# UNIT - 2

## ELECTROCHEMISTRY AND CORROSION

- Electrochemistry is the branch of chemistry that deals with the relation ship between electrical energy and chemical reactions
- Electrolytic cell: A Device which converts electrical energy to chemical energy or vice versa

The two main types of Electrochemical cells are

- Electrolytic cell
- Galvanic cell

- Electrolytic cell: The cell which converts electrical energy to chemical energy
- Galvanic cell: The cell which converts chemical energy to electrical energy.

**ANODE:** Anode is the electrode at which oxidation occurs.

**CATHODE:** Cathode is the electrode at which reduction occurs.

**ELECTROLYTE:** Electrolyte is a substance which in aqueous solution or molten state liberates ions and allows electric current to pass through, thereby resulting in its decomposition. ex: acids, bases etc.,

**HALF CELL:** Half cell is a part of cell, containing electrode dipped in a electrolytic solution. If oxidation occurs at the electrode that is called oxidation half cell. If reduction occurs at the electrode that is called reduction half cell.

**CELL:** Cell is a device consisting two half cells. The two half cells are connected through a wire and salt bridge

**SALT BRIDGE:**

- Salt bridge: It is a inverted U-shaped glass tube filled with electrolyte mixed With agar-agar or gelatin to impart gel like characteristics.
- The mouth of the tube are blocked with cotton plugs. All this precautions are taken to ensure that the contents of the salt bridge should not undergo mechanical mixing with the contents of the electrode.
- Common electrolytes used are KCl, $NH_4$ Cl etc. Glass tube Electrolyte + agar-agar powder Cotton plug

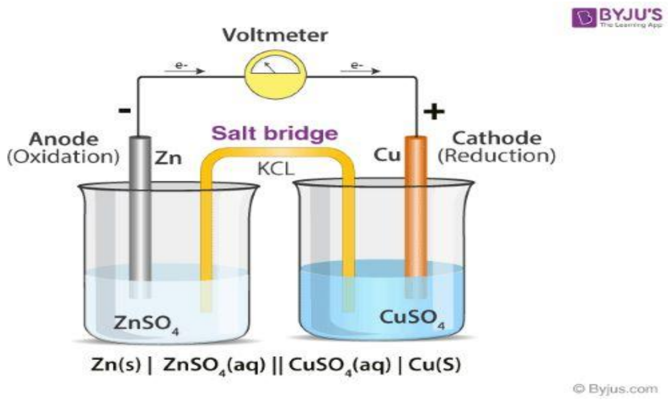
## ELECTRODE POTENTIAL (E):

- Electrode potential (E): It is the measure of tendency of an electrode to lose or gain electrons, when it is in contact with a solution of its own salt.
- Zn → Zn2+ + 2e- (oxidation) Cu2+ + 2e- → Cu (reduction)
- Factors affecting electrode potential:
- 1. The nature of the metal 2. The temperature 3. The concentration of ions in solution
- Standard electrode potential (Eo): It is the measure of tendency of an electrode to lose or gain electrons, when It is in contact with a solution of its own salt of 1 molar concentration at 25 oC
- Electrochemical cell or Galvanic cell An electrochemical cell is a device in which a redox reaction is utilized to get electrical energy (chemical energy is converted to electrical energy). ex: Daniel cell

## GALVANIC CELL:

- Electrochemical cell or Galvanic cell An electrochemical cell is a device in which a redox reaction is utilized to get electrical energy (chemical energy is converted to electrical energy). ex: Daniel cell
- Daniel cell: It consist of a Zinc electrode dipped in ZnSO4 solution and a copper electrode dipped in a CuSO4 solution.
- Each electrode is known as a half cell. The two solutions are inter connected by a salt bridge and the two electrodes are connected by a wire through the voltmeter.
- Oxidation takes place in the zinc electrode by the liberation of electrons, so this electrode is called negative electrode or anode.
- Reduction takes place in the copper electrode by the acceptance of electrons, so this electrode is called positive electrode or cathode.
- Daniel cell can be represented as Zn | ZnSO4 || CuSO4 | Cu
- The double bar || represents salt bridge.
- At anode: : Zn →Zn+2+2e
- At cathode :Cu+2+ 2e- → Cu

