(1) $2CO_{(gas)} + O_{2(gas)} \longrightarrow 2CO_{2(gas)}$

→ 3 moles of a gas produces 2 mole of gas
→ Hence ΔS decreases
$\Delta G = \Delta H - T\Delta S$ ΔG = Increases

(3) $C_{(solid)} + O_{2(gas)} \longrightarrow CO_{2(gas)}$

Oxidation of Solid Carbon:
→ 1 mole are producing only one mole
→ This leads to Reduction in Entropy.
$\Delta G = \Delta H - T\Delta S$ ΔG° = decreases or less

(5) $2C_{(gas)} + O_{2(gas)} \longrightarrow 2CO_{(gas)}$

→ one mole of gas produces a 2 mole of gas and Hence ΔS Increases
→ slope is Bowed downward downbowed.
→ ΔH decreases
→ Feasibility of a Reaction increases as ΔH becomes negative

Selection of Suitable Reducing Agent.
→ In industrial processes, the reduction of metal oxides is often preferred using Carbon as a reducing agent. Carbon act as a reducing agent

Q Why Carbon can't be used as a reducing agent for Chromic oxide

$2C_{(solid)} + O_{2(gas)} \longrightarrow 2CO_{(gas)}$

Carbon can act as reducing agent for all metal oxides Except of Cr because with Cr it forms CCr_2

$C + Cr_2 \longrightarrow CCr_2$ (Chromium carbide)

this CCr_2 gives undesirable properties of Chromium

Ease of Reduction :- The position of a given reaction on the Ellingham diagram shows the stability of oxide as a function of temp.

Applications

1) The main application is in metallurgy, where it helps to select the best reducing agent for various ores
2) It helps us to guide the purification of metals, specially removal of trace elements
3) Used to determine the relative ease of reducing a given metallic oxide to metal
4) Used to determine the ratio of carbon monoxide to carbon dioxide that will be able to reduce the oxide to metal
5) Determine partial pressure of O_2 that is in equilibrium with a metal oxide at given temp.

Water Chemistry :- Water is a universal solvent. It is used in every field of life. Many industries are based on the water.

Specifications of water for drinking purpose
1) water should be odourless and tasteless
2) It should be free from impurities and other radioactive contaminants.
3) It should be having appropriate hardness in between 100 - 300 ppm.
4) It should be free from germs and bacteria.

Hardness :- It is defined as the amount of Ca and mg salts present in water.

Hard water :- The water which do not make leather with soap.

Soft water :- The water which make leather with soap.

Degree of Hardness :- The extent to which water is hard.

Types of Hardness :- There are two type of hardness present.

1) Temporary – The hardness which is due to the presence of carbonates and bicarbonates of Ca and mg

$Ca(HCO_3)_2$, $Mg(HCO_3)_2$

2) Permanent :- which is due to the presence of chlorides and sulphates of Ca and mg

$CaSO_4$, $MgSO_4$, $CaCl_2$, $MgCl_2$

Degree of hardness is determined in terms of $CaCO_3$ equivalent because $CaCO_3$ is the most insoluble compound and it is having molecular weight equals to 100 which makes the calculation result easy.

Boiler :- Boiler is a device used in industries to produce steam as to generate power. Water used in the boiler should be soft otherwise it can lost the functioning and strength of boiler.

water fed in to the boiler should be free either it can lead to scales and sludge formation in the boiler.

Scales and sludges are the precipitates formed when water is boiled in the boiler. for Ex $CaCO_3$, $Ca(OH)_2$, $Mg(OH)_2$, $MgCl_2$

$$Ca(HCO_3)_2 \xrightarrow{\Delta} \underset{\text{scale}}{CaCO_3} + H_2O + CO_2$$

(Insoluble)

Scales are hard
sludges are soft.

So to avoid the formation of precipitates treatment over water should be done.
There are two types of treatment of boiler water

1) External Treatment :- The treatment of water which is carried outside the boiler.

2) Internal Treatment :- Treatment of water which is carried inside the boiler.

External Treatment :- Methods of External Treatment are

1) Zeolite process

2) Ion-Exchange or Deionized or Demineralized

1) Zeolite process :- In this process the Zeolites are used. Zeolites are the inorganic salts. For Exp Sodium Zeolites

In Zeolite process, the general principle involved is the exchange of Ca^{2+} and Mg^{2+} ions by Na^{+} ions of the Zeolite.

$$Na_2Ze + CaCl_2 \longrightarrow 2NaCl + CaZe$$

$$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$$

General Method :- In this process a Cylindrical Chamber is placed vertically having filling of Zeolite bed and Sand filter (three different layers of Sand) below the bed. As the water passes through the Zeolite bed Exchange of Na^{+} with Ca^{2+} will start take place and other impurities would retain in the sand filter and water get filtered at the bottom.

