

Corrosion and its prevention



Corrosion

➤ The process of decay of a metal from its surface due to unwanted chemical (or) electro chemical interactions with its environment is called corrosion.

1. **Ex:-** Formation of reddish brown layer of rust (Hydrated ferric oxide) on the surface of iron ($\text{Fe}_2\text{O}_3\text{H}_2\text{O}$).
 2. **Ex:-** Formation of green layer of basic carbonates on the surface of copper ($\text{CuCO}_3 + \text{Cu}(\text{OH})_2$).
- **Units:** milli inches /years (or) mm/ year.

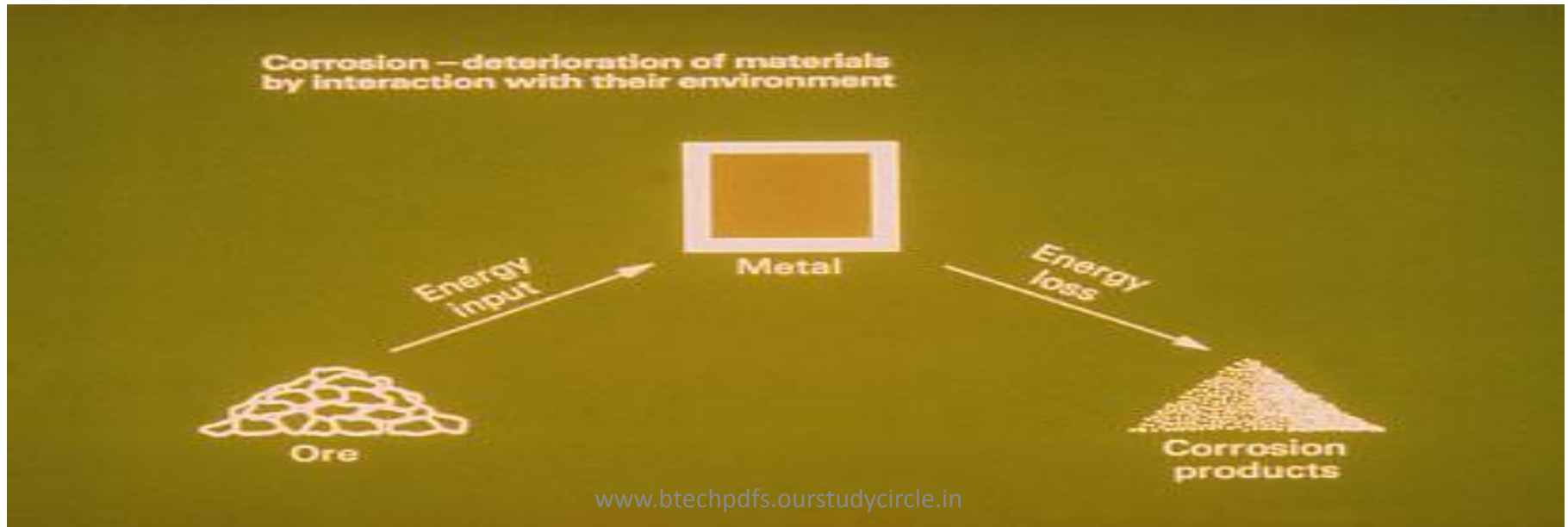
Causes of corrosion:-

- Metals exist in nature in the form of oxides, chlorides, sulfates, carbonates and sulphides.
- These combined states of metal has low energy is thermodynamically stable state for metals.
- During extraction of metals these are reduced to free metallic state which is unstable

➤ So metals have the natural tendency to go back to their stable combined state. Therefore they undergo corrosion to get stability.

Ore of Metal → **pure metal** → **corroded metal**
(Thermodynamically) *(Thermodynamically)* *(Thermodynamically)*
Stable *unstable* *Stable*

➤ Thus corrosion is a process “reverse of extraction of metals”



Effects of corrosion:

- The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
- The process of corrosion is very harmful and is responsible for the enormous wastage of metallic products.
- Losses occurring due to corrosion cannot be measured in terms of the cost of metals alone, but the high cost of fabrication into equipment/machine tool/ structures should also be considered.
- The approximate estimate of loss of metal due to corrosion, as 2 to 2.5 billion dollars per annum all-over the world.
- Hence an engineer must understand the mechanism of corrosion so that the effects can be minimized by avoiding the corrosion conditions and provide simultaneous protection against corrosion.

Theories of Corrosion :

Based on Mechanism

CORROSION OF METALS

DRY CORROSION(OR)CHEMICAL CORROSION

- 1. OXIDATION CORROSION
- 2. CORROSION BY OTHER GASES
- 3. LIQUID-METAL CORROSION

WET CORROSION (OR) ELECTROCHEMICAL CORROSION

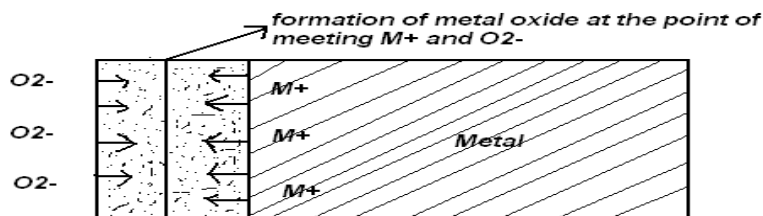
- 1. ELECTROCHEMICAL CORROSION BY EVOLUTION OF HYDROGEN AND ABSORPTION OF OXYGEN.
- 2. GALVANIC CORROSION
- 3. CONCENTRATION CELL CORROSION

1. Chemical (or) Dry corrosion:

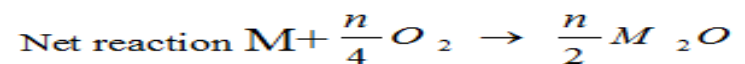
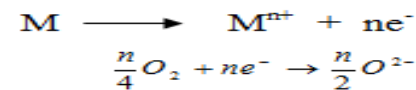
It proceeds in two ways

A. Oxidation corrosion

- It is brought about by the direct action of oxygen at low or high temperatures on metals, usually in the absence of moisture.
- At ordinary temperatures, metals are very slightly attacked. However alkali metals (IA) and alkaline earth metal (IIA) are even rapidly oxidized at low temperature.
- At high temperatures, almost all metals (except Ag, Au, Pt) are oxidized.
- **The reactions in the oxidation corrosion are,**



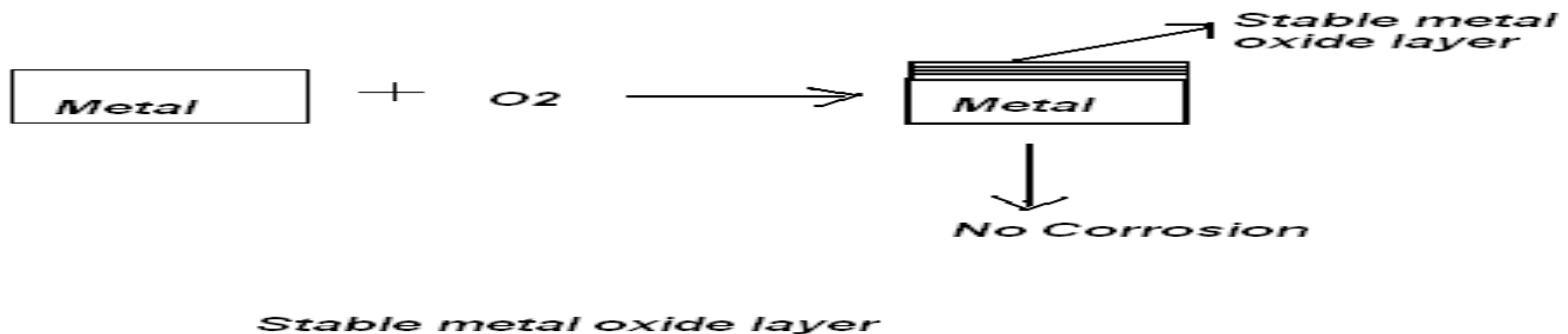
Oxidation mechanism of metals



Nature of the oxide formed plays an important role in oxidation corrosion process.