Cell reaction: Zn + Cu+2 → Zn+2 + Cu



## NERNST EQUATION:

- Nernst equation Nernst equation is used to calculate electrode potential of unknown metal.
- Consider a redox reaction Mn+ ne M
- E = Eo + 2.303 RT [ Mn+ ]
- when R = 8.314 J/K/mole; F = 96500 coulombs, T = 25 oC, the equation becomes
- E = Eo red+ 0.0592/n [ Mn+ ]
- Similarly for oxidation potential
- E = Eo oxid - 0.0592 /n log [ Mn+ ]

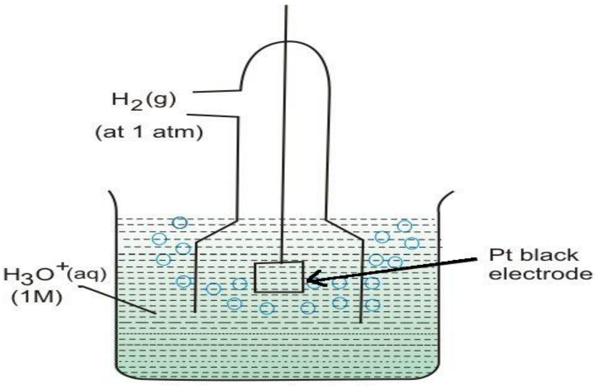
## STANDARD HYDROGEN ELECTRODE:

- To determine the single electrode potential it is combined with SHE is combined with potentiometer

and the EMF is measured.

- A standard Hydrogen electrode consists of a pt toil which is coated with platinum black, enclosed in a glass tube through which H2 gas passed at a pressure of lath and it is placed in IM HCl Solution.
- The following equibrium exists at the electrode.
- 2H+ (aq) + 2e- H2 (g) When S.H.E.is paired with another electrode in a galvanic cell it can be undergo either or reduction depending on the magnitude of potential of coupled electrode.
- The electrode reaction of this electrode is written as: ½ H2 → H+ + e-

- Applying Nernst equation
- $E_{H_2/H^+} = E^0_{H_2/H^+} - 0.0592/2 \log a_{H^+} / p^{1/2}_{H_2}$
- At 1 atm pressure
- $E_{H_2/H^+} = E^0_{H_2/H^+} - 0.0592 \log a_{H^+}$
- $E_{H_2/H^+} = E^0_{H_2/H^+} + 0.0592\ pH$

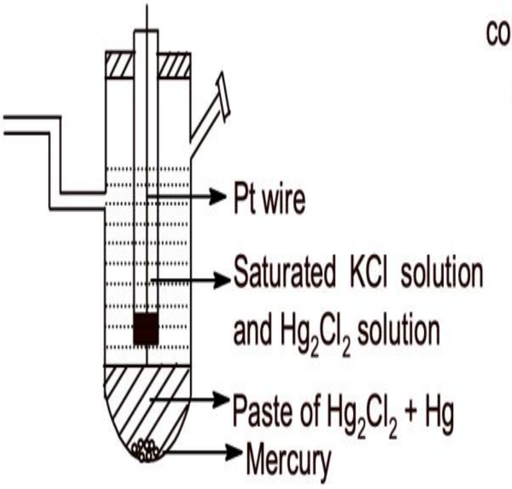


Hydrogen electrode

## CALOMEL ELECTRODE:

- Calomel electrode consists of a glass tube containing mercury at the bottom over which mercurous chloride (calomel) is placed.
- The remaining portion of the tube is filled with a saturated solution of KCl. The side tube is used for making electrical contact with salt bridge.
- One end of the pt wire is dipped in mercury and another is end is connected to potentiometer.
- $Hg_2Cl_2$ (s) 2e 2Hg (l) 2Cl
- The potential of the Calomel electrode depends on the concentration of the KCl solution.
- The electrode potentials for the various KCl concentrations at 25 oC are