Zeolite process

After some time the Zeolite bed get exhausted. It needs regeneration. Then to regenerate Zeolite we will inject dil solution of NaOH to have Na^+ ion again

Regeneration reactions

$CaZe + 2NaOH \longrightarrow Na_2Ze + Ca(OH)_2$

$MgZe + 2NaOH \longrightarrow Na_2Ze + Mg(OH)_2$

Now again it will start work

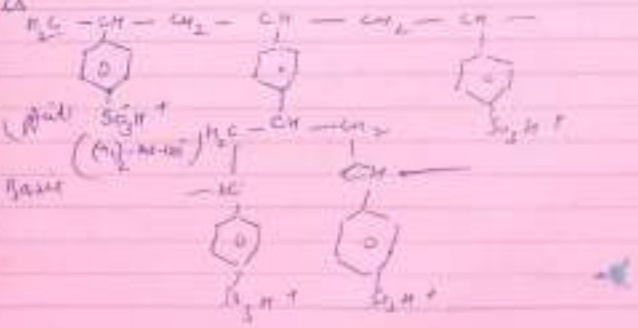
Disadvantages

1) Hot water can not be used other wise it will affect Zeolite bed.
2) Turbid water can not to be used otherwise it can block pores.
3) Acidic water can't be used.

(2) Ion - Exchange process :- In this process both cations and anions are removed. To exchange cations and anions we need Exchange Resins. Resins are Cross linked high molecular weight compounds.

Styrene divinyl benzene Co-polymer as a Resin is used, the Exchange property lies in the presence of the acidic or basic functional group at the para position

1) Cation Exchange Resins :- In this acidic group is attached Structure of Cation Resin is



Hence H^+ will replace Ca^{2+} or Mg^{2+}.
Exchange Resins reactions are -

For Simplicity we will write RH for Cation Resin

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca + 2H^+$$

2) Anion Exchange Resins :- Base groups are used and Represented as

$$ROH^- + Cl^- \longrightarrow RCl^- + OH^-$$

Hence $H^+ + OH^- \longrightarrow H_2O$

But after all the Exchange, the Resins get Exhausted and need Regeneration
Hence for Cation Resins - HCl (dil)
Anion Resins → NaOH (dil)

Regeneration Reactions

(1) Cation Resins

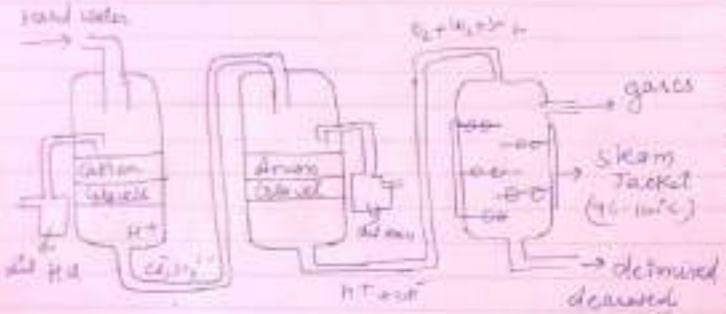
$$R_2'Ca + 2HCl \longrightarrow 2RH + CaCl_2$$

(2) Anion Resins

$$RCl^- + NaOH \longrightarrow ROH + NaCl$$

Process → First water which is going to be soft is fed in to the Cation Resin Chamber, Exchange of Cation will take place and then pass to the Anion Exchanger and hence anions are removed
Now the water left with Gases only. To remove gases like (O_2, CO_2, SO_2) one Mechanical degasser decarbonator is used which is heated up by using Dr. Steam Jacket (96-100°C)
Steel Chamber have perforated plates and an outlet for water and gases.

as the water percolate through the holes of the plate gases will remove out by using pump from upper end and water is heavier and will get drain at the bottom.



Ion - Exchange Process

Disadvantages

1. Acidic water can't be used
2. Turbid water can't be used
3. Hot water can destroy the resins
4. Apparatus is not easy to install

Advantages

1. Water of 0 - 2 ppm of hardness is achieved
2. Both cations and anions are removed
3. Gases are also removed
4. no problem of sludge

Disinfection - The process in which some chemicals are used to remove germs and bacteria present in water. These substances are called as disinfecting agents.

