UNIT-2

Electrochemical Cells & Corrosion

Single electrode potential (E)

- It is defined as the potential developed when an electrode is in contact with a solution of its own ions. It is denoted as E.
- When a metal rod is dipped in its salt solution, the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction).
- The process of oxidation or reduction depends on the nature of metal. In this process, there develops a potential between the metal atom and it's corresponding ion called the electrode potential. It is measured in volts.
- There is a dynamic equilibrium between the metal and metal ion and the potential difference between the two is called electrode potential. It is measured in volts.

Standard electrode potential (E^0)

- It is a measure of the tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1M concentration at 25^0C. it is denoted as E^0
- The potential exhibited by single electrode at unit concentration of its metal ion at 25^0C is called standard electrode potential (E^0)
- Eg: E of cu^{+2} / cu = E^0 when concentration of cu^{+2} is 1M. E^0 value of single electrode is determined experimentally by combining the single electrode with standard hydrogen electrode.

Q) What is Electro chemical series? Write the important applications of Electro chemical series.

- All the metals (or) metal ions are arranged in increasing order of redox potential (or) decreasing order of oxidation potential that series is known as **Electro chemical series.**
- Electro chemical series hydrogen above lying metals are called more active metals which can easily corroded.
- Hydrogen below lying metals are called noble metals (or) less active metals which are protected against the corrosion.
- When two dissimilar metals which are electrically contact with electrolytic solutions, whether which metal behaves as anode (or) cathode depend upon its redox potential values i.e metal having higher redox potential act as cathode other one act as anode.

Electrode	Electrode reactions	E°volts
$Li^+ \mid Li$	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05
$K^+ \mid K$	$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
$Mg^{2+} \mid Mg$	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37
$Al^{3+} \mid Al$	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66
$Zn^{2+} \mid Zn$	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76
$Fe^{2+} \mid Fe$	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
$Cd^{2+} \mid Cd$	$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.40 b*
$Ni^{2+} \mid Ni$	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.25
$Pb^{2+} \mid Pb$	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13
Pt, $H^+ \mid H$ a*	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Cu^{2+} \mid Cu$	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$I_2 \mid I^-$	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.54
$Fe^{3+} \mid Fe^{2+}$	$Fe^{3+}(aq) + 2e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$Hg_2^{2+} \mid Hg$	$Hg_2^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	+0.79
$Ag^+ \mid Ag$	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Br_2 \mid Br^-$	$Br(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.08
Pt, $Cl_2 \mid Cl^-$	$Cl_2(aq) + 2e^- \longrightarrow 2Cl^-(s)$	+1.36
$Au^{3+} \mid Au$	$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50

Applications of the electrochemical series:

1. Relative strength of the oxidizing and reducing agents in the electrochemical series.
2. **Calculation of EMF of the cell:**
   EMF of the cell is the difference of the reduction potential of the cathode and the anode.

$$E^0_{cell} = E^0_{Right} - E^0_{Left}$$

3. Predicting spontaneity or feasibility of a reaction
4. **Replacement tendency:** The metal on the top of the electrochemical series has the tendency to replace the one below it from its solution. This is because the metal placed at the bottom has a greater reduction potential and hence a greater tendency to accept electrons. For example, the standard electrode potential of Cu and Zn are as follows.

   $E\ Cu^{+2}$ = 0.34 volts and $E\ Zn^{+2}$ = 0.76 volts. The reduction potential of copper is greater than zinc, so copper can displace zinc from its solution.

Q) What are Reference electrodes? Explain the construction and working of it?

A) REFERENCE ELECTRODES: A reference electrode has a standard potential and it is used to compare the potential of other electrodes.

The two types of standard electrodes are

1. **STANDARD HYDROGEN ELECTRODE (SHE)**
2. **STANDARD CALOMEL ELECTRODE (SCE)**

These are mainly used for determination of unknown electrode potential.

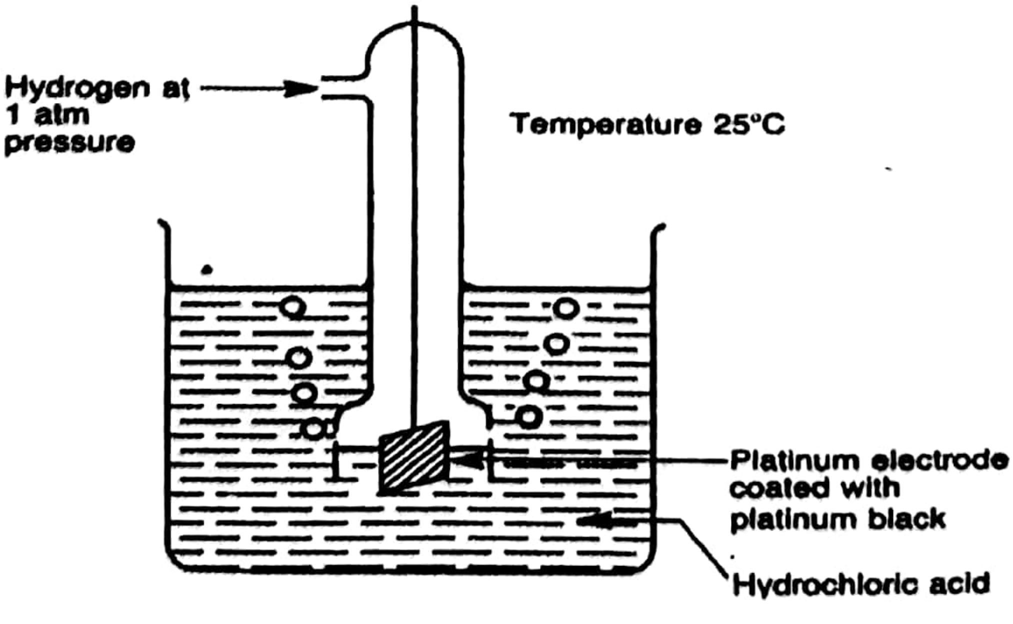
1. STANDARD HYDROGEN ELECTRODE (SHE):

- It is a redox electrode which is widely used as a reference electrode.
- It can be used either as an anode or a cathode depending upon the other electrode in the half cell.
- The standard hydrogen electrode consists of a platinum wire sealed in a glass tube and has a platinum foil attached to it.
- It is dipped into an acid solution with H+ ions of 1M concentration (IM HCl). Pure hydrogen gas at 1 atm pressure is constantly bubbled into the solution at a temperature or 298K the reaction occurs at the surface of the coil.
- The electrode is denoted as Pt/H_2 (aq)/ H^+ (aq).
- The following reaction occurs depending on whether the electrode acts as an anode or as cathode.

At Anode: $H_2 \rightarrow 2H^+ + 2e^-$ 0.0 V

At Cathode: $2H^+ + 2e^- \rightarrow H_2$ 0.0 V

- The electrode potential of an electrode is determined by connecting the half cell with a standard hydrogen electrode (SHE).
- The electrode potential of the standard hydrogen electrode is taken as zero
- The EMF of the cell gives the value of the electrode potential of the given electrode.