| KCl concentration | Electrode potential (in volts) |
|---|---|
| 0.1 N | 0.33 0.28 0.2 |
| 1.0 N | 0.28 |
| Saturated | 0.24 |



| conc$^n$ of KCl | St. red. potential |
|---|---|
| saturated | 0.2415 |
| 1.0N | 0.2800 |
| 0.1N | 0.3338 |

## CORROSION

The process of decay metal by environmental attack is known as corrosion.

- Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc.

E.g. Iron undergoes corrosion to form reddish brown colour rust [Fe2O3. 3H2O].

Copper undergoes corrosion to form a green film of basic carbonate [CuCO3 + Cu (OH) 2]

- Corrosion (Oxidation)
- Pure Metal <==========> Metallic compound + energy
- (Un stable) Reduction(extraction) (Stable)(Ores/Minerals)

## CAUSES OF CORROSION:

- The metals exist in nature in the form of their minerals or ores, in the stable combined forms as
- oxides, chlorides, silicates, carbonates, sulphides etc.
- During the extraction of metals, these ores are reduced to metallic state by supplying
- considerable amounts of energy.
- Hence the isolated pure metals are regarded as excited states than their corresponding
- ores. So metals have natural tendency to go back to their combined state (minerals/ores).
- When metal is exposed to atmospheric gases, moisture, liquids etc., and the metal surface reacts
- and forms more thermodynamically stabled compounds.

## EFFECTS OF CORROSION

- Wastage of metal in the form of its compounds.
- The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to
- corrosion.

- Life span and efficiency of metallic parts of machinery and fabrications is reduced.
- Poor appearance
- Maintenance and operating costs
- Plant shutdowns

There are two theories of corrosion

1. Dry/Chemical theory

2. Wet/Electrochemical/galvanic Corrossion

**DRY (OR) CHEMICAL CORROSION:** According to this theory this type of corrosion occurs

due to the direct chemical attack of atmospheric gasses ($O_2$, $H_2S$, $SO_2$, and $N_2$) on the metal surface

in the absenceof moisture.

There are three main types of dry Corrosion:

i. Oxidation corrosion

i. Corrosion of the other gases

ii. Liquid metal corrosion.

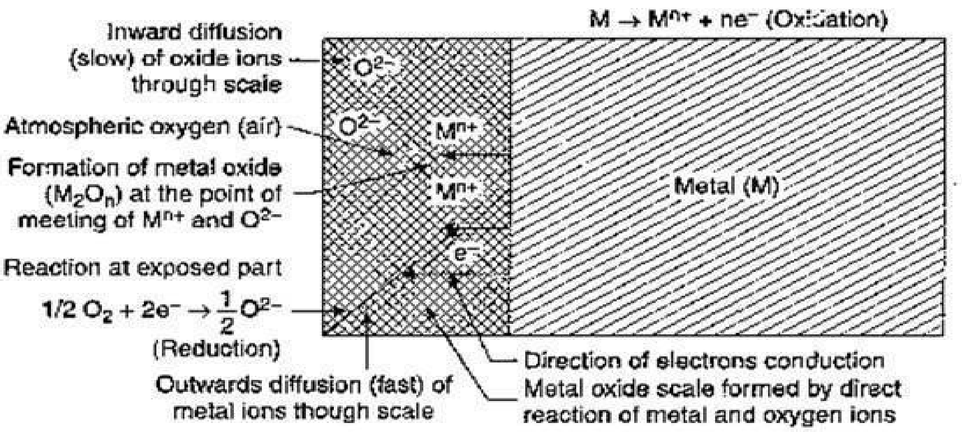
**OXIDATION CORROSION:**

- This is carried out by the direct action of oxygen in low or high temperatures on metals in absence of
- moisture.
- Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures.
- At high temperature all metals are oxidized (except Ag, Au, and Pt).
- Oxidation accurs first at the surface of the metal and result the formation of metal ions ($M^{2+}$ ) at metal