Chlorination - is a disinfection method

1. Cl_2 as liquid
2. Cl_2 as gas
3. Cl_2 as solid

Corrosion

→ It is a slow decay of the metal and metallic objects by chemical or electrochemical reactions with the env.

metals are stable when they are present in their ore and get corroded after extraction of metals.

Common example :- Rusting of Iron.

Types of corrosion

1) Dry or chemical corrosion :- In which corrosion of metals occur under dry conditions (gases :- CO_2, O_2, H_2S)

Corrosion by Oxygen → when metal is in close contact with O_2. corrosion of metal took place. A Redox reaction occurs

Oxidation $Fe \longrightarrow Fe^{+2} + 2e^-$

loss of electrons

Reduction

$\frac{1}{2}O_2 + 2e^- \rightarrow 2O^{2-}$ (gain of $\bar{e}$)

Over all Reaction

$Fe^{2+} + O^{2-} \rightarrow FeO$

Product of corrosion

Different metal oxide layers

(1) Stable layer :- When layer is stable in nature only the metal will remain safe. In case of Sn, Al, Cu, This type of layer is formed. As soon as the layer is on the metal, metal is safe.

(2) Unstable layer :- When layer is unstable in nature, it will dissociate to give metal and oxygen again and hence the metal is regenerated again

Metal Oxide $\rightarrow$ Metal + O_2

In Case of Ag, Pt and Au this type of layer is formed

(3) Volatile layer :- If the layer formed is volatile it will get decompose to the air and metal surface again come in contact with environment. In Case of alkali and alkaline earth metals, this type of layer is formed.

(4) Porous layer :- If the layer formed is Porous means having pores in nature then metal come in contact with env. again through these pores. In Case of Iron and Zinc this type of layer is formed.

Pilling Bed worth Rule

If the layer of metal oxide > metal than layer is protective
If the layer is < than metal layer layer is non protective.

(3) Corrosion of metal by CO_2 and SO_2

$CO_2 + H_2O \rightarrow H_2CO_3$ } Carbonic acid
$SO_2 + H_2O \rightarrow H_2SO_3$ } Sulphonic acid } corrosive

Specific Volume Ratio = $\frac{\text{Vol. of metal oxide}}{\text{Vol. of metal}}$

2) Corrosion by H_2S

$$Fe + H_2S \longrightarrow \underbrace{FeS}_{\text{metal Sulphide}} + H_2$$

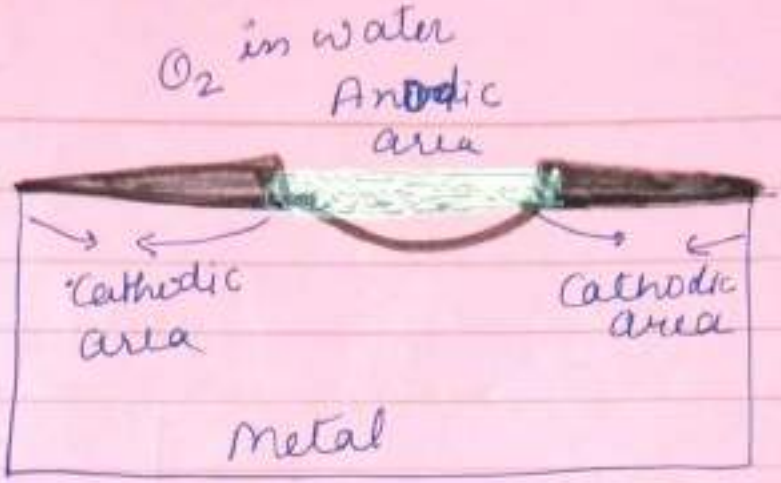
(2) Wet or Electrochemical Corrosion

In which Corrosion of metals occur in the presence of wet Conditions like Water, acid, Base wet corrosion also known as Concentration cell Corrosion

Mechanism of wet corrosion

(1) By absorption of O_2

When metal is in Contact with moisture then there is a formation of Concentration cell electrochemical cell. metal get Oxidised and Oxygen in water get Reduced



At anode $2[Fe \longrightarrow Fe^{+2} + 2e^-$ (oxidation)

At cathode $O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$ (Reduction)

