

BATTERIES AND CORROSION

Batteries

1) Primary & Lithium

2) secondary Lithium Ion

⇒ Reserve battery Zn-air

⇒ Fuel cells - Methanol-oxygen fuel cell

- solid oxide fuel cell SOFC.

⇒ Batteries is a device which convert chemical energy into electrical energy.

⇒ It has the capacity to store chemical energy which is later converted into electrical energy.

⇒ Battery is an arrangement of several cells connected in series which act as a source of current.

⇒ It is a type of electrochemical cell which consists of anode (oxidation) cathode (reduction) & an electrolyte, the sum of oxidation half reaction at anode & reduction half reaction at cathode give rise to redox reaction. (chemical energy)

⇒ Based on the type of redox reaction batteries are classified into two types.

1. Primary Batteries (1): -

* These are the batteries which are irreversible (not reversed) in which the redox reaction takes place only in one direction. Therefore once the redox reaction is complete the cell will stop working, which is called as "Dead Battery".

Primary Batteries cannot be recharged or reused again.

Eg:- Lithium cells.

2. Secondary Battery:-

⇒ These are the batteries which are reversible in which both the redox reaction takes place in both the directions.

⇒ Therefore the cell can be recharged & reused again.

Eg:- Lithium ion cells

⇒ Reverse Batteries:- In reverse batteries which has

It is a type of primary batteries which has the capacity to store large amount of electrical energy.

Eg:- zinc air battery → redox reaction

⇒ Fuel cells:- These are the cells which convert chemical energy into electrical energy but the materials acting as anode, cathode & electrolyte are supplied to the cell in the form of fuels.

So that chemical reaction takes place in the cell & get converted into electrical energy as well as an eco-friendly product is formed in the form of water.

Eg:- Methanol Oxygen fuel cell (SOFC)

Solid oxide fuel cell (SOFC)

Primary Battery :- Division of Lithium cells :-

Lithium primary battery, Lithium always act as anode.

* In primary battery, this is due to the lighter weight of lithium.

* It is classified into three types:-

1) Liquid cathode lithium cell.

2) Solid cathode lithium cell.

3) Solid electrolyte lithium cell.

1) LIQUID CATHODE LITHIUM CELL:-

The cell consists of liquid cathode: $SOCl_2$ & the anode material is made up of lithium in presence of lithium Aluminium chloride (LiAlCl₄) acting as electrolyte. The redox reaction can be written as

Anode - Lithium

Cathode - $SOCl_2$

Electrolyte - $LiAlCl_4$

Anode/Oxidation:-

$4Li \rightarrow 4Li^{+} + 4e^{-}$

Cathode/Reduction:-

$4Li^{+} + 4e^{-} + 3SOCl_2 \rightarrow 4LiCl + 3SO_2 + S$

Redox Reaction:-

$4Li + 3SOCl_2 \rightarrow 4LiCl + 3SO_2 + S$

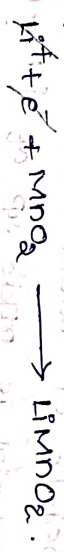
ii) solid cathode lithium cell
 It consists of MnO₂ as solid cathode and lithium anode. A mixture of 1,2 dimethoxy ethane & propylene carbonate is used as electrolyte

cathode - MnO₂
 anode - lithium
 Electrolyte - 1,2 dimethoxy ethane & propylene carbonate

Anode / oxidation:-



Cathode / Reduction:-



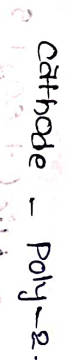
Redox Reaction:-



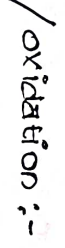
iii) solid electrolyte lithium cell :-
 It consists of lithium acting as anode & PVP as cathode in presence of iodine (I₂) where LiI - lithium iodide is used as solid electrolyte.