1.Stable:

- A stable metal oxide layer with fine-grained structure tightly adheres to the parent metal surface.
- Hence, such a layer can be of impervious nature to the attacking oxygen. Such film behaves as protective coating in nature, thereby shielding the metal from further corrosion.
- Ex; the oxide film on Al, Sn, Pb, Cu, Cr, W etc.



2.Unstable:

- If the metal oxide layer unstable, it decomposes back into the metal and oxygen.
- Consequently, oxidation corrosion is not possible in such a case.
- Thus, Ag, Au, and Pt do not undergo oxidation corrosion.

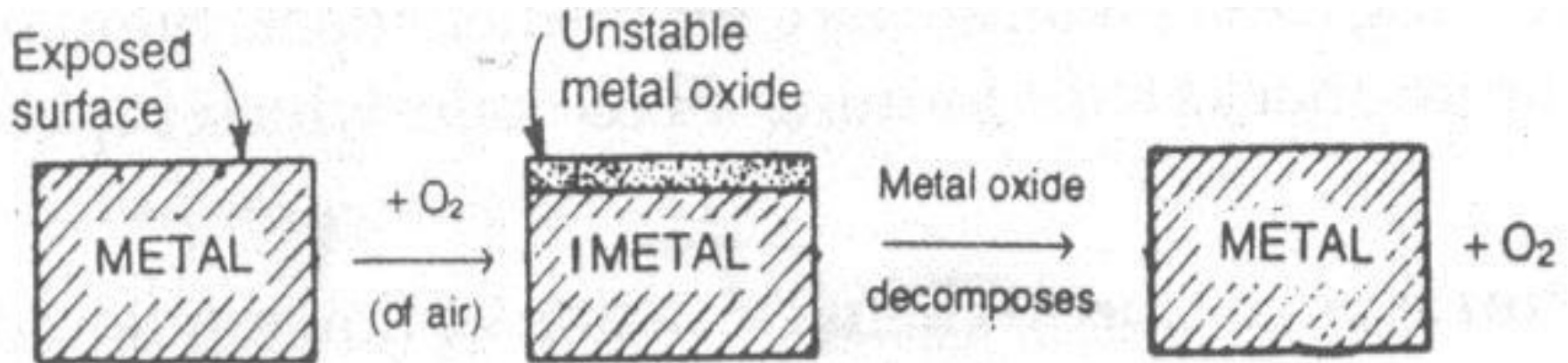


Fig. 2. Unstable oxide layer.

3.Volatile:

- If the metal oxide layer is volatile, it evaporates as soon as it is formed, leaving the underlying metal surface exposed for further attack.
- This causes rapid and continuous corrosion, leading to excessive corrosion.
- Ex: Molybdenum oxide (MoO_3) is volatile.

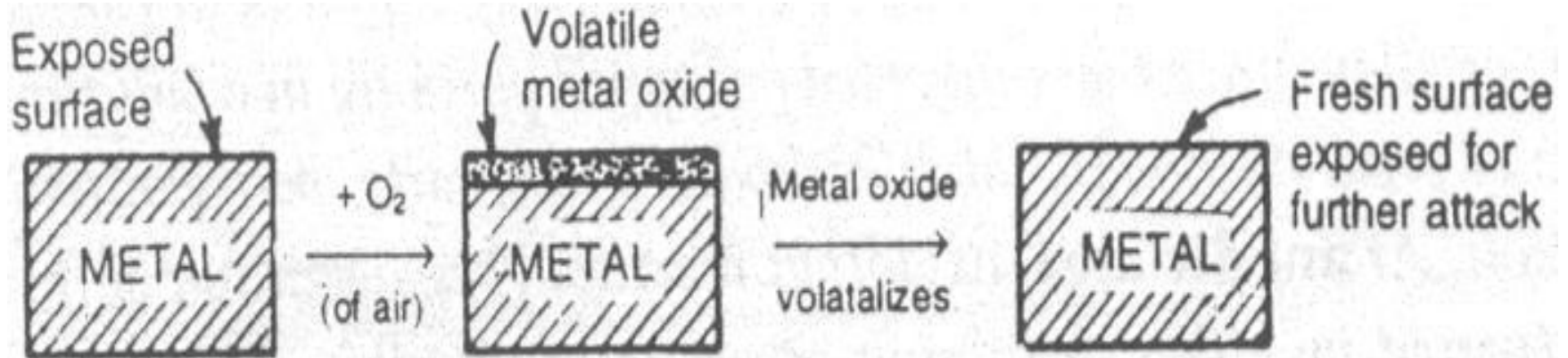


Fig. 3. Volatile oxide layer.

4.Porous:

- If the metal having pores or cracks provides access to the oxygen to reach the underlying surface of metal.
- As a result corrosion process continues unobstructed, till the entire metal is completely converted into its oxide.

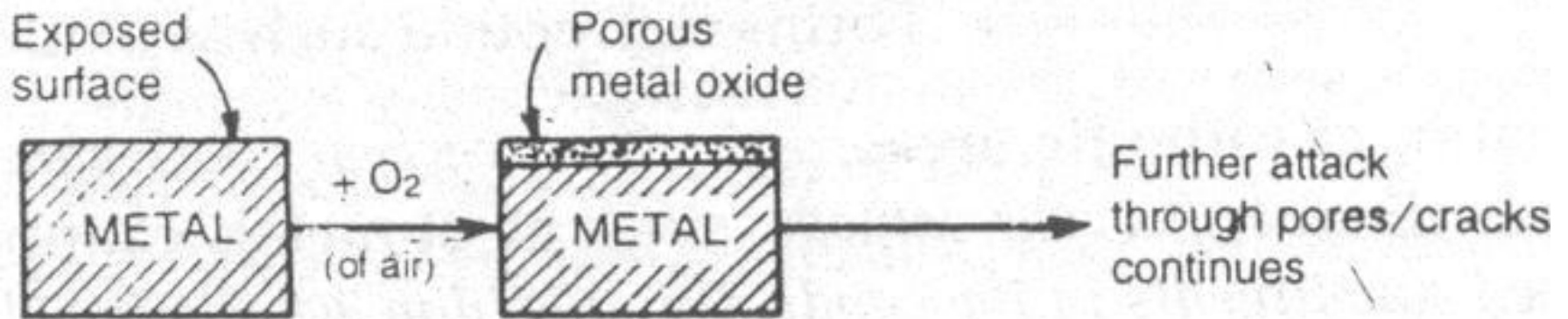


Fig. 4. Porous oxide layer.

➤ To express the extent of protection given by the corrosion layer to the underlying metal Pilling Bed worth rule was postulated.

Pilling Bed worth rule:

1. If the volume of the **metal oxide layer** is at least as great as the volume of **metal** from which it is formed is non-porous and becomes protective layer by tightly adhering to the base metal.
2. For example, the specific volume ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. Hence, the rate of corrosion is least in Tungsten (W).
3. If the volume of **metal oxide is less than** the volume of the metal, the **oxide layer is porous**, non continuous and non-protective and faces strains.
4. Hence cracks and pores are developed in the layer, creating access to atmospheric oxygen to reach the underlying metal. In this case corrosion is continuous and rapidly increases.

For example: **Li, Na and K.**

$$\text{SPECIFIC VOLUME RATIO} = \frac{\text{VOLUME OF METAL OXIDE}}{\text{VOLUME OF METAL}}$$

B. Corrosion by other gases:

- The gases like SO_2 , CO_2 , Cl_2 , H_2S and F_2 etc, also causes chemical corrosion and the extent of corrosion depends mainly on the chemical affinity between the metal and the gas involved.
- The degree of attack depends on the formation of protective or non-protective films on the metal surface.
- If the film formed is protective or non-porous, the intensity or extent of attack decreases, because the film formed protects the metal from further attack.

Ex: AgCl film, resulting from the attack of Cl_2 on Ag.

- If the film formed is non-protective or porous, the surface of the whole metal is gradually destroyed.