$M \rightarrow M^{2+} + 2e^-$ (Oxidation)

- Oxygen changes to ionic form ($O^{2-}$) due to the transfer of electrons from metal at oxide film. $O_2 + 2e \longrightarrow 2O^{2-}$ (Reduction)
- Oxide ions reacts with the metal ion to form the mrtal-oxide film.

$M + O_2 \rightarrow M^{2+} + 2O^{2-} = (MO)$(Metal oxide)



**MECHANISM:** Initially the surface of metal undergoes oxidation and the resulting metal oxide forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide(MO).

i).If the metal oxide is stable, it behaves has a protective layer which prevents further

Corrosion.

E.g., the oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

ii).If the metal oxide unstable, the oxide layer formed decomposes back into metal and oxygen. Oxidation

corrosion is not possible.E.g., Ag, Au and Pt do not undergo oxidation corrosion.

iii).If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the

underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive

in molybdenum oxide (MoO3).

iv).If the metal oxide layer is porous, the oxide layer formed has pores or cracks. This cause continuous

corrosion till conversion of metal into its oxide is completed.

Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)

**CORROSION OF THE OTHER GASES:**

This type of corrosion is due to gases like SO2, CO2, Cl2, H2S, F2 etc. In this

corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas

involved.

## LIQUID METAL CORROSION:

This corrosion is due to chemical action of flowing liquid metal at high temperatures

on solid metal or alloy.

Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

## WET (OR) ELECTROCHEMICAL CORROSION

- This type of Corrosion occurs where a conducting liquid is in contact with the metal.
- This corrosion occurs due to the existence of separate anodic and cathodic parts, between which
- current flows through the conducting solution(Mositure).
- At anodic area, oxidation reaction occurs there by destroying the anodic metal either by dissolution
- or formation of compounds. Hence corrosion always occurs at anodic parts.

**MECHANISM:** Under the above conditions,one part of metal becomes Anode and other part becomes

Cathode.

At anode:In anodic part oxidation of metal occurs.

$M \rightarrow M^{n+} + ne^-$

<u>At Catode:</u> The cathodic reaction consumes electrons with either evolution of hydrogen (or) absorption of oxygen which depends on the nature of corrosive environment.

i. Evolution of hydrogen: This type of corrosion occurs in acidic medium.

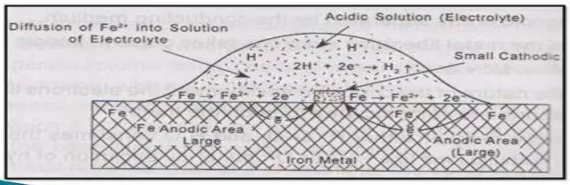
Ex: Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation

of electrons.

<u>At Anode:</u> Iron undergoes dissolution to give $Fe^{2+}$ ins with the liberation of elctrons

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

**Mechanism of wet corrosion by hydrogen evolution**

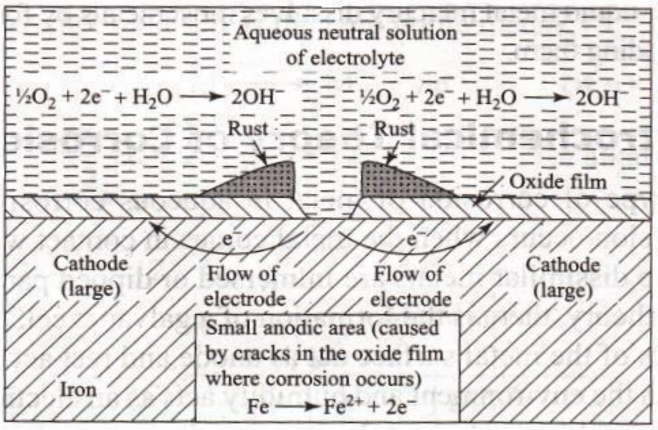


At Cathode: The liberated electrons flow from anodic to cathodic part,where $H^+$ ions get to reduced to $H_2$.