Q) Describe the construction of Batteries. Write the cell reactions and mention its applications?

A) Batteries: A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation- reduction (redox) reaction. Batteries are classified as follows:

1. **Primary battery**
2. **Secondary battery**
3. **Fuel battery**

Primary cells (or batteries): In which the cell reaction is not reversible. Thus, once the chemical reaction takes place to release the electrical energy, the cell gets exhausted, no more electricity is produced and the battery becomes dead. They are use and throw type. **Eg: Dry cell (Leclanche cell), Lithium cell etc.**

Secondary cells (or batteries): In which the reaction can be reversed by passing direct electric current in opposite direction. Thus a secondary battery may be used through a large number of cycles of discharging and charging. **Eg: Nickel cadmium (Ni-Cd), Nickel metal hydride (Ni-MH), Lithium cells, Zinc-air cells etc.**

Fuel cells (or batteries): Fuel cells are different from batteries in that they require a constant source of fuel and oxygen/air to sustain the chemical reaction, they can however produce electricity continually for as long as these inputs are supplied. **Eg: Hydrogen –oxygen fuel cell, Methyl alcohol –oxygen alkaline fuel cell, Phosporic acid fuel cell, Molten carbonate fuel cell.**

Dry battery (Leclanche cell):

- It is called a dry battery as it does not have any liquid electrolyte in it.
- The zinc vessel serves as the anode The cathode is a graphite rod in the centre of the cell.
- It is surrounded by the electrolyte which consists of a paste of NH_4CI, $ZnCl_2$, MnO_2.
- The cell is represented as Zn / Zn^{2+} , NH_4 / MnO_2,

The cell reactions involved are:

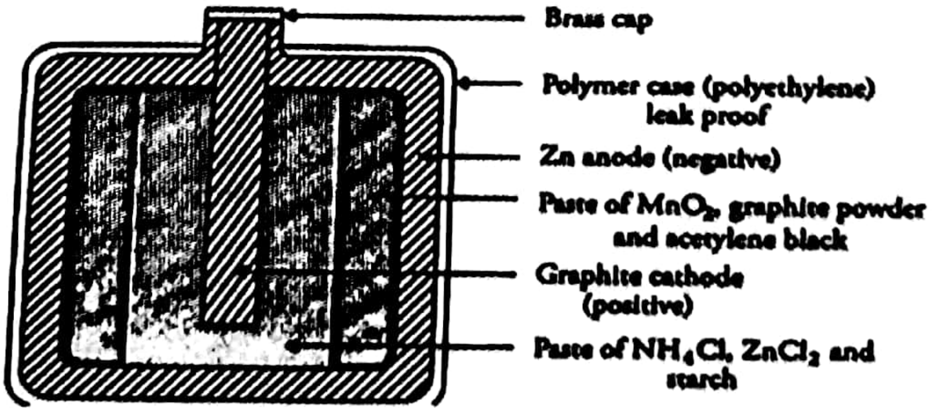
At Anode: $Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2e^-$

At Cathode: $2NH_4^+\,(aq) + 2MnO_2\,(s) + 2e^- \longrightarrow 2NH_3\,(aq) + Mn_2O_3\,(s) + H_2O\,(l)$

Cell Reaction: $Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \longrightarrow Zn^{2+}(aq) + 2NH_3(aq) + Mn_2O_3(s) + H_2O(l)$

The NH_3 liberated reacts with Zn^{2+} to form a complex $[Zn\,(NH_3)_2]\,Cl_2\,(s)$.

The cell is a primary cell and gives a voltage of 1.5V. Gradually, the products are formed and the cell voltage drops.



Advantages of Leclanche cell:

- The compact size of a dry cell makes it suitable for powering small electronic devices
- Dry cells are used in flash light, portable radio, tape recorder etc.
- The cost of this battery cell is quite low.
- Various shapes, sizes and capacities of these cells are easily available.
- Long traditional reliability (performs consistently well).

Disadvantages of Leclanche cell:

- Its energy density is quite low.
- It gives poor service in low temperature.
- Self-life is not very good.
- Its voltage falls steadily with discharge.
- The dry cell cannot be recharged once it loses its electrical power.

Lithium Cells:

Lithium cells are primary cells with Lithium acts as anode. It has high standard oxidation potential and good conductivity. As reactivity of Li in aqueous solution is more, lithium cells use non-aqueous solvents as electrolyte. Li cells are classified into two types: a) Lithium cells with solid cathode and b) Lithium cells with liquid cathode.

A) **Lithium cells with solid cathode:** The electrolyte in these systems is a solid electrolyte. The most widely used cell is lithium-manganese dioxide cell. MnO_2 should be heated to over 300°C to remove water before keeping it in the cathode, thereby increasing the efficiency of the cell.

Anode: Lithium Metal

Cathode: MnO_2 as an active material.

Electrolyte: $LiBF_4$ salt in a solution of propylene carbonate and dimethoxy ethane.

The cell reactions are given below:

At Anode: $Li \longrightarrow Li^+ + e^-$

At Cathode: $MnO_2 + e^- \longrightarrow MnO_2^-$

B) Lithium cells with liquid cathode:

Lithium-thionyl chloride cell is an example of liquid cathode. It consists of high surface area carbon cathode. Thionyl chloride acts as an electrolyte and as a cathode. The cell voltage is 3.3-3.5 V. The cell reactions are given below:

At anode: $4Li \rightarrow 4Li^+ + 4e^-$

At cathode: $2SOCl_2 + 4Li^+ + 4e^- \rightarrow 4LiCl + SO_2 + S$

Net reaction: $4Li + 2SOCl_2 \rightarrow 4LiCl + SO_2 + S$

Applications: i) The coin type cells are used in watches and calculators.

ii) Cylindrical cells are used in fully automatic cameras.

Uses: i) These are used for military and space applications.

ii) These are widely used in medicinal devices.

iii) These are used in electric circuit boards for supplying fixed voltage.