Ex: dry Cl_2 gas attacks on tin (Sn) forming volatile SnCl_4

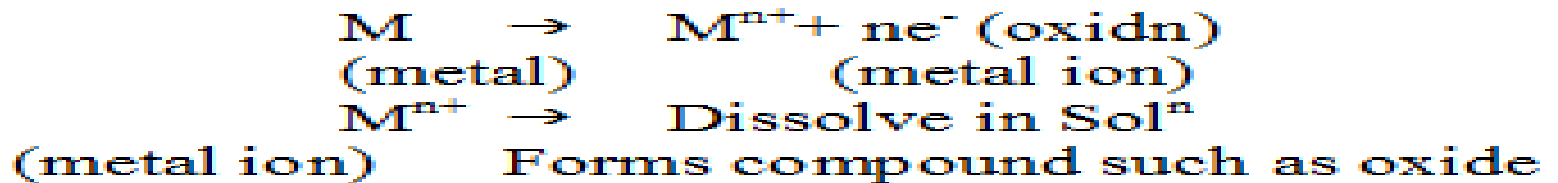
C. Liquid metal corrosion

- It is due to chemical action of flowing liquid metal on solid metal at high temperatures.
- Such corrosion occur in devices used for nuclear power. The corrosion reaction involves either dissolution (the act of breaking up) of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.
- Both these methods of corrosion cause weakening of the solid metal.
- **Ex:-** Coolant Sodium leads to corrosion of Cadmium in nuclear reactor.

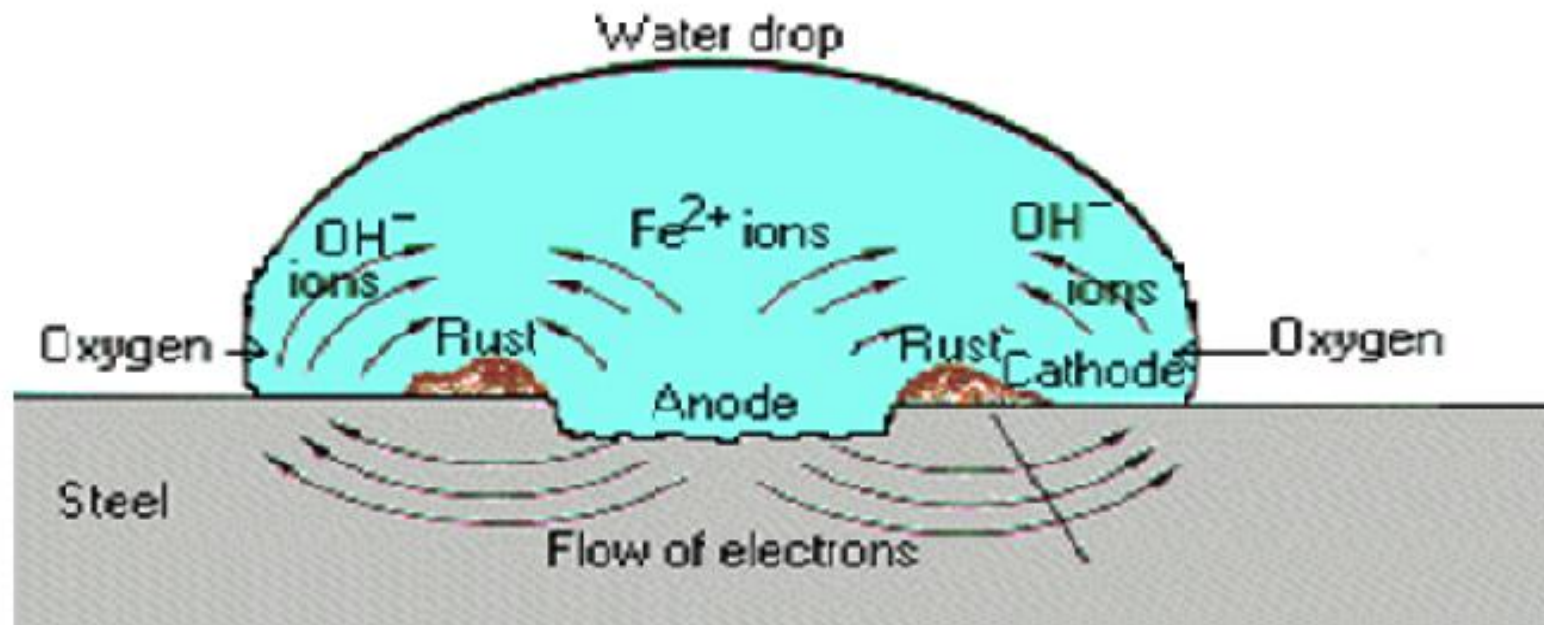
2. Electrochemical or Wet Corrosion:

- This type of corrosion occurs where a conducting liquid is in contact with metal or when two dissimilar metals or alloys are either immersed or dipped partially in a solution.
- This corrosion occurs, due to the existence of separate. “anodic and cathodic” areas, between which current flows through the conducting solution.
- At anodic area, oxidation reaction (i.e. liberation of free e⁻s) takes place, so anodic metal is destroyed by either dissolving in combined state (such as oxide etc). Hence, corrosion always occurs at anodic areas.

At anode :



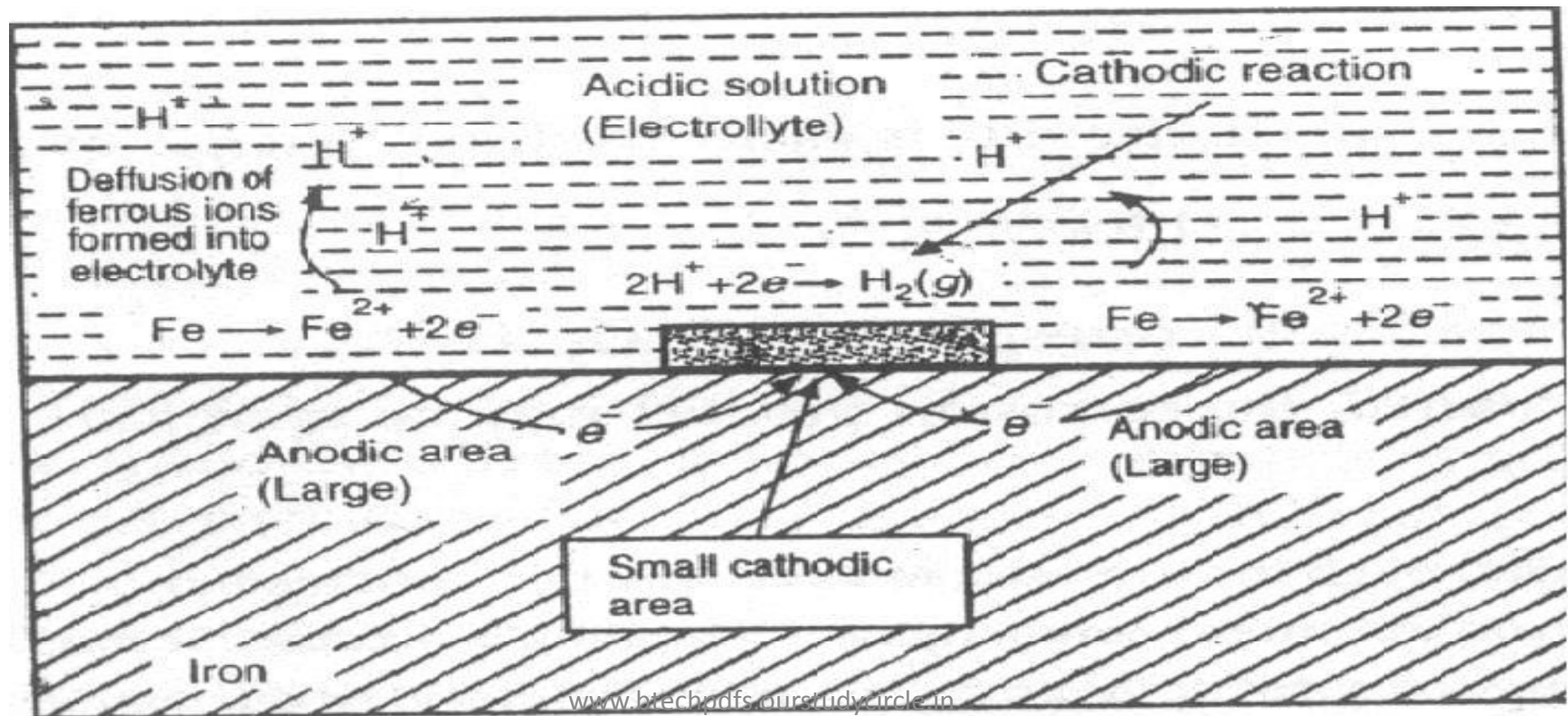
1.Absorption of O₂



- Rusting of iron in neutral aqueous solution of electrolytes in the presence of atmospheric oxygen is a common example of this type of corrosion.
- The surface of iron is, usually, coated with a thin film of iron oxide.
- However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well metal parts act as cathodes.
- It follows that the anodic areas are small surface parts; while nearly the rest of the surface of the metal forms large cathodes.
- At the anodic areas of the metal (iron) dissolve as ferrous ions with liberation of electrons.