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

Overall reaction: $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$

The anodes are large areas, whereas cathodes are small areas.



(b)

II. ABSORPTION OF OXYGEN:

- This type of corrosion occurs in

(or) basic medium.

Ex: Rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen.

At Anode: Iron dissolves as $Fe^{2+}$ with liberation of electrons

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

At cathode: The liberated of electrons flow from anodic part to cathodic part of through metal,where the

electrons are taken up ny the dissolved oxygen to form $OH^-$ ions

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (Reduction)

Overall reaction: $Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe(OH)_2$

If oxygen is in excess, ferrous hydroxide ($Fe(OH)_2$) is easily oxidized to ferric hydroxide ($Fe(OH)_3$).

$4 Fe^{2+} (OH)_2 + O_2 + 2 H_2O \rightarrow 4 Fe(OH)_3$

## TYPES OF CORROSION:

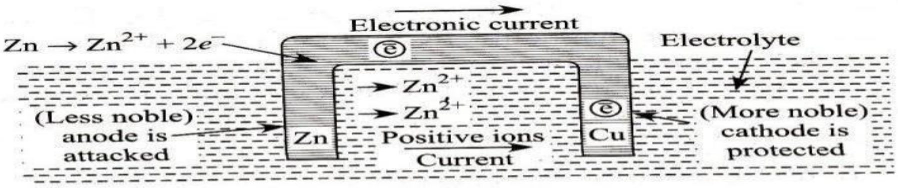
(i). Galvanic Corrosion

(ii). Waterline Corrosion

(iii). Pitting corrosion

**I).GALVANIC CORROSION** : This also called bimetallic corrosion or dissimilar metal corrosion.

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



Galvanic corrosion

**At anode:** $Zn \longrightarrow Zn^{++} + 2e^-$ [Oxidation] corrosion

**At cathode:** $Cu^{++} + 2e^- \longrightarrow Cu$ [Reduction] unaffected

• In the above Zn and Cu metals are contact with each other,Here Zn metal is Higher position in

electrochemical series and act as anode ,so undergoes corrosion.

• Cu metal is lower position in electrochemical series and act as cathode ,so protected fro

corrosion.

### (II). WATERLINE CORROSION:

- This is also known as differential oxygen concentration corrosion.
- It has been observed in the case of 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.

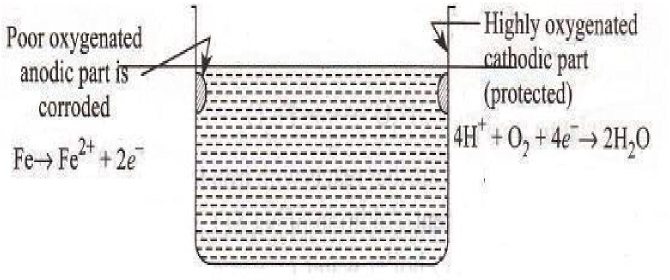
At anode:Fe → Fe2+ +2e-

At cathode: 2H+ +½O2 + 2e-→ H2O

Overall reaction: $Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe^{2+} + 2OH^-$ $(Fe(OH)_2$