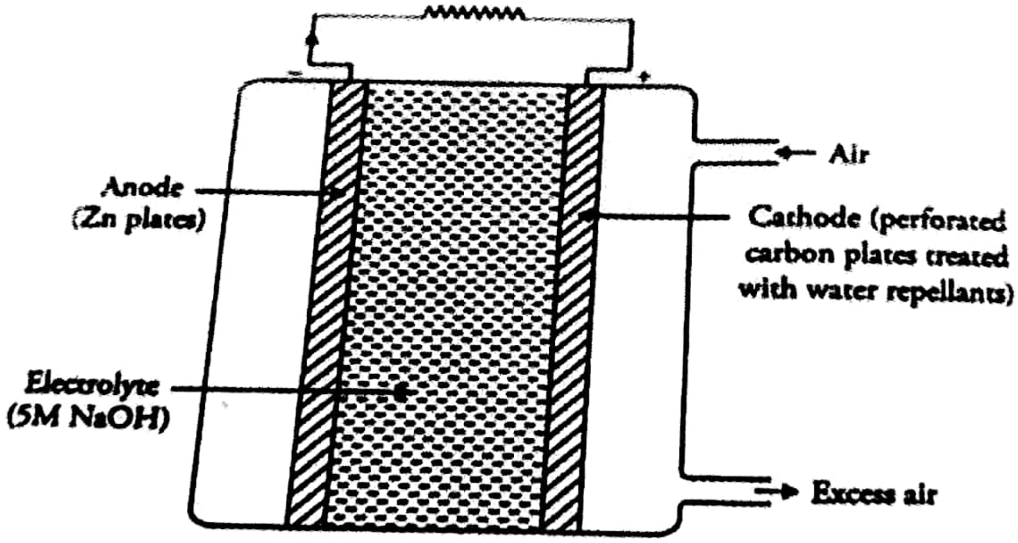
Zinc-Air Battery:

- The cell consists of zinc plate acts an anode.
- A perforated carbon plate treated with water repellants acts as a cathode. Sodium hydroxide or potassium hydroxide used as an electrolyte.
- The cathode allows contact of oxygen from the air.
- At anode, the zinc reacts with electrolyte to form zinc oxide and water.
- The electrons travel from anode to cathode where oxygen of the air accepts the electrons to form hydroxide ions.
- These are electrically non-rechargeable, however they can be recharged mechanically by converting zinc oxide to zinc metal.
- The theoretical cell output is 1.65 V.
- In reality just 1.3= to 1.4 V is given as output. These batteries have properties of both fuel cell and batteries.
- The Cell Reactions:

At Anode: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

At Cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

Net Reaction: $Zn + \frac{1}{2} O_2 \longrightarrow ZnO$



Advantages of Zin-Air Battery:

- These are used in watches, hearing aids, cameras and also for electric propulsion of vehicles.

Fuel cells

- A Fuel cell is a device that **converts chemical energy form of a fuel into electricity** though a chemical reaction with oxygen or another oxidizing agent.

Advantages:

- Fuel cells increase thermal efficiency.
- Fuel cells produce electricity for longer periods.
- Fuel cells generate power with little pollution.

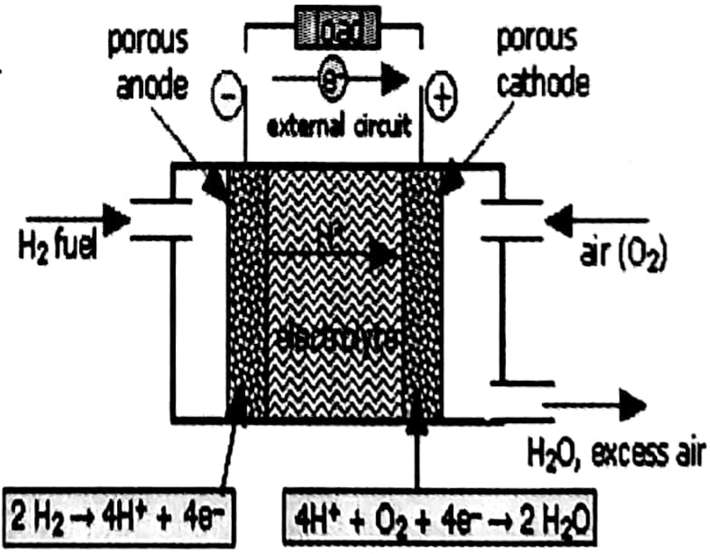
Types of fuel cells:

1. Hydrogen –oxygen fuel cells 2. Methyl alcohol–oxygen alkaline fuel cell 3. Phosphoric acid fuel cell 4. Molten carbonate fuel cell

1. Hydrogen–oxygen fuel cells:

- H_2-O_2 Fuel cell in which hydrogen is the **fuel** (reducing agent) and oxygen is the oxidizing agent.
- The cell consisting of two inert porous electrodes which are made of graphite covered with pt or Ag catalyst.
- An electrolytic solution is KOH
- The hydrogen gas is passed through the anode while the oxygen gas is passed through the cathode.
- The product discharge in water and its standard emf is E^0=1.23 volts

At Anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$
At Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$
Overall Reaction: $2H_2 + O_2 \longrightarrow 2H_2O$



Applications:

- The energy conversion is very high.
- The product H2O is drinking for water source for astronauts.
- It is a storage system for space applications and use for fossil fuels, low noise and thermal pollution.

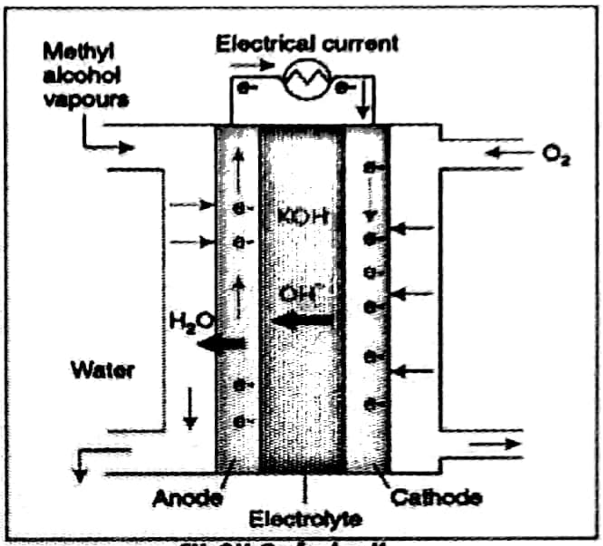
2. Methyl alcohol–oxygen fuel cells:

- In this fuel cell CH_3OH used as a fuel and O_2 as oxidant to generate electrical energy.
- The methyl alcohol oxygen fuel cell has two electrodes.
- Anode consists of porous nickel electrode covered with Pt catalyst.
- Cathode consists of porous nickel electrode covered with Ag catalyst.
- The electrolyte KOH is taken in between two electrodes.
- CH_3OH and O_2 are sent continuously in to respective electrodes.

At Anode: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

At Cathode: $3/2O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

Overall Reaction: $CH_3OH + 3/2O_2 \longrightarrow CO_2 + 2H_2O$



CH_3OH-O_2 fuel cell

Advantages of Methyl alcohol-oxygen alkaline fuel cell:

- It is reasonably stable at all environmental conditions.
- Easy to transport do not require complex stream reforming operations.
- Methanol has less risk for use of plants and animals and human beings then gasoline.
- It is zero emission by the cells hence the fuel cells are ecofriendly.

Applications:

- The major application of this fuel cell used as fuel for motor vehicles like NECAR -5 in japan and USA.