2. Evaluation of H₂

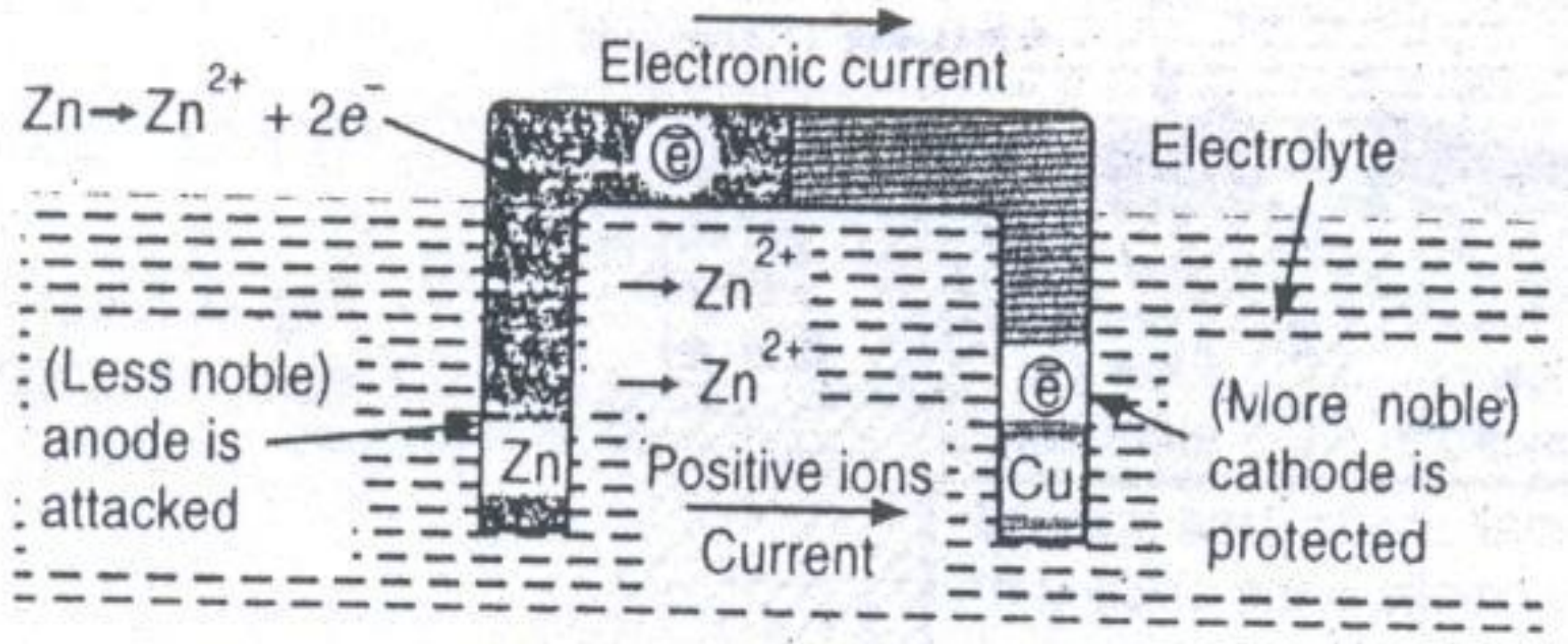
- This type of corrosion occurs usually in acidic environments. Considering metal like Fe, the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons.
- These electrons flow through the metal, from anode to cathode, where H⁺ ions are eliminated as hydrogen gas





Types of electrochemical Corrosion

A. Galvanic Corrosion :



- This type of electrochemical corrosion is also called bimetallic corrosion.
- When two dissimilar metals are connected and exposed to an electrolyte, they will form a galvanic cell.
- The anodic metal (high oxidation potential) will be oxidised and it will undergo corrosion.
- Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell.
- Zinc acts as anode and undergoes corrosion while cathode will be unaffected

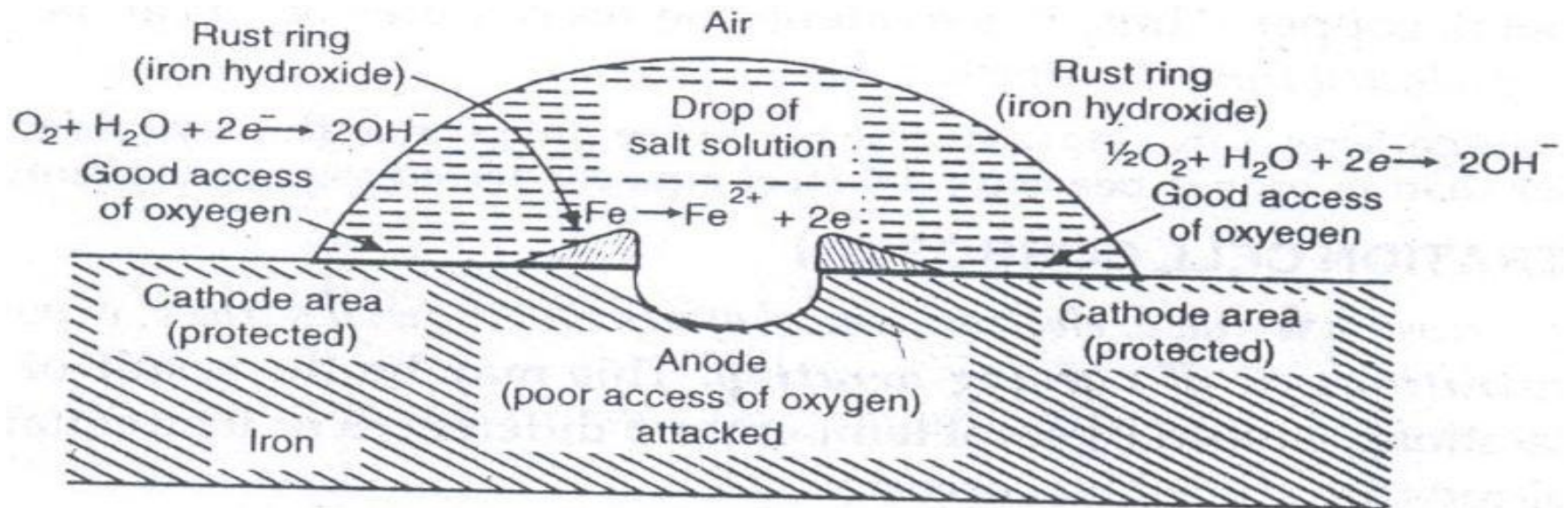
1. Galvanic corrosion can be avoided by coupling metals close to the electrochemical series.
2. Fixing insulating material between two metals.
3. By using larger anodic metal and smaller cathodic metal.

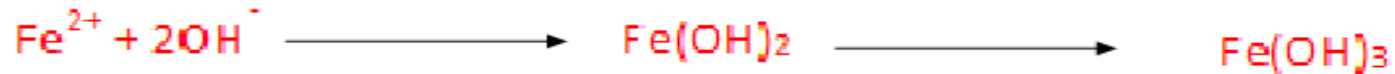
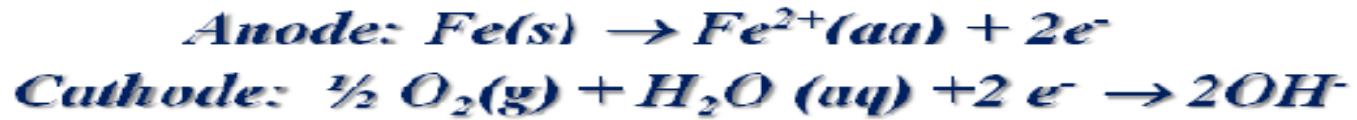
Example of galvanic corrosion:

1. Steel screws in brass marine hardware
2. steel pipe connected to copper plumbing
3. steel propeller shaft in bronze bearing
4. zinc coating on mild steel
5. lead–tin solder around copper wires.