Anode - Li
 Cathode - Poly-2-vinylpyridine - PVP/I₂
 Electrolyte - LiI

Anode / oxidation:-



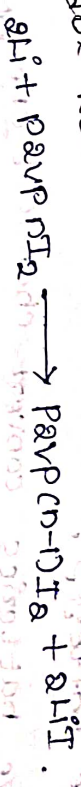
Cathode / reduction:-



Cathode / reduction:-



Redox reaction:-



* Secondary Battery
 Lithium ion cell :-

* In secondary battery lithium ion is used for the generation of electric current. The electrical energy depends on the movement of Li⁺ ion from anode to cathode as well as from cathode to anode.

* The cell consists of several layers of carbon graphite acting as anode & several layers of lithium metal oxide, LiCoO₂ acting as cathode.

Eg:- lithium cobalt oxide acting as cathode.

* The anode & cathode is separated by an organic solvent consisting of polymer gel.

Anode = layers of carbon graphite
 cathode = layers of lithium oxide LiCoO₂

Anode :-



Cathode :-



Reserve Batteries :-

Reverse batteries convert chemical energy to electrical energy which have a greater capacity to store the energy.

Eg:- zinc Air Battery = Zn + air

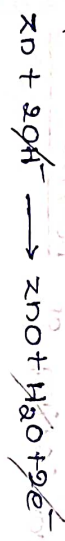
The battery consists of zinc dust (an) zinc granules (or) zinc powder acting as anode & oxygen (or) air act as cathode. Both the electrodes are separated by KOH - Potassium Hydroxide as electrolyte.

Anode - Zn dust / granules

Cathode - Air / O_2

Electrolyte - KOH

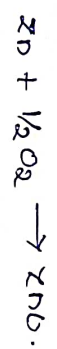
Anode / Oxidation :-



Cathode / Reduction :-



Redox Reaction :-



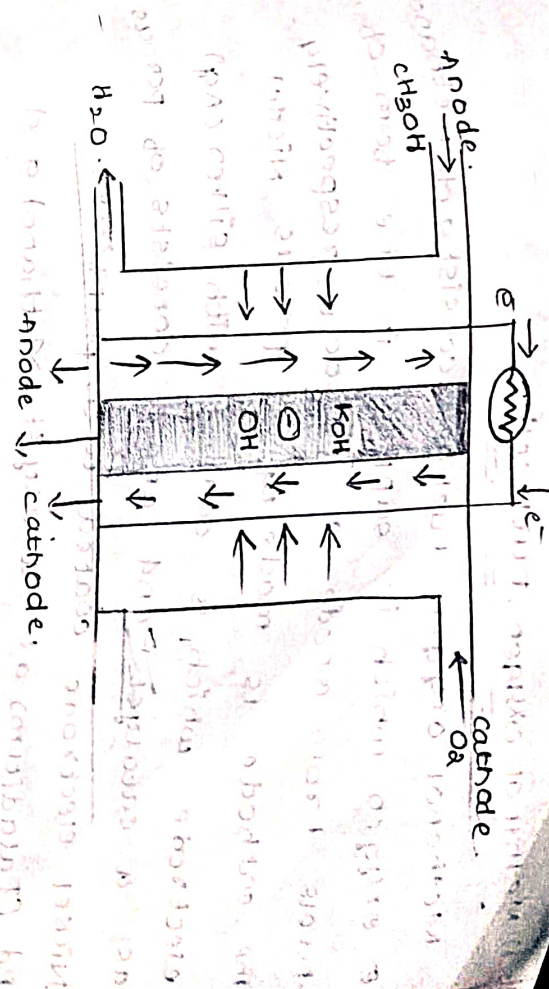
Fuel cells

Eg:- Methanol Oxygen Fuel cells.

Anode / Oxidation :- $CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$

Cathode / Reduction :- $\frac{3}{2}O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$

Redox Reaction :- $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$



Solid Oxide Fuel Cells - SOFC

Anode = H_2

Cathode = O_2

Electrolyte = oxide material.