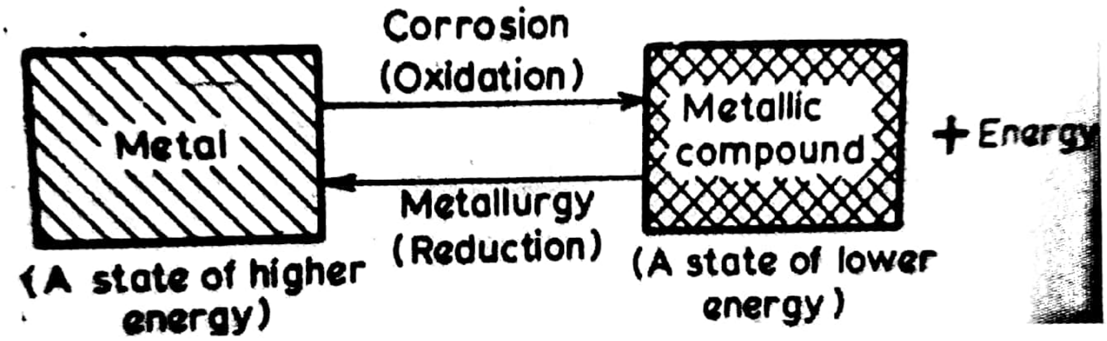
Advantages of fuel cells: Fuel cells can be used for portable, backup, transportation, and stationary power applications.

1. **Portable Power:** Portable fuel cells are lightweight, long-lasting, portable power sources that prolong the amount of time a device can be used without recharging.
2. **Backup Power:** Fuel cells used for backup power come in many sizes and types and typically use hydrogen as their fuel.
3. **Transportation Applications:** Fuel cells can be used for many transportation applications including automobiles, buses, utility vehicles, and scooters and bicycles. The operating temperature of an automotive fuel cell is between 60 to 80 °C.
4. **Stationary Power Applications:** Stationary fuel cells can be used as a primary power source. In hybrid power systems, fuel cells can be connected to photovoltaics, batteries, capacitors, or wind turbines, providing primary or secondary power.

CORROSION

INTRODUCTION:

All metals (except noble metals (like Au, Pt, Ag) exist in nature as combined form such as their oxides, carbonates, hydroxysulphides, Halides and silicates etc. These are reduced to their metallic state form during extraction process.



Causes of corrosion:

- Pure metals (higher energy state) is always trying to get back to its combined form (low energy state) by the action of environment (dry gases (or) moisture liquid) by the result of destruction of the metal starts at the surface. Corrosion is a chemical oxidation of metals, by this process metallic destruction occurs.
- **Definition:** Any process of deterioration or destruction and consequent loss of a solid metallic material through an unwanted chemical or electrochemical attack by its environment at its surface is called corrosion. Thus corrosion is a reverse process of extraction of metals.
- **Ex:** Rusting of iron–when iron is exposed to the atmospheric conditions, reddish scale and powder of Fe_3O_4 is formed.
- When Cu is exposed to CO_2 moisture atmosphere, Formation of green film of basic carbonate- [$CuCO_3$ +$Cu(OH)_2$.

Theories of corrosion: Corrosion can be explained by the following two theories.

1. Dry or Chemical corrosion. 2 .Wet or Electrochemical corrosion.

1. **Dry or chemical corrosion:** This type of corrosion occurs mainly through the direct chemical action of environment atmospheric gases such as O_2, H_2S, SO_2, NO, Halides, inorganic liquids with metal surfaces.Which are of following three types.

1. Oxidation corrosion 2. Liquid corrosion. 3. Corrosion by other gases

Oxidation corrosion:

- It occurs by the direct action of oxygen (O2) over the metal surface
- At ordinary temp generally all the metals are slightly attacked. However alkali metals like Li, Na, K, Rbetc and alkaline earth metals–Be, Ca, Sretc are attacked very rapidly and get oxidized readily.
- The reactions in the oxidation corrosion are

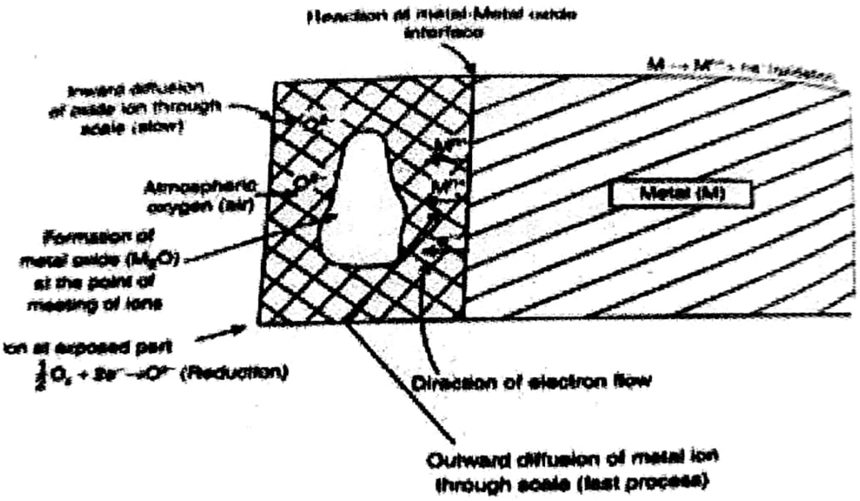
$$M \longrightarrow M^{n+} + ne^- \text{ (Oxidation)}$$

$$1/2\ O_2 + ne^- \longrightarrow O^{2-} \text{ (Reduction)}$$

$$\text{Or } M^{n+} + O^{2-} \longrightarrow MO \text{ (Metallic Oxide)}$$

Mechanism of oxidation corrosion:

Oxidation occurs first at the surface of the metal. Scale of **metal oxide** is formed on the surface of the metal and it tends to act as a barrier for further oxidation.



Nature of the Oxide film formed:

1. Stable 2. Unstable 3. Volatile 4. Porous

Stable layer: Stable non-porous oxide layer is adhered tightly to the metal surface which acts as protective coating over the metal for their oxidation, thus corrosion is prevented.

Eg: Al, Sn, Pb and Cu.

Unstable: The oxidation layer is formed and decomposes back into the metal & oxygen

Eg: Ag,Au, Pt

Volatile: Oxide layer over the metal volatilizes as soon as formed there by leaving the metal surface exposed for further attack

Eg: Mo-molybdenum forms volatile MoO_3 layer.

Porous: Oxide layers contain the pores (or) cracks so, the atmospheric O_2 is easily access through this pores further corrosion occurs until entire metal is converted into its oxide.

Eg: Alkali & Alkaline earth metal.

Pilling Bed worth Rule:

According to this rule formation of oxide film volume over the metal surface whether it is protective or non-protective against the corrosion of the metal.

Case-1:

When the formation oxide film volume is exactly equal or excess volume of metal. It should be non-porous and protective against the corrosion.