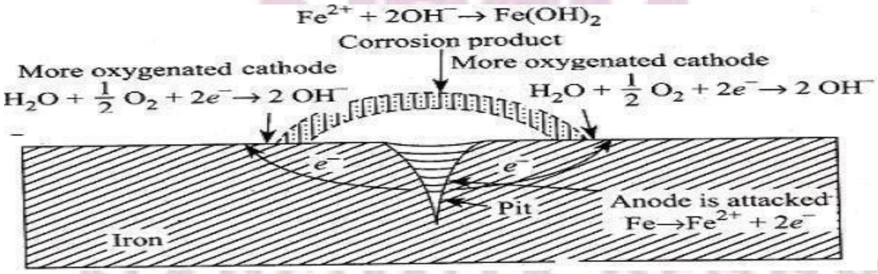
. The area above the waterline (highly oxygenated) acts as cathodic and is not affected by corrosion. However, if the water is relatively free from acidity, little corrosic occurs.

. This type of corrosion is prevented to a great extent by painting the sides of the by antifouling paints.



**(III). PITTING CORROSION:**

- Pitting corrosion is due to crack on the surface of a metal, there is a formation of a “local
- galvanic cell” (Pinholes, pits and cavities) in the metal.
- Pitting is usually the result of the breakdown or cracking of the protective film on a metal at
- specific points. This gives rise to the formation of small anodic and large cathodic areas. In the corrosive environment this produces corrosion current.



Specific Volume Ratio = Volume of metal oxide

Volume of metal

**FACTORS AFFECTING RATE OF CORROSION:**

The rate and extent of corrosion depends on the nature of the metal and nature of corroding .environment.

Those are

1. NATURE OF METAL: Different properties of a metal are responsible for corrosion. These properties are given below.

a. Position of metal in galvanic(emf) series

b. Over voltage

c. Nature of surface/oxide film

d. Volatility of corrosion product

e. Purity of Metal

**Position of metal in galvanic series:**

- A metal having higher position in galvanic series(EMF series) undergoes corrosion when
- connected to another metal below it.
- The Metal which is Higher position in galvanic(EMF)Series is faster in corrosion
- The Metal which is Lower position in galvanic(EMF)Series is slow in corrosion
- Ex: Li Corrodes faster than Mg.
- Because Mg metal is lower position than Li metal in the emf series .

**Over voltage /Potential :** Over voltage of a metal in the corrosive environment is inversely proportional to corrsion rate.

Ex:In case of Zinc metal placed in a normal solution of $H_2SO_4$,,over oltage of Zn is 0.7volts.Here the rate of corrosion is very low due to high overvoltage of zinc metal (0.7 V) By adding small amount of $CuSO_4$ to $H_2SO_4$ . Over voltage of Zn is reduced to 0.33 V and rate of corrosion is increased.

**Nature of surface/oxide film:** Nature of surface/oxide film:. The ratio of the volumes of metal oxides to the metal is known as specific volume ratio(Pilling Bedworth Rule). Greater the spedific volume ratio lesser the corrosion rate.

Pilling Bedworth Rule: Smaller the ratio greater the corrosion rate

**Nature of the corrosion products:**

- If the corrosion product is soluble in the corroding medium, the corrosion rate will be faster.
- If the corrosion product is insoluble in the corroding medium ,the corrosion rate will be slow.
- If the corrosion product is volatile, rapid and continuous corrosion occurs.

**Purity of the Metal:**

- . 100% pure metal does not undergoes any type of corrosion
- The rate of corrosion increases with the increasing exposure and extent of the impurities
- % purity of Zn 99.999 99.990 99.95
- Corrosion rate 1 2650 5000

2. NATURE OF ENVIRONMENT: Different properties of an environment are responsible for corrosion.

These properties are given below.

a) Effect of pH

b) Temperature

c) Humidity

d) Amount of oxygen in atmosphere

e) Presence of corrosive gases

f) Presence of suspended particles

**a. Effect of pH:**

• Rate of corrosion is inversely proportional to temperature.

• Rate of corrosion can be reduced by increasing the pH of the solution by adding alkali.