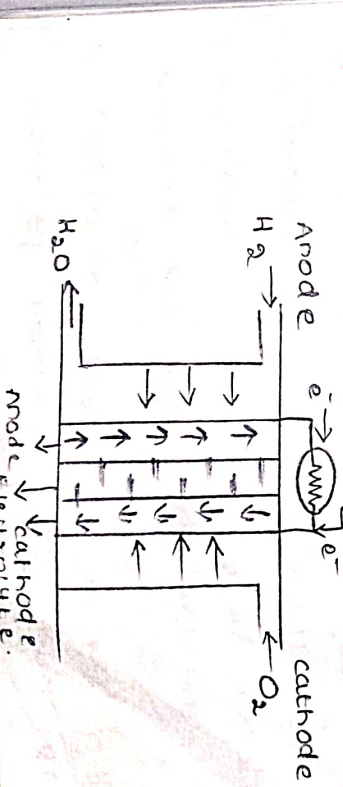
Anode / Oxidation :-



Cathode Oxidation :-



Redox Reaction :-



1) Methanol oxygen Fuel cell

Methanol oxygen fuel cell consists of methanol & oxygen which is supplied in the form of fuels from anode & cathode respectively.

The cathode is made up of porous Nickel electrode which is coated with silver (Ag) as a catalyst and anode consists of porous Nickel electrode coated with platinum or Pd (Paladium) as catalyst. Methanol and oxygen undergoes reaction in the cell producing electricity and an eco-friendly product like water.

Applications & Advantages of SOFC

1. SOFC have many applications & advantages due to the electrolyte being solid oxide material.
2. The electrolyte can withstand high operating temperatures.
3. The rate of corrosion is minimum due to the solid oxide electrolyte.
4. It has the capacity to extend the battery life with minimum cost.
5. The efficiency of electricity generated is high with negligible pollution.

Description :-

SOFC converts chemical energy to electrical energy directly by oxidation of fuels, consisting of anode, cathode & electrolyte. The electrolyte is a solid oxide material which has the high capacity to bear high temperatures. It separates the anode through which hydrogen is passed & cathode through which oxygen is passed. Thus hydrogen flows through anode & oxygen through cathode making the electrons flow resulting in "electric current".

* Applications & Advantages of Lithium Ion batteries for electrical vehicles.

1. Lithium ion batteries possess high specific capacity, prolonged life, cycle good.

mechanical stability at all operating conditions.

2. They possess physico chemical properties, which is the key factor for its storage applications.

3. The electrode materials are environmentally friendly which possess high performance for electrical vehicles.

4. They are used in plug-in in fuel battery electric vehicles.

5. The technology of the batteries is most suitable for electric vehicles due to high energy output.

6. They are used in consumer electronics like mobiles, laptops, computers, digital cameras and video game players.

7. They possess high energy performance, longer life cycle and high potential to enhance energy density.

8. Advantages or applications of Methanol oxygen fuel cell :-

* Methanol oxygen fuel cell are highly stable at all operating conditions

* It is easy to transport as they are used for portable applications

* Due to high hydrogen concentration of Methanol the fuel cell doesn't require complex steam reforming operation

* It is used as an excellent fuel cell due to its high safety to aquatic plants & animals

* It ~~poses~~ poses less fire risks because Methanol have low flammability limit

Corrosion

Introduction:-

Corrosion refers to the destruction of the metal due to chemical or electrochemical reaction with the environment resulting in loss of metallic material.

In general metals are extracted from ores which are obtained from earth's crust. Ores occur in nature in stable form & during the metal extraction process, it is subjected to high temperature, heat & energy. Therefore the metal which is obtained from ores are highly unstable & thus have greater tendency to revert back to nature in stable form.

Theories of corrosion :-

- 1) Acid attack theory.
- 2) Chemical attack theory.
- 3) Electro chemical attack theory.

Chemical Attack theory (or) Chemical

Corrosion (or) Dry Corrosion :-
When the metal reacts with the available chemicals present in the environment it is

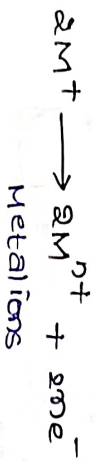
called chemical corrosion.

It is also called as dry corrosion. As the metal reacts with dry gases present in the environment to form metal oxide as the corrosion product which gets deposited on the surface of the parent metal.

Based on the metal oxide layer, corrosion can be prevented & the theory of chemical corrosion can be discussed by the following points.