Ex: stable oxide layer like Cl, Ni, Cu, Sn, Pt

Case-2:

When the formation of oxide volume over the metal is less than that of metal volume it should be porous and non-porous and non-protective against the corrosion

Ex: Alkali & Alkaline earth metal.

$$\textbf{Pilling bed worth rule} = \frac{\textbf{volume of metal oxide layer}}{\textbf{Volume of the metal}}$$

2. Wet (or) electro chemical corrosion:

- This type of corrosion occurs where conducting liquid electrolytic solution in contact with metal or dissimilar metal or alloys which are partially immersed in electrolytic solution. Which can be divided into two parts, i.e. anodic part and cathode part.
- Anodic part of metal atom undergoes oxidation to give metal ion. Which on dissolution into electrolytic solution, the releasing electrons travel from anodic to cathode area.
- **Corrosion (Oxidation) always takes place at anodic part.**
- At anodic part $M \longrightarrow Mn^{+} + ne^{-}$(oxidation or Corrosion)
- On the other hand, reduction takes place at cathode area. Where releasing electrons are accepted by cathode part's surrounding electrolytic ions but not cathode metal.

Mechanism of wet electro chemical corrosion:

Mechanism of wet corrosion is two types based on nature of electrolyte – (nature of corrosive environment)

1. Evolution of hydrogen – (electrolyte is taken as acid (HCl or H_2SO_4).
2. Absorption of oxygen - (electrolyte is taken as neutral aqueous solution ($NaCl+H_2O$)

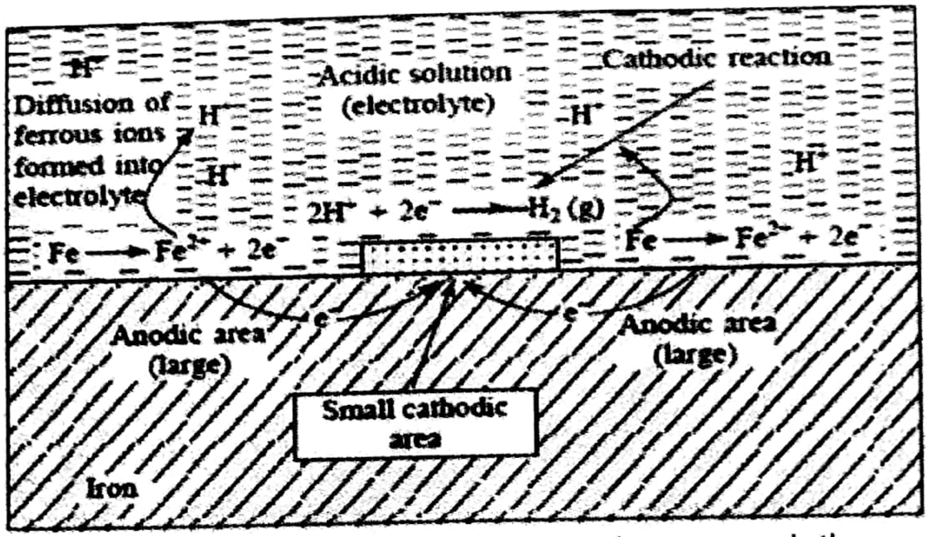
1. **Evolution of hydrogen:** This type occurs in acidic environments. For eg: In the corrosion of iron metal the anodic reaction is dissolution of Fe as ferrous ions with liberation of electrons.

$$Fe \rightarrow Fe^{2+} + 2e \quad \textbf{(Oxidation)}$$

$$\underline{2H^{+} + 2e^{-} \rightarrow H_2 \quad \textbf{(Reduction)}}$$

$$Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$$

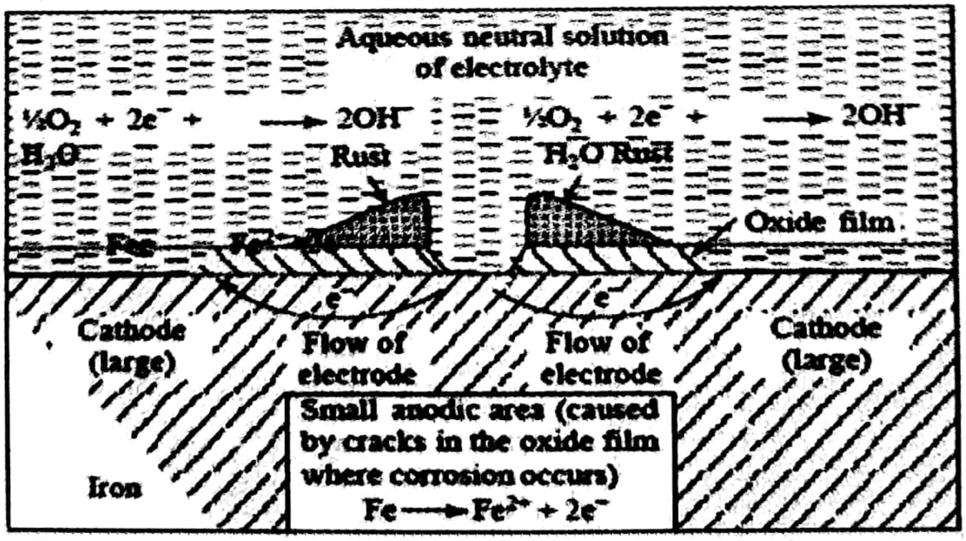
- This type of corrosion causes "displacement of hydrogen ions from the acidic solution by Metal ions.
- In hydrogen evolution type corrosion, the anodes are very large areas, where as cathodes are small areas.
- All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.



Mechanism of wet corrosion by hydrogen evolution

Absorption of oxygen type corrosion:

- Rusting of Fe in neutral aqueous solution of electrolytes like NaCl in the presence of atmospheric oxygen is a common example of this type of corrosion.
- In this mechanism small anodic and large cathodic area is formed.
- Sever corrosion occur at anodic part while cathodic part is protected:-Thus at the anodic part iron metal dissolves as Fe^{2+} ions with the liberation of electrons
  $Fe \rightarrow Fe^{2+} + 2e^-$
- The liberated e- s flow from anodic to cathode areas through iron metal during which they interact with dissolved oxygen and moisture.
  $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
- The Fe2+ and OH- ions diffuse and form ferrous hydroxide precipitate when they meet with each other.
  $Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$
- If enough O2 is present Fe(OH)2 is easily oxidized to Fe(OH)3 (ferric hydroxide)
  $4 Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$



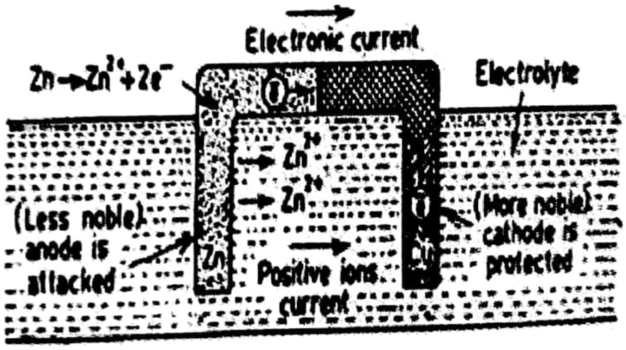
Mechanism of wet corrosion by oxygen absorption

Types of wet corrosion

1. Galvanic corrosion 2 Concentration cell corrosion 3.water line corrosion. 4. Stress corrosion

Galvanic Corrosion:

- When two dissimilar metals such as Zn and Cu are electrically connected and exposed to electrolyte solution.
- Metal having higher redox potential in electro chemical series which acts as cathode other one act as anode. So that Zn (-0.76V) act as anode where as Cu act as cathode (+0.34ev).So that Zn undergoes oxidation.