• Acidic pH increases the rate of corrosion (pH is less than 7).

• Basic pH decreases the rate of corrosion (pH is more than 7).

Thus rate of corrosion will be maximum when the corrosive environment is acidic.

**b.Temperature:**

• Rate of corrosion is directly proportional to temperature, because the rate of reaction and

diffusion of ions increased with increase the temperature.

• Hence With the increase of temperature the corrosion rate is increases.

**c. Humidity :**

- Rate of corrosion is directly proportional to Humidity.
- Rate of corrosion will be more ,when the humidity is high in environmente.
- e. 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.
- e.Presence of corrosive gases:
- acidic gasses like CO2, SO2 produces electrolytes which are acidic and increases corrosion.
- f.Presence of suspended particles:

- particles like Nacl, $(NH_4)_2SO_4$ produces electrolytes which increases corrosion.

## CORROSION CONTROL METHODS:

### 1. CATHODIC PROTECTION

- The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.

There are two types of cathodic protection

(a) Sacrificial anode method

(b) Impressed current method.

### (a) SACRIFICIAL ANODE METHOD:

- In this protection method, the metallic structure to be protected (base metal) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- The more anodic metal itself gets corroded , while the parent structure (base metal) is protected.
- The more active metal is called sacrificial anode.
- Commonly sacrificial anodes are Mg, Zn, Al and their alloys

Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which

undergoes corrosion leaving the base metal protected.

Eg. The underground water pipelines and water tanks are also protected by sacrificial anode

method.

The important applications of this method are:

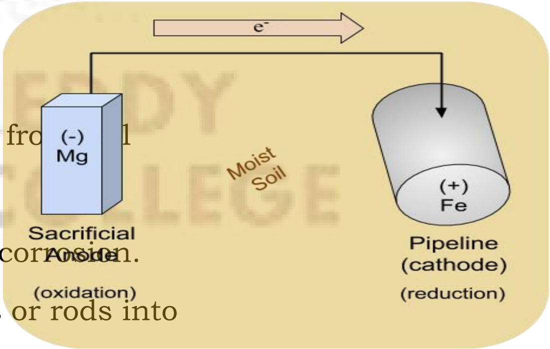
1. Protection of underground cables and pipelines fro l

corrosion.

2. Protection of ships and boat hulls from marine corrosion.

3.Prevention of rusty water by inserting Mg sheets or rods into

domestic water boilers or tanks.



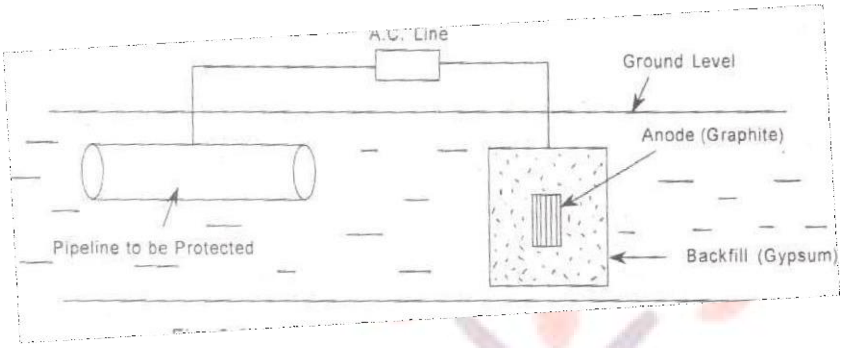
Eg: Sacrificial anode method: ship hull and underground water

pipeline

### (b) IMPRESSED CURRENT METHOD:

- In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.

- The impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current is taken from a battery or rectified on A.C. line.
- The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.



**ADVANTAGES:**

1. Operating and maintenance costs are less.

2. Suited for large structures and long term operations.

**APPLICATIONS:**

1.Tanks and pipelines,

2.Transmission line-towers,

3.Marine piers, Ships etc.