B) Pitting Corrosion

- Consider a drop of water resting on the surface of metal, the metal surface which is covered by the drop has low oxygen concentration and thus acts as an anode and suffers corrosion.
- The uncovered metal surface due to high O₂ concentration acts as cathode.





1. Pitting of the metal occurs when there is a **break in the protective layer**. Pitting corrosion is a non uniform corrosion resulting in the formation **pits, cavities and pin-holes** in the metal.

2. Once a small pit is formed the rate of corrosion will be increased.

DIFFERENCES OF CHEMICAL CORROSION WITH ELECTROCHEMICAL CORROSION:

Chemical (or) Dry corrosion	Electrochemical (or) Wet corrosion
This corrosion occurs at dry conditions	This corrosion occurs at wet conditions in presence of an electrolyte medium
Corrosion is uniform	Not uniform, the anodic area is small, pitting is frequent
it is slow process	It is a rapid process
It involves direct chemical attack of metal by environment	It involves the formation of large number of electrochemical cells.
It is explained by absorption mechanism	Explain by mechanism of electrochemical reactions
Corrosion products are produced at the place where corrosion takes place	Corrosion at anode, and corrosion products occurs at cathode.

FACTORS AFFECTING THE RATE OF CORROSION

1. Nature of metal

2. Nature of corroding environment

Galvanic Scale of Metals in Sea Water		
NOTE: Potentials vary with the actual composition of the material.		
	Material	Potential
More Active (Less Noble) ↑ ↓ More Passive or Noble	Magnesium and its Alloys	- 1.50
	Zinc	- 1.03
	Aluminum and its Alloys	- 0.75
	Cast Iron	- 0.61
	Carbon Steel	- 0.61
	Type 430 Stainless (Active)	- 0.57
	Type 304 Stainless (Active)	- 0.53
	Type 410 Stainless (Active)	- 0.52
	Silicon Bronze	- 0.40
	Copper	- 0.36
	Yellow Brass—268	- 0.36
	Red Brass—230	- 0.33
	Aluminum Bronze	- 0.32
	Tin Bronze—(G & M)	- 0.31
	Admiralty Brass	- 0.29
	Copper—Nickel	
	90—10	- 0.28
	80—20	- 0.27
	70—30	- 0.25
More Passive or Noble	Nickel—200	- 0.20
	Silver Solder	- 0.20
	Inconel—600	- 0.17
	Monel	- 0.13
	Stainless Steel (Passive)	- 0.10
	Silver/Silver Chloride half cell (Reference)	0.00
	Graphite	(note sign change) + 0.20

1 Nature of Metal

(i) Position of the metal in galvanic series:

Decides the corrosion rate

A metal having higher position in the galvanic series undergoes corrosion when connected to another metal below it. Eg: Zn-Cu

More difference in the position of galvanic series will cause faster corrosion at anodic metal. Eg: Fe-Cu

(ii) Purity of metal:

Pure metal resists corrosion

Impurities in a metal form a local galvanic cell and result in the corrosion of metal.

Rate of corrosion increases due to more exposure of impurities.

(iii) Relative areas of anode and cathode:

Smaller the area of anode compared to cathode faster corrosion of anode.

When the cathode area is larger, the demand for electrons will be more, and this results in increased rate of dissolution of metals at anodic regions

Small cathodic area → corrosion will be less.

iv) Physical state of the metal:

Small granular metal will corrode faster than the larger one.

The areas under stress tend to be anodic and suffer corrosion.

Caustic embrittlement takes place in stressed parts such as bends, joints and rivets in boilers

(v) Nature of oxide film:

If the oxide film is porous and oxygen can be diffused through it, more corrosion is expected .

If the corrosion product is volatile and soluble, the corrosion will be faster. MoO_3 , SnCl_4 are volatile , so faster is corrosion.

(vii) Volatility and solubility of corrosion product

In both case corrosion will be faster

In case of soluble corrosion product corrosion enhanced by water

MoO_3 – volatile – faster corrosion

(VIII). PASSIVITY or PASSIVATION:

Passivation is the phenomenon by which a metal or alloy shows high corrosion resistance due to the formation of highly protective layers, very thin (about 0.0004mm thick) and quit invisible surface film

Passivation of metal takes place only in certain environments, which tend to maintain protective film on the surface. Ex: Ti, Cr and Al containing stainless steel alloys exhibit outstanding corrosion resistance in presence of oxygen. This is due to formation of thin, protective oxide film on their surfaces. Whenever any damage occurs, this film is automatically repaired in oxidizing environments.

2. Nature of corroding environment

(i) Temperature:

Temperature increases, the rate of corrosion increases.

(ii) Humidity of air:

Moisture or humidity present in the atmosphere helps in the setup of an electrochemical cell and facilitates corrosion.

(iii) Presence of impurities in the environment:

Pollutants like H_2S , SO_2 , CO_2 and acid vapours cause more pollution. In sea water (salty in nature which acts as an electrolyte) corrosion rate increases.

(iv) pH :

Acidic medium, ($\text{pH} < 7$) - more corrosive than basic or neutral medium.

(v) Nature of ions present in environment:

Cu⁺² ions present in the vicinity of Fe, accelerate corrosion

Silicates present in the vicinity resist corrosion (forms insoluble compounds).

(vi) Conductance of corroding medium:

Greater the conductance of the medium, the easier is the current flow and severe is the corrosion,

e.g., a metal piece buried in clay soil is more intensely corroded than a piece buried in sand

(vii) Oxygen concentration and oxygen concentration cell:

The rate of corrosion increases with increasing supply of oxygen. The region where oxygen concentration is lesser becomes anodic and suffers corrosion.

EX: Fe rod partially immersed in water



Protective Coatings



CORROSION CONTROL METHODS

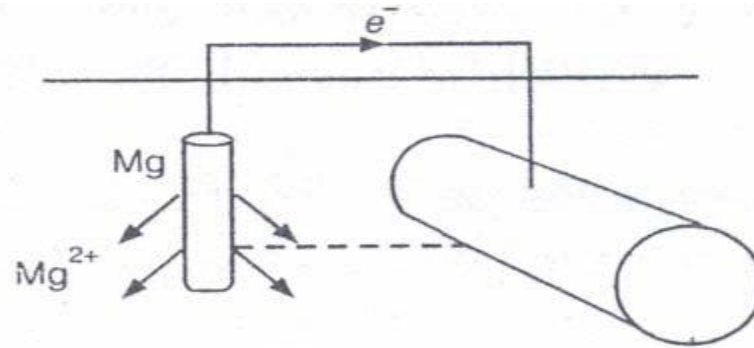
- Metal undergoes corrosion by its oxidation, when they behave like an anode.
- We can prevent the corrosion of metals by forcing the metals to behave like cathode. This is the principle of cathodic protection.

There are two types of cathodic protection.