At anode – $Zn \rightarrow Zn^{+2} + 2e^-$ (oxidation)

At cathode – $2H^+ + 2e^- \rightarrow H_2$ (Reduction)

Galvanic corrosion.

Applications

(i) Steel screws in a brass marine hardware.

(ii) Lead-antinomy solder around copper wire.

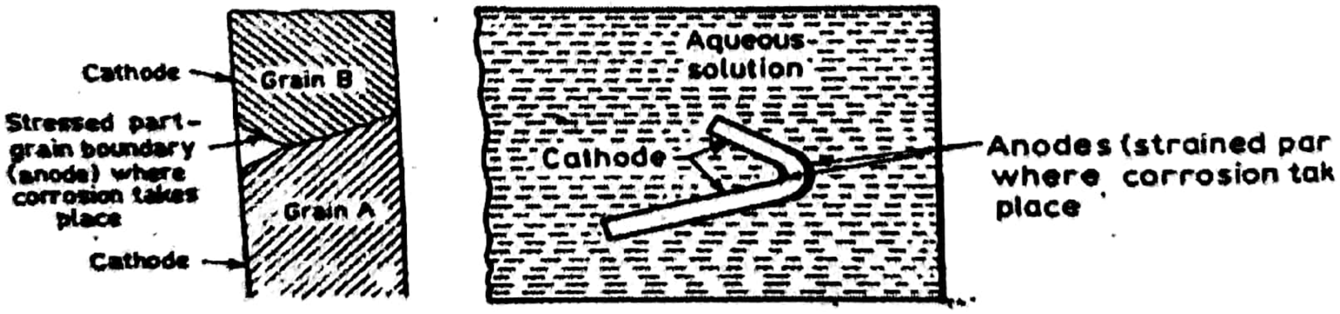
(iii) A steel propeller shaft in bronze bearing.

(iv) Steel pipe connected to copper plumbing.

Stress corrosion:

This type of corrosion observed in the metal parts which are under continuous mechanical operations such as hammering, annealing. The part which undergoes stress acts as anode and gets corroded.

For example, Low carbon steel does not corrode in conc. HNO_3 due to protection effect of passive film. However in dil. HNO_3 it does not form stable passive film and therefore dissolves steel. Some of the metals themselves they form protective oxide film in air, water and dil. Acids. Eg: Al, Si, Ti, and Cr.



Stress corrosion.

(h) **Waterline corrosion:** It has been observed in the case of an iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration. Corroding portion is poor in oxygen and acts as anode (Fig. 2.5).

Reactions:

At anode: $Fe \longrightarrow Fe^{++} + 2e^-$

At cathode:

$$H_2O \longrightarrow H^+ + OH^-$$
$$(4H^+ + O_2 + 4e^- \longrightarrow 2H_2O)$$
$$Fe^{++} + 2OH^- \xrightarrow{(0)} Fe(OH)_2 Fe(OH)_3$$

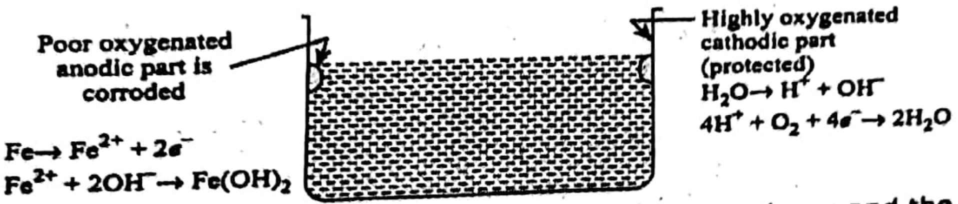
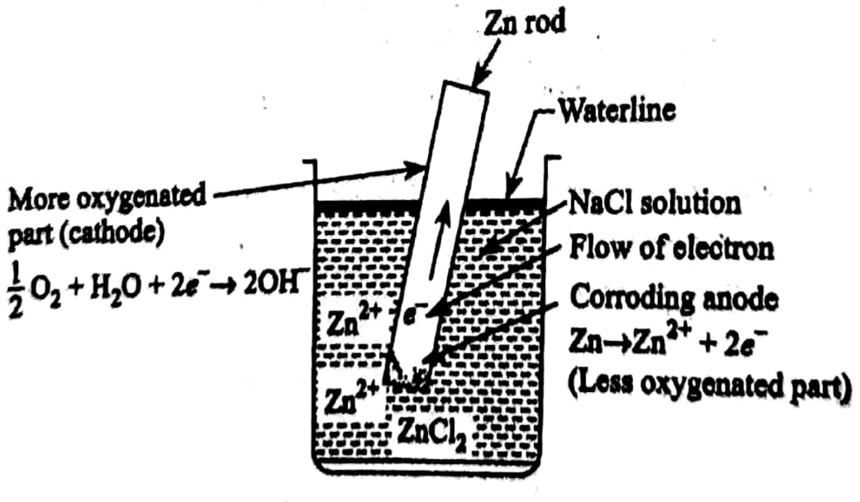


Fig. 2.5 Waterline corrosion occurs just underneath the meniscus and the water level

(i) **Differential aeration corrosion:** If a metal rod is dipped in an electrolyte, the portion dipped in water is poor in oxygen concentration and works as anode which gets corroded and the portion above water acts as cathode which is protected. The system will act as a concentration cell and the chemical reactions for zinc dipped in water are given as:

$$Zn \longrightarrow Zn^{++} + 2e^-$$
$$H_2O + \frac{1}{2}O_2 + 2e^- \longrightarrow 2OH^-$$
$$\overline{Zn + H_2O + \frac{1}{2}O_2 \longrightarrow Zn(OH)_2}$$

$Zn(OH)_2$ appears as corrosion product (Fig. 2.6).



g. 2.6 Mechanism of differential aeration attack caused by partial immersion of metal

- **Galvanic series:** Electrochemical series does not account for the corrosion of all metals and alloys, and it gives no information regarding the position of alloys. Consequently, a more practical series, called galvanic series have been prepared by studying the corrosion of metals and alloys in a given environment.
- Galvanic series relationships are useful as a guide for selecting metals to be joined, will help the selection of metals having minimal tendency to interact galvanically or will indicate the need or degree of protection to be applied to lessen the expected potential interactions.
- In general, the further apart the materials are in the galvanic series, the higher the risk of galvanic corrosion, which should be prevented by design. Conversely, the farther one metal is from another, the greater the corrosion will be.