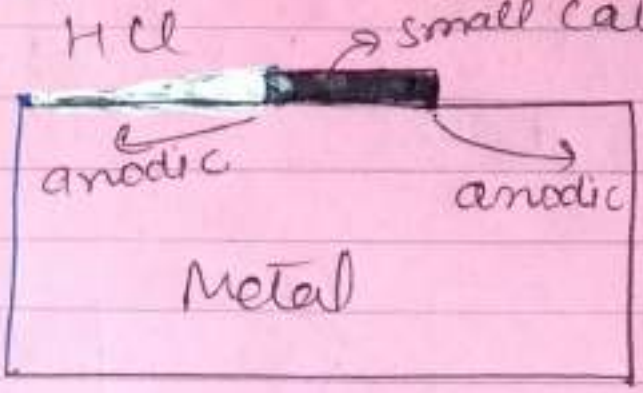
$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{+2} + 4OH^-$$

$$Fe^{+2} + 2OH^-$$

$Fe(OH)_2$ or $Fe_2O_3 H_2O$
Rust

Cathodic area is larger than the anodic area so corrosion occurs at faster rate.

(2) By Evolution of H_2 gas
when acidic Conditions are there, then H_2 gas get evaluate.



$HCl \rightarrow H^+ + Cl^-$

At anode

$$Fe \longrightarrow Fe^{+2} + 2e^-$$

At Cathode

$$2H^+ + 2\bar{e} \longrightarrow H_2 \uparrow$$

Corrosion occurs at slower rate because of small Cathodic area than anodic area.

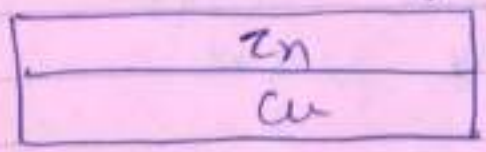
Types Of Wet Corrosion

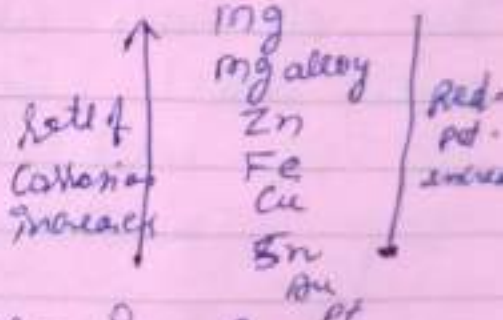
(1) Galvanic Corrosion :- It is also known as bimetallic Corrosion

In this type one of the metal will remain safe and other will get corroded. Rate of corrosion depends on the position of metal in the galvanic series. Acc to galvanic series the metals and its alloys are arranged according to their reduction potential for Exp Zn + Cu (Brass)

Zn is having low Reduction potential than Cu. Hence Zn will get corroded and Cu will remain safe.

Basic exp is Statue of liberty which is an alloy.



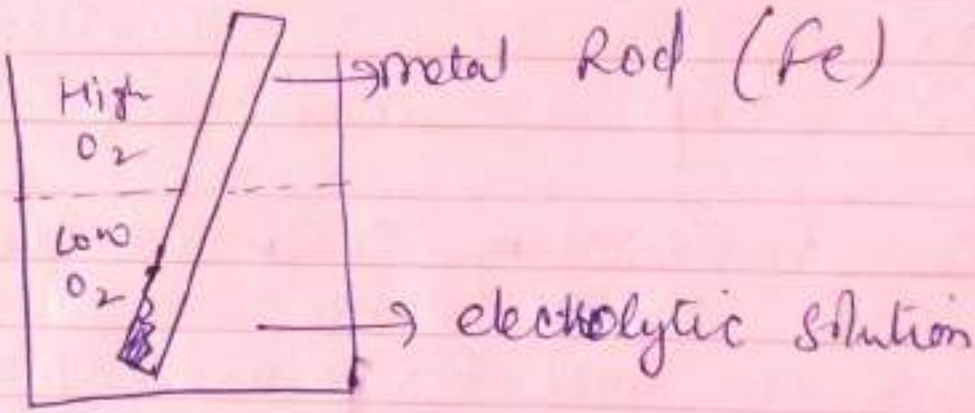


(2) Concentration Cell Corrosion :-

When two different Conc. of the same compound occurs then Generation

of an electrochemical cell occurs.

→ When an electrode made up of metal is dipped in to a solution (electrolyte). Hay portion is immersed in solution and hay is Expesed to air.