1. Sacrificial anodic protection
2. Impressed current cathodic protection

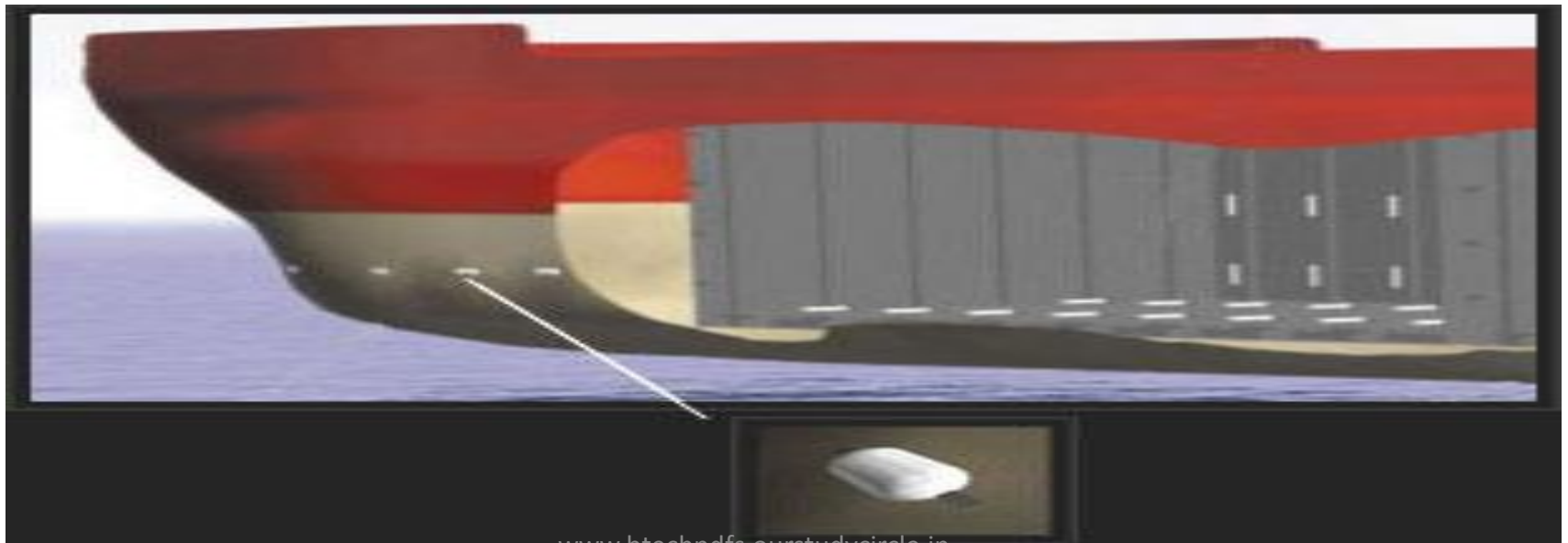
1. Sacrificial anodic protection

- In this method of protection, the metallic structure to be protected called “base metal” is connected to more anodic metal through a wire, so that all the corrosion is concentrated at the more anodic metal.
- As the more anodic metal is sacrificed in the process of saving base metal from corrosion. Hence, it is known as *sacrificial anode*. The corroded sacrificial anode block is replaced by a fresh one.
- Metals commonly used as sacrificial anodes are Zn, Al, Mg and their alloys.
 - a. To protect marine structures and ship parts which are made of steel are connected to a sacrificial anode (Zn (or) Mg).
 - b. Buried pipelines, underground cables and water tanks also protected by sacrificial anode (Mg) method.



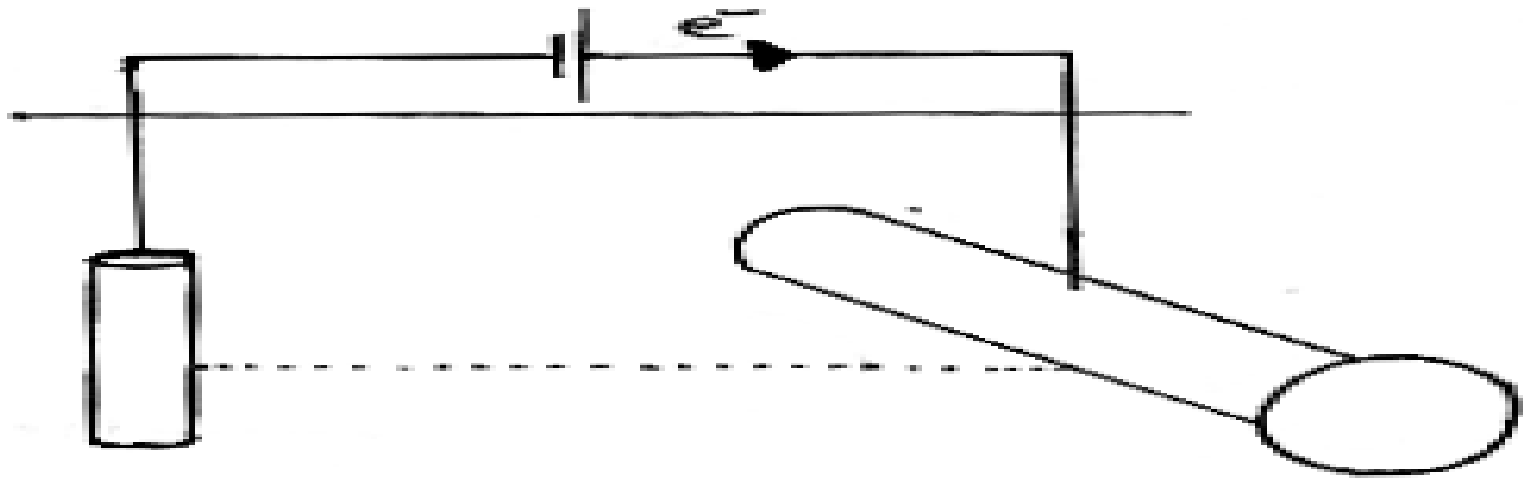
In cathodic protection, an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (*e.g.* a pipeline, bridge, ship hull or boat).

Applications: Ship hulls, piers

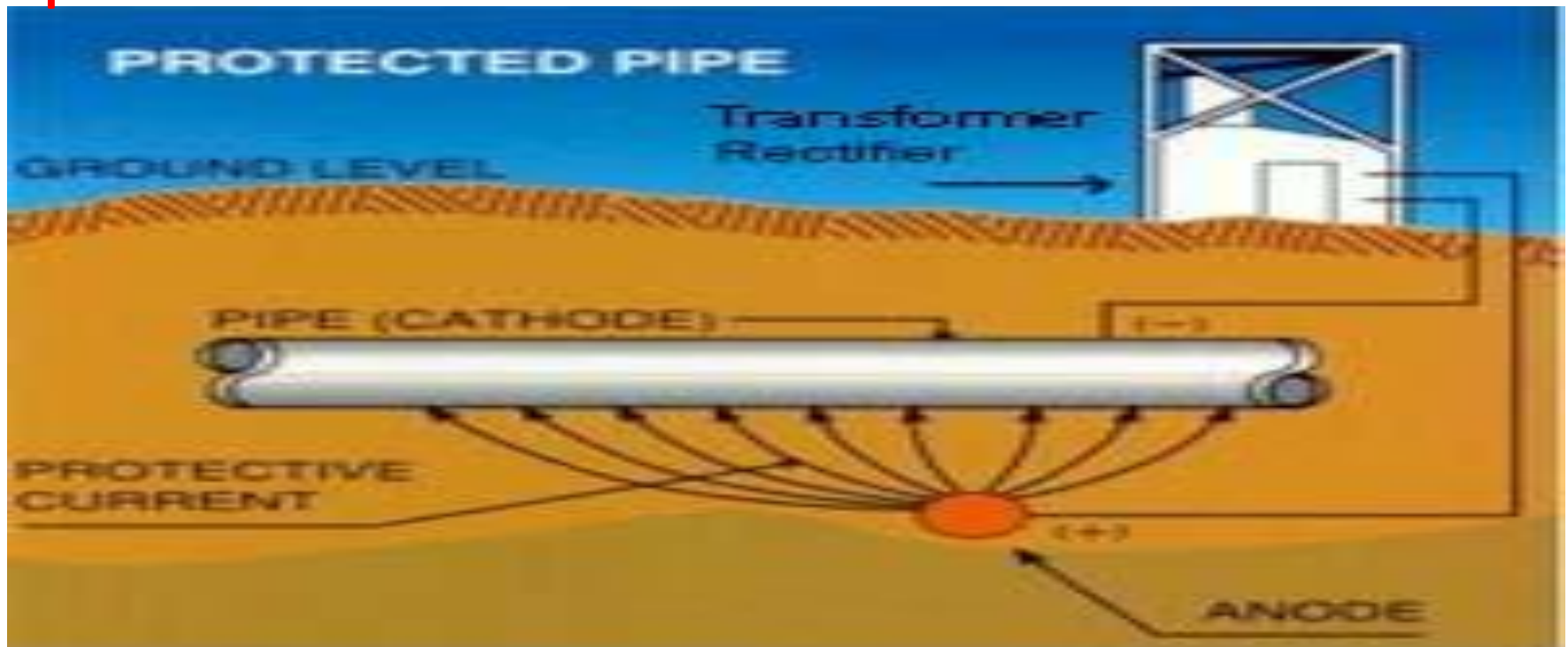


2. Impressed current cathode method.

- In this method current from an external source is impressed (applied in the opposite direction) to nullify the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The anode may be either an inert metal or one which deteriorates and will have to be replaced periodically.
- The commonly used anodic materials are graphite, carbon, stainless steel, scrap iron, high silica iron and platinum.
- The anode is buried in back fill such as gypsum to increase the electrical contact between itself and the surrounding soil.