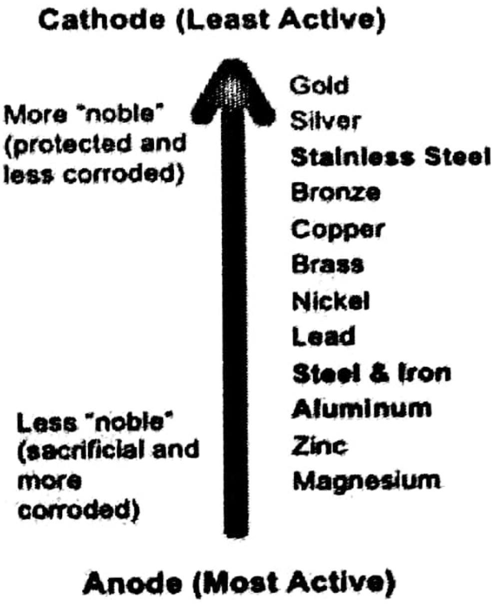


Table 7.3 Electrochemical series versus galvanic series

S.No	Electrochemical series	Galvanic series
1	Electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration, without any oxide film on them	This series was developed by studying the corrosion rates of metals and alloys in different environments like sea water without removing their oxide films if any
2	The position of metal is fixed in the electrochemical series	The position of metal may shift in the galvanic series depending on the environment
3	It gives no information regarding the position of alloys	Alloys have also been included and hence their corrosion rates can be studied from this series
4	This series comprises metals and non-metals	This series comprises metals and alloys
5	It predicts the relative displacement tendencies	It predicts the relative corrosion tendencies

Factors influencing rate of corrosion: 1. Nature of metal 2.Nature ofEnvironment

Nature of metal

1. **Metal position in galvanic series:-**

The metal higher in series is more active and suffers corrosion. Potential difference increases between the two metals in galvanic series the rate of corrosion is also increased.

2. **Over voltage:**

When Zn is placed in 1N H_2SO_4 solution to evolve the H2 and generate the high over voltage (-0.76) of Zn metal rate of corrosion is slow but if add few drops of $CuSO_4$ solution which deposit over the Zn, there by Cu, becomes cathode, while Zn becomes anode so that Cu voltage (0.34ev) able to diminish the Zn voltage, rate of corrosion is increased.

3. **Relative area of anodic & cathodic parts:-**

Large anode & small cathode (evolution of H2) area ratio, in which anode is slowly corrosive. On the other hand, large cathode, small anode (absorption of O_2) rate of corrosion speedily occur on the anode.

4. **Purity of metal:-**

The rate of corrosion decreases with increase in the purity of metal while any impurity causes heterogenety (impure) and the rate of corrosion is increased

Eg: Zn metal containing impurity such as Pb (or) Fe undergoes corrosion.

5. **Physical state of metal:-**

The rate of corrosion is also depend on physical state of metal such as grain size, crystals , stress etc. For small size, under stress area the rate of corrosion is increased.

6. **Nature of surface film:-**

The oxide film formed is of thickness over the metal surface, the rate of corrosion decreases while the rate of corrosion is increased with decrease of oxidation film thickness over metal surface

Eg:- Thickness	Ni	Cr	w
	16	2.0	3.6

7. **Solubility of corrosion product:-**

If the corrosion product is soluble in electrolytic solution, then corrosion proceeds with faster rate.

Factors due to nature of corrosive environment

1. **Temperature**: the rate of corrosion reactions increases with increase in temperature.
2. **Humidity in air**: The moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell, and rate of corrosions increases with humidity.
3. **Presence of impurities**: Atmosphere is contaminated with gases like CO_2, SO_2, H_2S; fumes of H_2SO_4, HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion.
4. **PH value**: pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.
5. **Amount of oxygen in atmosphere:** As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

Corrosion control methods (Protection against from corrosion)
(Proper designing and Cathodic protection)

Design and material selection:

i. The metals containing impurities even in small quantities and if that impurity is cathodic to the metal, then the metal acts as anode and rapid corrosion takes place.
For ex: If lead is an impurity (0.02%) in zinc, the latter is corroded rapidly. Similarly if iron (0.003%) is the impurity in magnesium, the magnesium is corroded. This type of corrosion is avoided by alloying.

ii. Contact with dissimilar metals must be avoided.

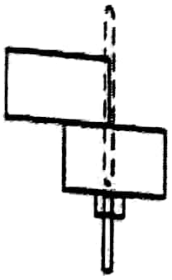
iii. When two dissimilar metals are in contact with one another then anodic material should have large area as much as possible and cathodic area is as small as possible.

iv. Whenever direct joining of two metals is unavoidable, then some insulator like rubber or plastic piece must be placed in between the metals.

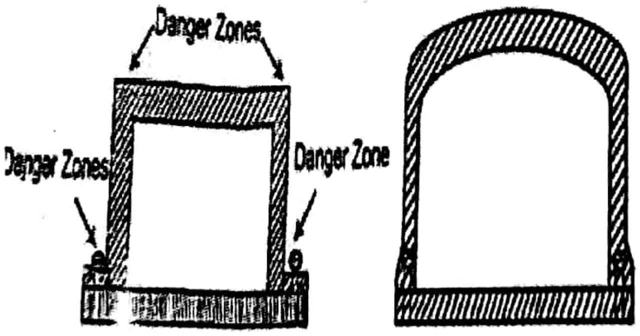
v. The smaller part is noble metal and larger part is anodic metal. The anodic -metal should not be painted or coated.

vi. The equipment should be designed, so as to avoid localized stress. Further equipment design should be avoided sharp bends, rivettes, corners and lap joints.

vii. Whenever possible , the equipment should be supported on legs to allow free circulation of air.

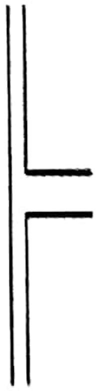

Poor design


Best design



a) Bad
b) Good

Design of Electrical Box.


Poor design


Best design

Cathodic protection:-

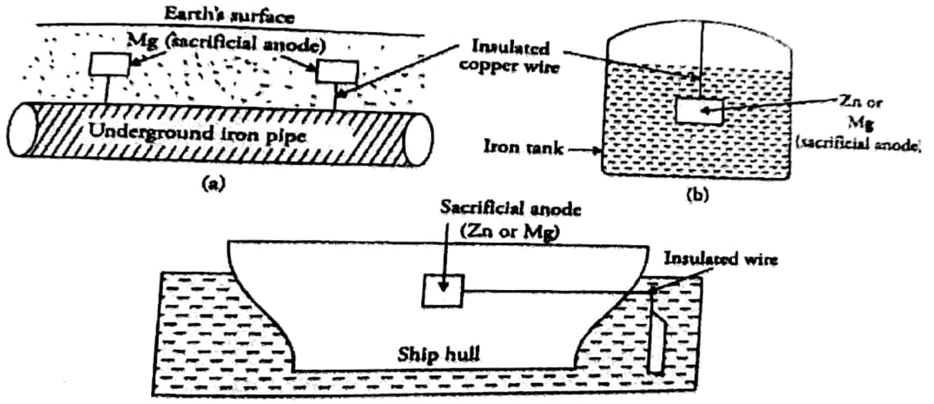
The principle involved in the cathodic protection is the base metal (which metal want to protect from corrosion) to be protected is forced to behave like a cathode as it is not effected by the corrosion.