- a) oxidation corrosion
- b) oxidantless corrosion by gases.
- c) corrosion by liquid metals.
- d) oxidation corrosion :-

In this process the metal undergoes oxidation forming metal ions by loss of electrons



The electrons combine with oxygen forming oxide anions



The metal ions & oxide anions combine to form metal oxide layer as thick or thin film as the corrosion product which gets deposited on the surface of the parent metal.

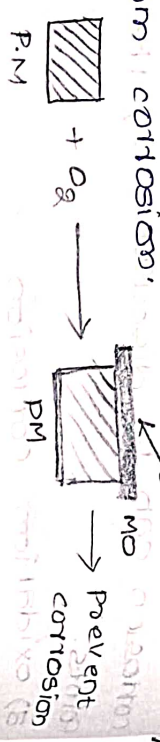
Therefore



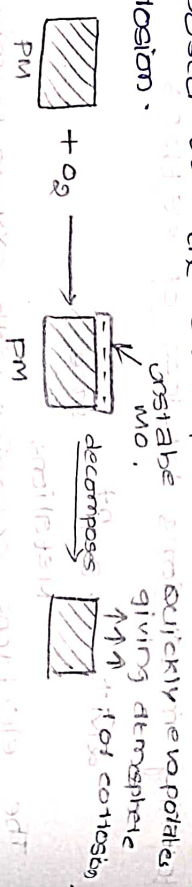
Based on the nature of metal oxide layer corrosion can be divided into two types:

- (i) stable metal oxide :-
- (ii) unstable metal oxide :-

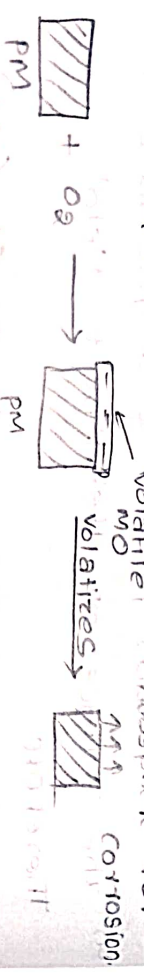
(i) stable metal oxide :-
 It is tightly or densely formed on the parent metal surface & it is strongly formed & tightly held to the metal surface. So that, it acts as a protective barrier & prevents the metal from corrosion.



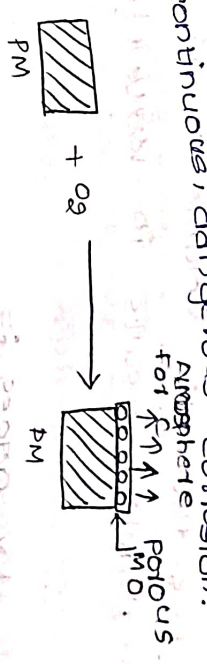
(ii) unstable metal oxide :-
 It is very thin layer which is loosely held to the parent surface & it quickly get deposited leaving the metal surface to get exposed to the atmosphere for further corrosion.



(iii) volatile metal oxide :-
 When a metal reacts with volatile materials present in the atmosphere then it forms volatile metal oxide layer which get volatilised, leaving the metal surface to get exposed to the atmosphere for further corrosion.



(iv) porous metal oxide :-
 Porous metal oxide layer consists of cracks & pores through which the metal surface is continuously exposed to the atmosphere resulting in continuous, dangerous corrosion.



- * Piling Bedworth Rule :-
- * to calculate the volume of MO layer from piling Bedworth Rule.
- * Piling Bedworth rule states that the resistance of the metal (R) depends on molar volume ratio of the metal oxide formed on the parent metal.
- * It can be represented as

$$R \propto \frac{M}{D} \frac{m}{d} \quad (M.P)$$

$$R \propto \frac{M}{D} \times \frac{d}{m}$$

where
 M = molecular weight of metal oxide.
 m = atomic weight of the metal.
 D & d = Density of metal oxide & parent metal respectively.
 When $R > 1$, the volume of metal oxide formed is greater than the volume of parent metal.

in such condition, the metal oxide formed act as a protecting covering & prevents the parent metal from corrosion.