Applications



Protective Coatings

Surface coatings- metallic coatings

- Surface coating made up of metals is known as metallic coatings.
- The metallic coatings often used are of zinc, tin, nickel, chromium, aluminum, copper etc.
- Metallic coatings are produced by coating one metal on the surface of another metal.
- The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

Types of metallic coatings

These are of two types.

- Anodic coatings**
- Cathodic coatings**

A. Anodic coatings:

- In these coatings, the metal which is used for coating is more anodic than the metal which is to be protected. So an anodic metal coated over the surface of base metal.

Ex:- coating of Zn, Al and Cd anodic metals coated on the surface of steel. Here the base metal steel acts as cathode.

- If it is exposed when pores, break(or) discontinuities occurs in anodic c the base metal a galvanic cell is formed between coating metal and base metal not corroded, till all the coating metal is consumed.
- Galvanization is one type of anodic coating technique.

2. Cathodic coating

➤ These coatings protect the base metal, due to their higher corrosion resistance.

➤ In these coatings, a cathodic metal (high reduction potentials) coated over the surface of base metal.

Ex:- coating of tin on the surface of iron.

➤ If breaks, pores or discontinuities occur in the cathodic coatings, more the corrosion of base metal is speeded up. This is due to the fact that exposed metal acts as anode and coating becomes the cathode.

➤ Tinning is one type of cathodic coating technique

Anodic Coating

1. Protects the underlying base metal sacrificially
2. E^0_v value of coating metal is lower than that of the base metal
3. If pores, breaks or discontinuities occur in such a coating the base metal is not corroded till all the coating metal is consumed
4. Coating of Zn on iron is an example

Cathodic Coating

1. Protects the underlying base metal due to its noble character and higher corrosion resistance.
2. E^0_v of coating metal is higher than that of the base metal.
3. If pores, breaks or discontinuities occur in such a coating, the corrosion of the base metal gets speeded up
4. Coating of Sn on iron is an example.

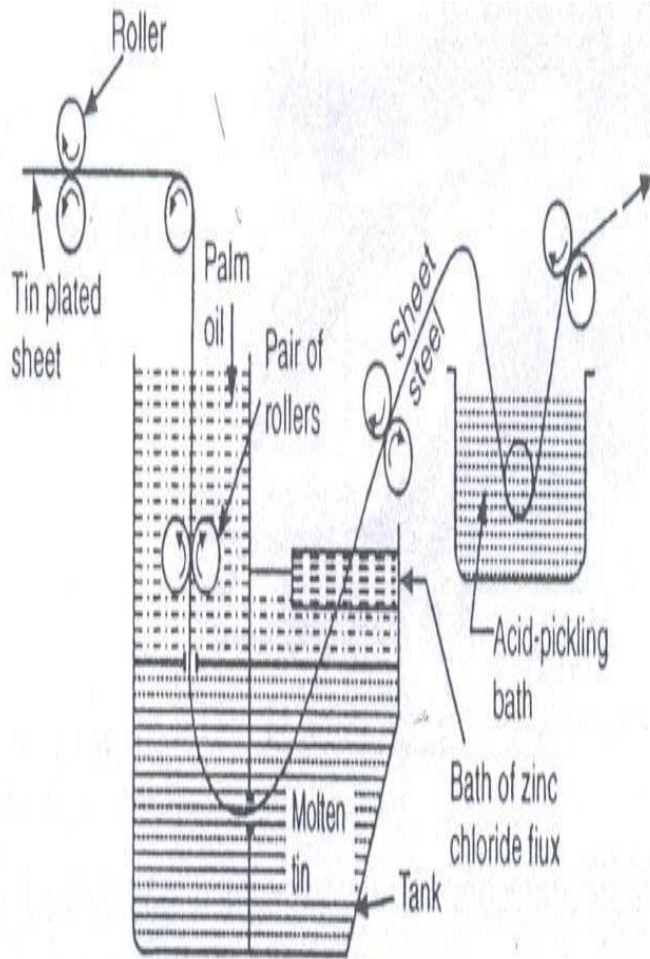
Methods of applying metallic coatings

I. Hot dipping:

- This is a method of coating a **low melting metal such as Zn , Sn , Pb, Al, etc.**, on iron, steel and copper which have relatively higher melting points.
- The base metal is dipped in a molten bath of the coating metal which is covered by a molten flux layer which cleans the base metal surface and prevents the oxidation of the coating metal.
- For good adhesion of the coating metal on the surface of base metal, the base metal surface must be very clean.
- The most commonly used hot dipping methods are Galvanizing and Tinning

a) Tinning

- Coating tin over iron or steel articles is called tinning.
- In this process the surface of the base metal i.e., iron sheet is cleaned by acidic pickling with $\text{dil.H}_2\text{SO}_4$ and passed through a bath of zinc chloride flux.
- The flux help the molten metal to adhere to the metal surface. Then the sheet is passed through molten tin bath and pressed in between two rollers from a layer of palm oil.
- Palm oil helps to protect the tin coated surface against oxidation. The rollers remove excess of tin and produce a thin film of uniform concentration. An alloy of the base metal coating metal at their junction.



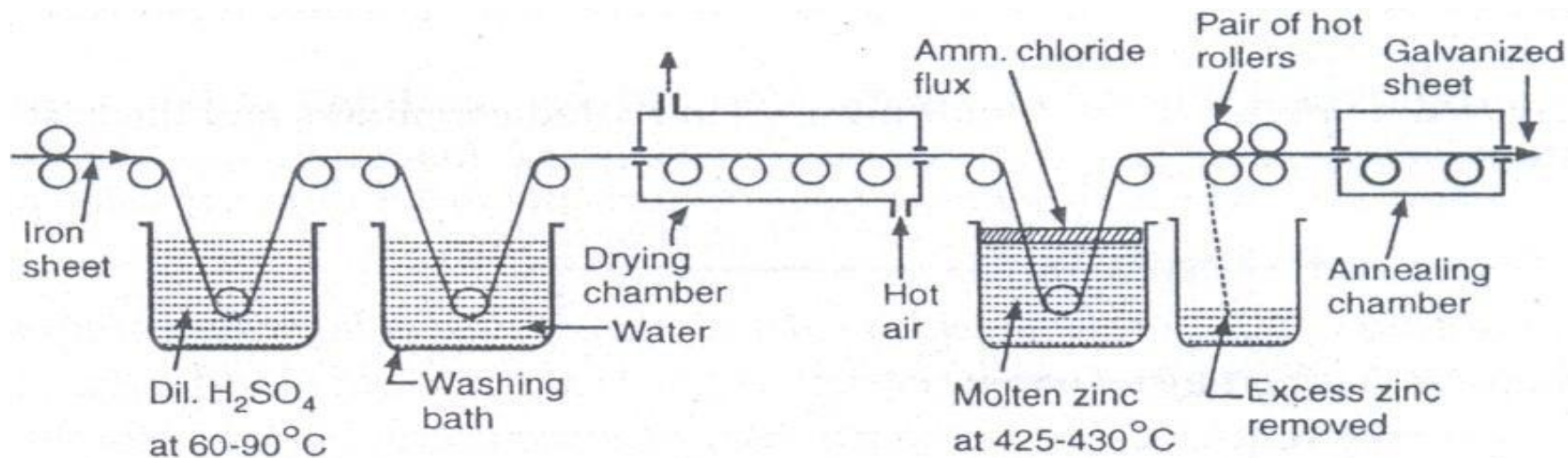
Tinning of sheet steel. The sheet passes through a layer of flux into the molten tin and then emerges between pairs of rollers from a layer of palm oil.