The electrode which is under solution will start Corrode Hence absorption of O_2 will take place

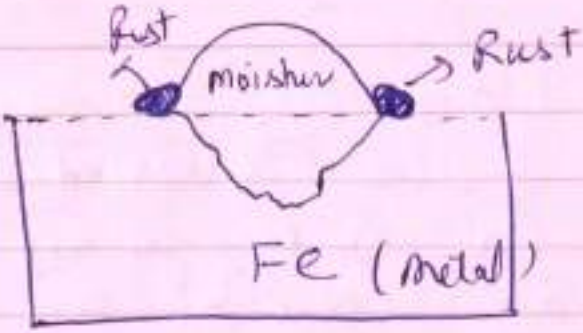
Exp Rusting of Fe

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

At Cathode $O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$

Overall $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
Rust

(3) Pitting Corrosion :- It is a localised corrosion It occurs only in that part where moisture / Acidic / Basic solution is present.



Due to corrosion, A cavity will form at anode. Product of corrosion occurs near cathode. Due to pit generation it is regarded as Pitting Corrosion

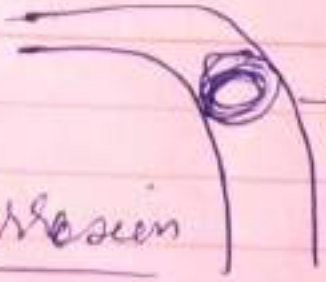
Rusting of Fe (Same Rx)

4) Stress Corrosion :- It is a localised corrosion. During the manufacturing of metals they are under stress due to welding, bending and Hammering. The stressed part act as Concentration cell.

Stress Corrosion of Zn and Cu (Brass)

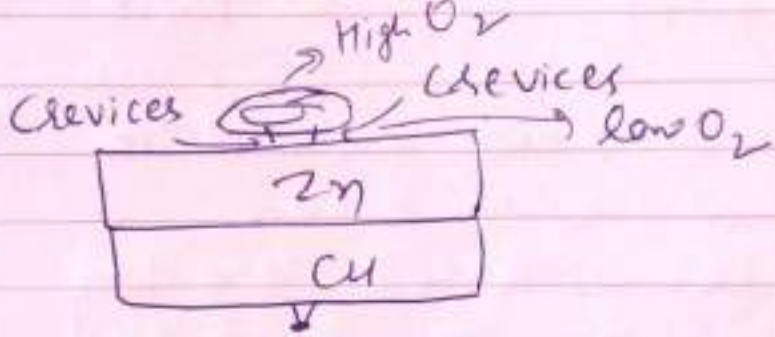
When some traces of ammonia are present the stressed portion of Zn and Cu will form Complexes with ammonia which are the precipitates and loss in metal strength

$Cu(NH_3)_4$ $Zn(NH_3)_4$



Stress Corrosion

5) Crevice Corrosion → It is also a localised corrosion. It occures in the crevices area. In the crevices (small opening) concentration cell occurs.



In crevices any moisture drop can retain and leads to absorption of O_2 as Zn metal loose its electrons.

(Rusting of Fe) Same exp.

Protective Methods

Corrosion can be controlled by various methods.

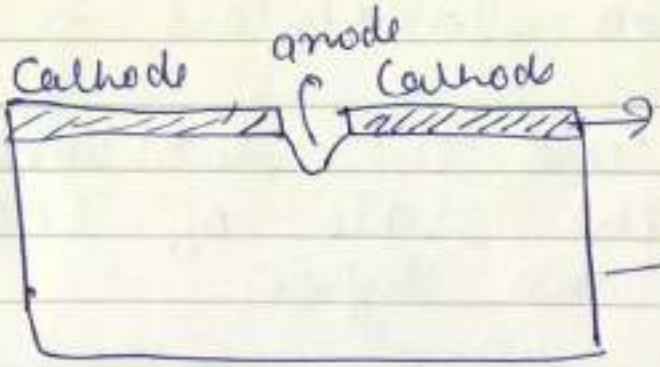
① Modifying the corrosive env. → By modifying the corrosive env. we can control corrosion
→ If there is acidic condition then neutralise it with Base
→ Same for Basic condition
→ moisture can be absorbed by increasing the temp.

② Metallic Coating → It is the most useful methode to save metal from corrosion.
→ One metal is coated over the other metal

→ One will act as Anode Second will act Cathode

Two types of metallic coating

① Cathodic coating → A metal which is having more reduction potential is coated over the Base metal which is to be protective.