Cathodic protections are two types

1. **Sacrificial anodic protection 2. Impressed current cathodic protection.**

Sacrificial anodic protection:

Underground iron pipes are protected from corrosion by this method.

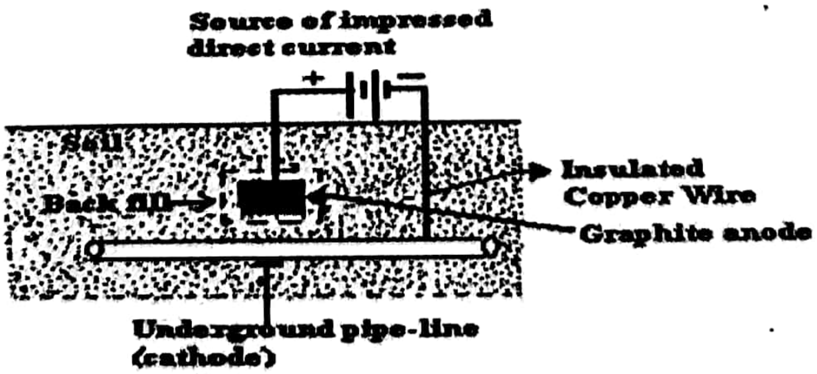


.14 Sacrificial anodic protection

- Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.
- Underground pipe line able to connect to more active metal. Like Mg rod there by Mg act as anode and base metal (iron metal) behaves as a cathode due to Mg redox potential is lower than Fe
- So that Mg acts as anode and Fe acts as cathode. Corrosion always occurs at anode there by Mg rod is corroded while base metal Fe pipe is protected.

Application:-Protection from corrosion of underground cable, pipeline, ship hulls, water tanks.

Impressed current cathodic protection



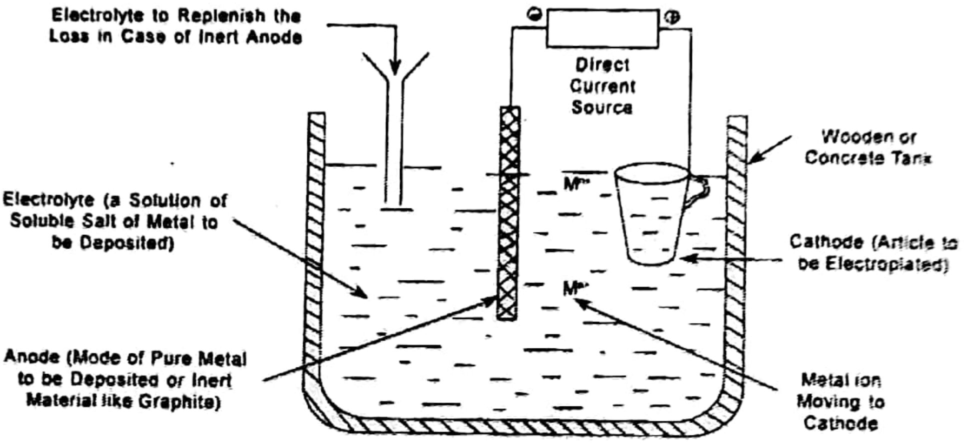
- In this method underground buried iron pipeline (base metal) is connected to graphite (or) Pt anode. Through the Cu wire.
- Graphite is placed in back fill which contain coke breeze or gypsum to increase the electrical contact between itself and the surrounding soil.
- Graphite and pipeline is also connected to the battery which supply the impressed or applied current
- Corrosion current (from anode to cathode) and impressed current, both travel in opposite direction are cancelled out (nullify) with each other. By the result graphite is converted into cathode.
- **Applications:-** This type of protections is used in buried structures such as tanks and pipelines, transmission line towers, marine pipes, laid up ships etc.,
- **Advantages:** - They can be automatically controlled which reduce maintenance and operational costs.

Passivity:-

- The process in which a metal exhibits higher corrosion, resistance is called passivity.
- When a very thick and highly protective film is formed on the surface of metal (or) Alloy. It is called passivity.
- Passive film on metal surface is determined by pourbaix diagram which depend on electrode potential and PH
- Passive film is formed on the surface of A1,Cr1 Si, Ti in air, water. The film is insoluble, non-porous, self-healing and chemically inert.

Electro plating:

- It is on electro chemical process in which Base metal is coated by Zn, Ag, Cr, Cu, Sn etc to protect it from corrosion and also give shinning and decorative look.
- In this process – the base metal is taken as cathode and coated pure metal (deposited metal) is taken as anode. Both are dipped in electrolyte solution and connected to Battery.
- When current is passed coated metal ions migrate to cathode (Base metal) and gets deposited.



Electro less plating (Auto catalytic redox reaction)

Definition: "The process of depositing a metal over substrate by controlled chemical reduction of metal ion by a reducing agent without using electric current is called electro less plating"

Metal ions +reducing agent   Metal + oxidized product

Differences between electroplating and electro less plating:

Property	Electro plating	Electroless plating
1) Driving force	Passage of current	Auto catalytic redox reaction
2) Anode	A separate anode is used	Catalytic surface of the substrate acts as anode
3) Reducing agent	Electrons bring about reduction	Chemical reagents bring about reduction
4) Applicability	Applicable only to conductors	Applicable toboth conductors nonconductors

Electroless Ni plating

Pre-treatment of surface:

a) CO, Ni, steel andAl can be directly plated.
b) Pb, Cd and Sn are first electroplated with Ni prior to electroless plating.
c) Non-conductors are activated in SnCl, and HCI followed by dipping in PdCl, and HCL On dry ing, thin Pd layer is formed.

Bath composition: $NiCl^{2}$, coating solution, sodium hypophosphite reducing agent, NaOAc buffer, sodium succinate (complexing agent) pH=4-6, temperature = 85-95C.

Process: Pre-heated surface is immersed in bath; the reduction ofNi occurs and Ni gets deposited over the surface.

$Ni^{2}+H2PO^{2}+H,O- \rightarrow Ni+H2PO^{3}+2H$

Properties:

(a) They possess greater corrosion resistance than electroplated Ni deposit.
(b) They give harder surface with better wear resistance.
(c) Coating is soldarable and weldable.

Applications:

(a) They are used in electronic industry for fabricating printed circuits and diodes. They are used to prevent the galling of aluminum stainless steel.