Applications:

1. Tin metal possess good resistance against atmospheric corrosion. Tin is non toxic and widely used for coating steel, copper, and brass sheet.
2. The containers coated with tin is used for storing food stuffs, ghee, oils etc. and packing food materials.
3. Tinned copper sheets are used for making cooking utensils and refrigeration equipment

b. Galvanizing

- It is a process of coating iron or steel sheets with a thin coat of Zn to prevent iron from rusting.
- The base metal iron or steel sheet is cleaned by acid pickling method with $\text{dil. H}_2\text{SO}_4$ for 15-20 minutes at 60-90 °C.
- The sheet is then washed well and dried. It is dipped in a bath of molten zinc maintained at 425-435 °C.
- The surface of the bath is kept covered with ammonium chloride flux to prevent oxide formation.
- The sheet is taken out and excess Zn is removed by passing it between a pair of hot rollers.
- Then the sheet is subjected to annealing process at 650 °C and cooled slowly.
- An alloy of iron and zinc were formed at the junction of the base metal and coating metal.



Galvanizing of sheet steel.

Applications:

It is mostly used to protect iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets and tubes.

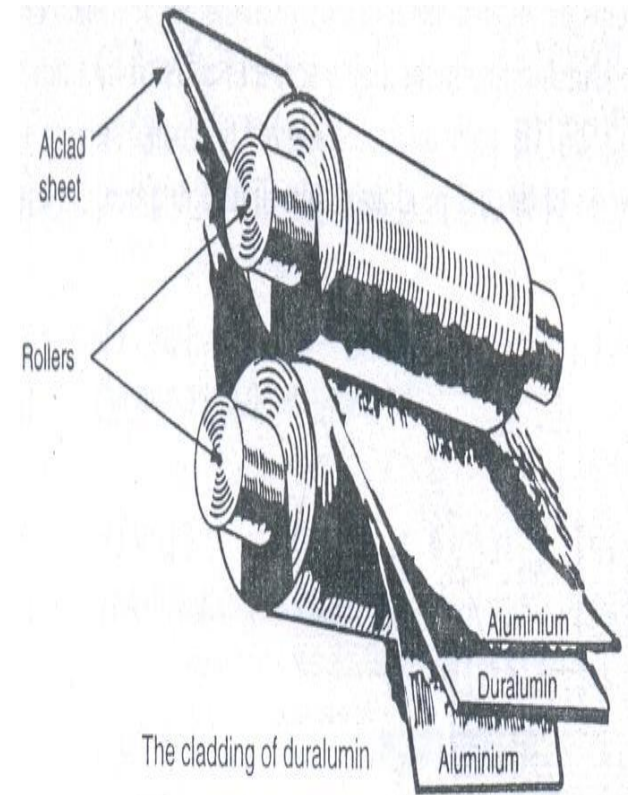
Galvanizing utensils cannot be used for preparing and storing food stuffs especially acidic in nature, because zinc dissolves to form highly toxic or poisonous compounds.

ii. Metal Cladding (Al-Cladding):

- In this process a dense, homogeneous layer of coating metal is bonded (cladded) firmly and permanently to the base metal on one or both sides. The metal cladded is called cladding metal.
- The choice of cladding metals depends on the corrosion resistance required for any particular environment.
- The corrosion resistant metals like Ni, Cu, Pb, Ag, Pt etc. and alloys like stainless steel, Ni alloys, Cu alloys, Pb alloys are used as cladding materials.
- The common base metals cladded are mild steel, aluminium, copper, nickel and their alloys.
- A 99.5% pure aluminium is subjected to cladding to protect duraluminium to produce 'Al-clad', which is widely used in air craft industry.

➤ The process of metal cladding is a kind of “metal sandwiching” where the base metal is arranged with protecting metal on either side like sandwich and passed through roller under the action of heat and pressure.

➤ In this method the cladding metal is bonded/attached firmly to the base metal.



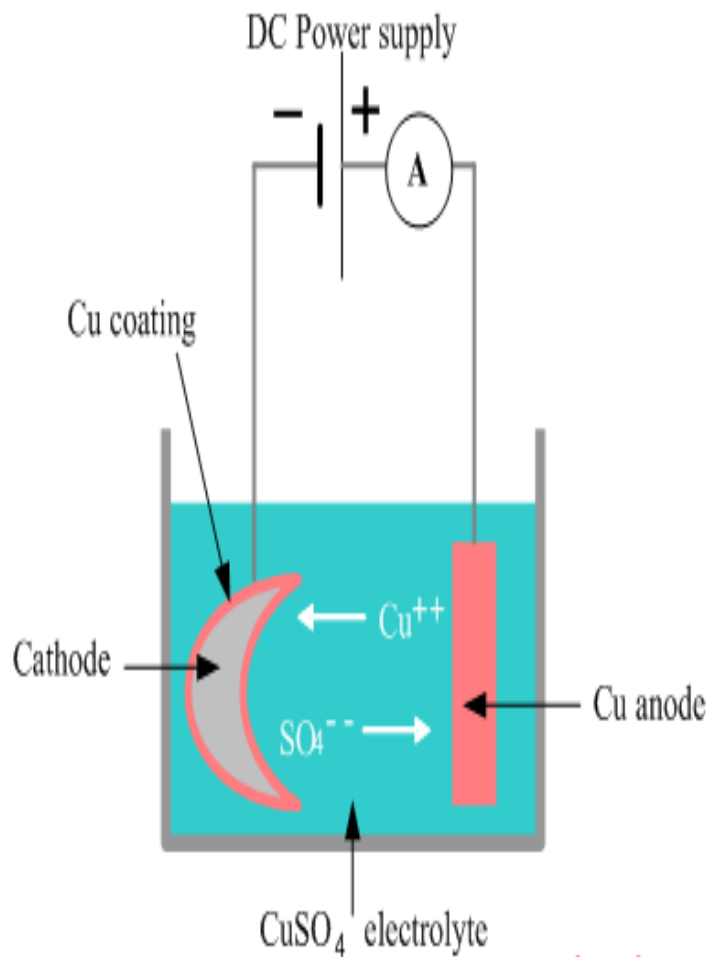
Applications:

➤ this method is widely adopted in aircraft industry and automobile industry.

III. Electro plating (or) electrodepositing(Copper plating)

- The process of depositing the coating metal on the surface of base metal by electrolysis is called electroplating.
- Oils, greases are first removed from the surface of metal to be electroplated by treatment with organic solvents like tetra chloral ethylene.
- Surface scales, oxides are removed by treating with H_2SO_4 . The cleaned metal is made cathode of an electrolytic cell.
- The anode is either inert material like graphite (or) coating metal itself.
- The electrolyte is a solution of a soluble metal salt to be deposited.
- When direct current is passed; coating metal ions migrate to the cathode and get deposited on metal surface.

Electroplating of Cu



www.substech.com

Application:

- Electroplating is a most important and frequently used technique in industries to produce metallic coatings.
- Both metals and non metals can be electroplated.
- In metals the electroplating increase resistance to corrosion, chemical attack, hardness, wear resistance and surface properties.
- In non metals electroplating increases strength and decorates the surface of non metals like plastics, wood, glass etc.

IV. Electroless plating:

- It is technique of depositing a noble metal (from its salt solution) on a catalytically active surface of a less noble metal by employing a suitable reducing agent without using electrical energy.
- The added reducing agent causes the reduction of the metallic ions to metal, which eventually gets plated over the catalytically activated surface giving a highly uniform, but thin coating thus:

Metal ions + Reducing agent $\rightarrow$ Metal + Oxidised products

(Deposited over
catalytically
active surface)

Electroless plating (Nickel plating).

- Before performing electroless nickel plating, the material to be plated must be cleaned by a series of chemicals, this is known as the pre-treatment process.
- Failure to remove unwanted "soils" from the part's surface result in poor plating.
- Each pre-treatment chemical must be followed by water rinsing (normally two to three times) to remove chemicals that may adhere to the surface.
- De-greasing removes oils from surfaces, whereas acid cleaning removes scaling.

Composition of bath:

Coating solution – NiCl_2 solution (20g/l)

reducing agent – sodium hypophosphite (20g/l) ;

buffer – sodium acetate (10g/l);

complex agent cum exhalant – sodium succinamate (15g/L)

pH = 4.5 ; **temp** = 93°C

Reactions:



Net reaction :