When R₂O, the volume of metal oxide formed is less than the volume of the parent metal which results in water & further corrosion.

b) corrosion by gases :-

When the metal react with the gases like H₂S it forms metal sulphide & liberate hydrogen gas.



When Excess of hydrogen gas get accumulated in the metal it develops pressure resulting in "cracks & blisters" on the metal surface leading to a corrosion condition called as "hydrogen embrittlement".

When atomic hydrogen combine with carbon present in steel, then it forms methane (CH₄) gas, which creates excess pressure causing "cracks & blisters" on the metal surface leading to a corrosion called as "decarburization".

c) corrosion by liquid metals :- liquid metals like mercury (Hg) reacts with metals resulting in the formation of

"always (or) amalgams". This deactivates the metal surface causing corrosion & in some cases. It the concentration of alloy is high then it makes the metal-metal bonds weaker causing damage to the metal.

→ Electro chemical Attack Theory (ECAT)
Electro chemical corrosion / wet corrosion :-
⇒ corrosion in presence of wet medium / environment is called wet corrosion.

⇒ It is also called as electro chemical corrosion due to the formation of cathode & anode regions.

⇒ According to electrochemical theory, wet corrosion is a two step process.

⇒ The metal undergoes Electrochemical corrosion, when it is placed in a wet medium when a metal piece is in contact with a liquid medium, then a part of the metal undergoes oxidation losing electrons as well as metal ions. These metal ions are held near the metal acting as a tiny galvanic cell forming the anode region.

The other parts of the metal gains the electrons, lost by anode & it forms the corrosion product & thus the metal part act as cathode gaining electrons. Thus, in electrochemical corrosion a part of the metal act as anode & another part of the metal ions which are formed anode the metal undergoes liquid medium undergo dissolution in the liquid medium due to the smaller grain size of the metal from undergoing corrosion. Therefore the anode part of the metal undergoes corrosion.

Factors responsible for the formation of anode & cathode regions :- (cont)

Types of corrosion :-

In wet corrosion when metal is placed in the liquid medium there is a formation of cathode & anode regions. The various factors responsible for the formation of cathode & anode regions are.

- 1) Presence of impurities.
- 2) Difference in oxygen concentration.
- 3) Cracks on the surface film.

(4) Presence of impurities :-

Reactions involved in Electrochemical Corrosion

At Anode :- Anode undergoes oxidation losing electrons & metal ions

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

At cathode :- The electrons, lost by anode is gained by cathode & two possible reactions may occur at cathode.

1) Evolution of Hydrogen :-

$$2H^{+} + 2e^{-} \rightarrow H_2$$

Therefore,

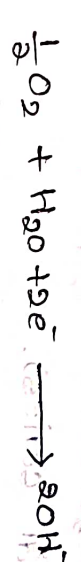
Redox reaction :-

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (\text{Anode})$$

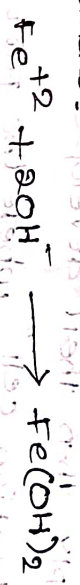
$$2H^{+} + 2e^{-} \rightarrow H_2 \quad (\text{Cathode})$$

$$Fe + 2H^{+} \rightarrow Fe^{2+} + H_2 \quad (\text{Redox})$$

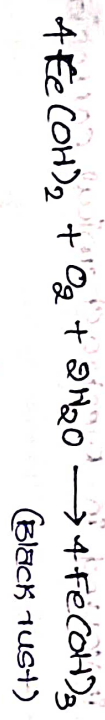
2) Absorption of Oxygen :- The cathode gains electrons & absorb oxygen forming $2OH^{-}$ ions.



$2OH^{-}$ ions formed combine with Fe^{2+} ions, formed at anode forming $Fe(OH)_2$ (Ferrous Hydroxide).



In presence of excess oxygen supply Ferric Hydroxide is converted into the rust of Ferric Hydroxide.



When the concentration of oxygen is less, then Fe_3O_4 - magnetite (Yellow rust) is formed.

(1) Presence of impurities :- 1
 When two dissimilar metals are in electrical contact then the metal having higher oxidation potential will have greater tendency to lose electrons undergoing oxidation & it acts as anode. which undergoes corrosion.