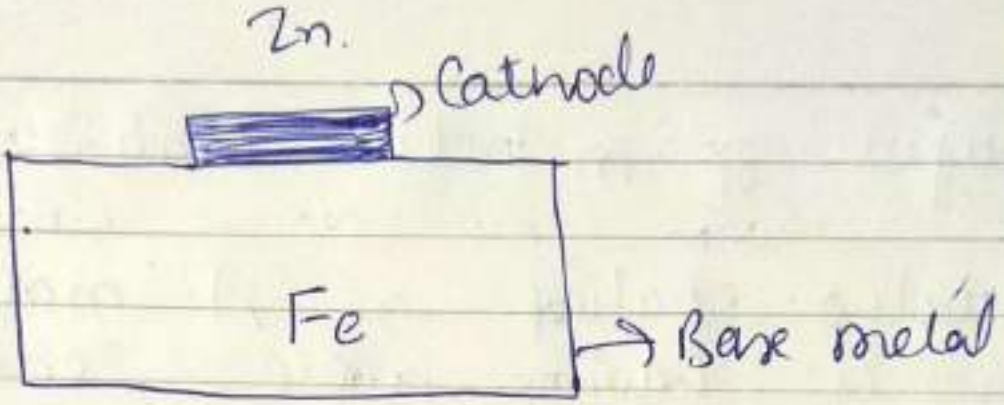


for exp. Coating of Cu over Zn.

Coating of Sn over Fe (Tinning)

② Anodic coating → Coating of metal having low reduction potential over the Base metal (High Reduction potential)

for exp Zn over Fe (Galvanization / Sheradizing)



(3) Corrosion Inhibitors :-

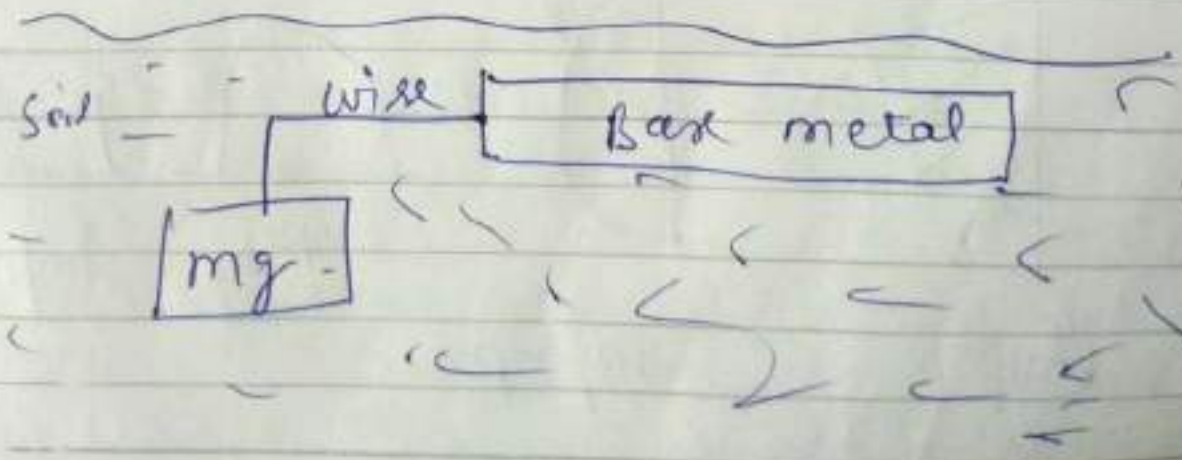
Inhibitors are the substances which inhibits the rate of corrosion.
It is of two types

(1) Cathodic Inhibitors :- acidic and Basic solution will corrode the metal.
At cathode diffusion of H^+ can be controlled towards Right side by using solutions like amine and soap.
O_2 can be absorbed from water by using Sodium Sulphite.

(2) Anodic Inhibitors :- In case of anode metal ions are produced and they will form / Complexes with sulphates and nitrates

(4) sacrificial Protection :- In this method one of the metal will sacrifice itself for the sake of other metal.

In order to protect the metal pipes under soil, metal (Sacrificial) will use to protect it



Mg metal is reactive metal used to sacrifice its life for the protection of Fe. In accordance with the galvanic series.

Mg is placed above Fe.

We have normally observed Mg blocks are attached to the ship to protect it from corrosion. After some time they get disappeared.

(3) Proper Design of metals

→ metal & design should be proper
→ Do not have crevices