusted & suitable current density is applied for electrolysis.
- viii) As electrolysis proceeds, the anode metal gets oxidized & enters the electrolytic soln. The metal ion then get reduced & deposited on cathode to give uniform coating on the surface of base metal.
- ix) The metal ions getting reduced & deposited at cathode are reformed by anode metal oxidation. Thus, there is no change in salt concentration of electrolyte.

	Reaction at anode.	Reaction at cathode.	Salts for electrolyte
For Nickel plating	$\text{Ni} \rightarrow \text{Ni}^{+2} + 2e^-$	$\text{Ni}^{+2} + 2e^- \rightarrow \text{Ni}$	$\text{NiCl}_4, \text{NiSO}_4$
For copper plating	$\text{Cu} \rightarrow \text{Cu}^{+2} + 2e^-$	$\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}$	$\text{CuSO}_4$
For Silver plating	$\text{Ag} \rightarrow \text{Ag}^+ + e^-$	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	$\text{AgCN}$

fig



## \* Factors affecting electroplating process -

- i) Control of current density
- ii) Control of temperature
- iii) Control the rate of deposition.
- iv) Control of metal ion concentration & pH of electrolyte.
- v) Control of anode surface area & position.

## \* Applications of electroplating -

- i) Electroplating can be used (for getting decorative surface).  
eg → gold, chromium, brass coating on steel are used in ornaments, wrist watches, belts, pens etc.
- ii) It is used for protecting surface against corrosion eg → chromium plating on steel.
- iii) Non-metallic materials like wood, paper, glass, feather, resins can be electroplated for decoration, preservation of surface from corrosion.  
eg - Synthetic resin are electroplated with Cu
- iv) Automobile, aircraft, radio & communication industries use electroplated parts.

## \* Advantages:-

- i) Coating thickness can be controlled.
- ii) Coating of metal having high melting points like Cr, Ni, Ag, Au etc can be easily applied.
- iii) Process is non-expensive.
- iv) Fine coatings can be obtained with improved hardness.