The metal having lower oxidation potential act as cathode forming the corrosion product such a type of corrosion which occurs due to difference in oxidation potential. between the metals is called differential metal corrosion.

(ii) Galvanic corrosion.
 When zinc & copper are connected in series then zinc having higher oxidation potential act as anode undergoing corrosion. (Electro chemical series).

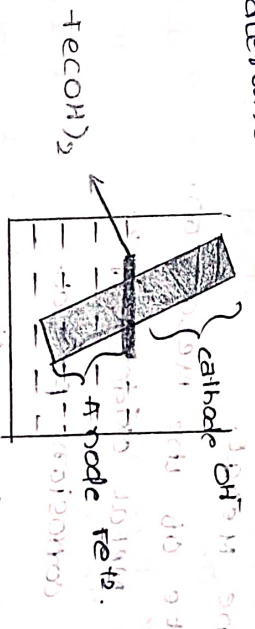
(2) Difference in oxygen concentration :-
 When the metal surface is unevenly exposed to oxygen supply then they develops an "oxygen concentration cell" where the part of the metal which is well exposed to oxygen supply, it act as cathode & the parts of the

metal which is not exposed (or) less exposed to oxygen supply then it act as anode, undergoing corrosion. Such a type of corrosion which occurs due to the formation of oxygen concentration cell it is called as differential corrosion.

Partial line corrosion :-

eg:- water line corrosion :-
 When a metal is partially submerged in water then the part of the metal which is well above the "waterline" is exposed to sufficient oxygen supply & thus it act as cathode whereas the part of the metal which is submerged in water have less oxygen supply.

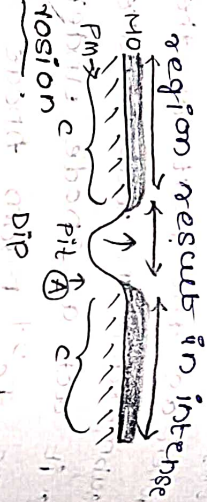
It act as anode undergoing corrosion. There fore Fe^{2+} form anode & OH^- from cathode combine & form the waterline called as "waterline corrosion".



Cracks on the surface film :-

When porous metal oxide layer is formed having cracks or holes on the metal surface it leads to intense corrosion. In this process when there is a crack on the metal oxide layer then the

cracked part slowly develops into a pit or dip through which the metal surface is exposed to the atmosphere for corrosion. The cracked part which develops into a pit acts as anode where corrosion takes place. In the pit it is called as 'pitting corrosion'. The cracked part poses a small area acting as anode & the metal parts in which the metal oxide layer is firmly held to the parent surface having larger area act as cathode thus a small anode region & a very large cathode region results in intense dangerous corrosion.



Factors Affecting Corrosion

- 1) Nature of the metal.
- 2) Position of metal in galvanic series.
- 3) relative areas of cathode & anode region.
 - a) purity of the metal.
 - b) Physical state of the metal ion.
 - c) Physical state of the metal oxide layer.
 - d) Nature of corrosion product.
- 4) Nature of corroding medium.
 - a) Effect of Temperature
 - b) Effect of Humidity
 - c) Nature of ions present
 - d) Presence of impurities in atmos.
 - e) Difference in oxygen concentration.

Factors Affecting Corrosion

Nature of the metal :-

- 1) Position of metal in galvanic series :-
(Electrochemical series) :-
The metals which are placed on the top of electrochemical series/galvanic series have higher oxidation potential having greater tendency to undergo oxidation acting as anode which consequently undergoes corrosion.

Therefore the metal placed on the top position of galvanic series undergoes corrosion.

- 2) Relative areas of cathode & anode region :-
When there is a crack on the metal surface the cracked point develops into a pit causing pitting corrosion. which is associated with the small anode region & large cathode region resulting in intense corrosion.

Therefore when the area of anode is smaller having larger cathode region it forms dangerous corrosion.

- 3) Purity of the metal :-
When two dissimilar metals are in electrical contact leading higher electrical contact leading higher the metals then the metal having higher oxidation potential according to electrochemical

series will act as anode that undergoes corrosion.

4) Physical state of the metal ion :- when the grain size of the metal ion is smaller then it readily undergoes dissolution leading to corrosion.

5) Nature of metal oxide layer formed :- when the metal oxide layer formed is porous in nature then the parent metal surface is exposed to atmosphere for continuous corrosion.

6) therefore porous metal oxide layer leads to dangerous corrosion. compared to stable or volatile metal oxide.

7) Solubility of corrosion product :- if the corrosion product formed on cathode is highly soluble then it undergoes dissolution in the wet medium leading to the formation of more corrosion products on cathode.

8) If the corrosion product is insoluble then it act as a protective covering on the metal surface & it prevents further cathode reaction. & it reduces the corrosion.

9) Therefore, if the corrosion products are soluble then corrosion increases further.

B) Nature of Corroding Medium

1) Effect of pH :- when pH is less than 7 (pH < 7) it refers to acidic medium in which corrosion is faster.

2) Effect of temperature :- At higher temperatures the rate of corrosion increases.

3) Effect of Humidity :- The rate of corrosion increases when Humidity (or) moisture increases.

4) Nature of ions present in the atmosphere :- their nature of metal oxide formed depends on the nature of metal ions present in the atmosphere. i.e. if the metal is reacting with stable ions present in the atmosphere then the metal will form stable metal oxide layer which prevents corrosion further.

5) If the metal is reacting with unstable or volatile materials present in the atmosphere then it leads to the formation of unstable (or) volatile metal oxide layer which enhance corrosion.

6) Presence of impurities in the atmosphere :- when the metal is reacting with the impurities like dry gases, H_2S , moisture & other pollutants then the metal undergoes corrosion.

6) Difference in oxygen concentration :-

When the metal surface is unevenly exposed to oxygen supply then their develops an "oxygen concentration cell" where the part of the metal which is well exposed to oxygen supply, it act as cathode & the parts of the metal which is not exposed cor less exposed to oxygen supply then it is act as anode, undergoing corrosion.

⇒ Corrosion control methods :-
corrosion control method refers to infinite the corrosion rather than preventing the corrosion completely.

~~for~~ cathodic protection ~~pro~~ method :-
In this method corrosion is prevented by protecting the anode part of a metal because anode is the one which undergoes corrosion.

The anode part of the metal, is made to behave as cathode. So that, corrosion can be prevented.

- It consists of two methods.
- 1) Sacrificial anodic protection method.
 - 2) Impressed current cathodic protection

1) Sacrificial anode protection method

In this method the anode part of the metal is protected by making the anode to behave as cathode so that corrosive part be prevented.

can be done by connecting the actual anode to a more active metal having higher oxidation potential than actual anode. So that the more active metal act as anode & the actual anode behave as cathode.

The more active metal is connected to actual anode through an external circuit & it undergoes corrosion their by protecting the actual base anode from corrosion. The more active metal which undergoes corrosion is called "sacrificial anode" because it prevents corrosion of anode by getting corroded itself.

eg:- The metal iron acting as anode can be protected by connecting to zinc metal through an external circuit where zinc having higher oxidation potential than iron act as anode & thus zinc undergoes corrosion sacrificially called as sacrificial anode.

In the method when the more active metal gets corroded it is removed & replaced by a fresh metal having higher

Oxidation potential.

Impressed current cathodic potential

In this method impressed current is passed at anode which opposes the anodic current. so that the corrosion reaction occurring at anode is prevented. The impressed current can be passed by a battery which is connected through an external circuit. This method can be applied to the buried pipe lines which are used for big structures for long term operations.

SURFACE COATINGS

1) Hot dipping method

2) Galvanizing (or) Galvanization

3) Finishing Coating of zinc

4) Electroplating Electrolysis

5) Hot dipping method :-

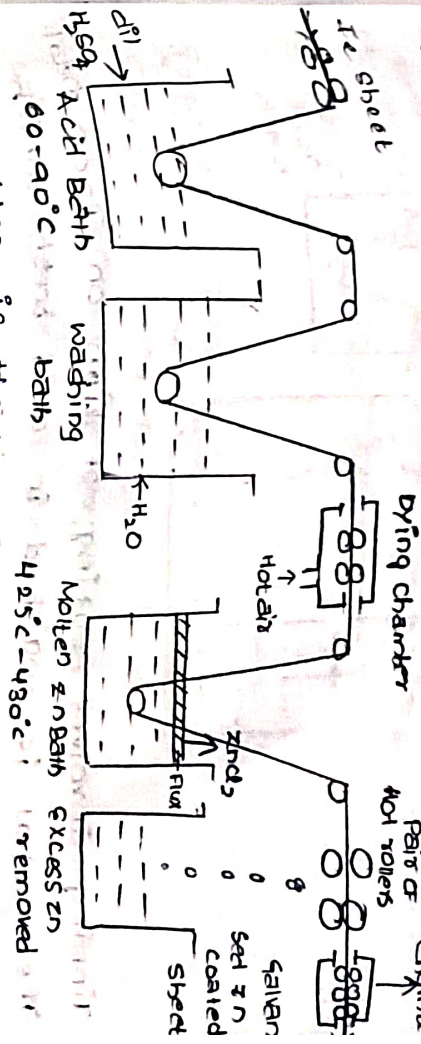
This method involves the coating of base metal which is dipped in the molten hot coating material where coating takes place on the waste metal.

This method is applicable for the base metals having higher melting point which are coated with the coating material having lower melting point. The coating material is kept in a bath in presence of, coating material

& flux which prevents oxidation of the base metal.

this consists of two methods.

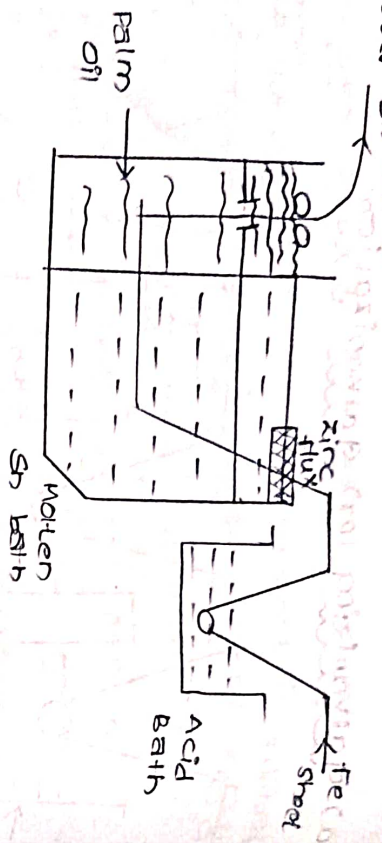
a) Galvanizing (or) Galvanization



Galvanization is the process of coating of iron on

1000. The iron base metal which is to be coated is immersed in acid bath containing H_2SO_4 which removes rust & scales then it is washed in washing bath & dried in drying chamber in presence of hot air then it is immersed in molten zinc material kept in a bath maintain that $425^\circ C - 430^\circ C$ in presence of flux which prevents oxide formation. Thus, coating of zinc on iron sheet takes place, which is further passed in between a pair of hot rollers, which removes excess zinc coating, then the iron sheet is finally rolled in an annealing chamber to produce zinc coated galvanized sheet.

b) Tinning Sn coated sheet



Tinning involves coating of tin on iron metal. The metal is washed in acid bath, which removes rust & it is dried & then dipped in molten tin tank where coating of tin takes place. The coating is further made smooth & polished by passing the tin coated sheet in between the pair of rollers through palm oil to produce tin coated iron sheet.

2) Electroplating :-

It involves the coating of base metal by a process of electrolysis. The base metal which is to be coated is connected as cathode & a graphite rod is connected as anode. The coating material like Nickel, Chromium, Silver, salts are taken as electrolyte.

When current is passed the cations present in the electrolyte as coating material move towards the base material acting as cathode & thus get deposited on cathode. i.e

Not on Cu ions get coated on the base material taken as cathode. This process of coating the material through electrolysis is called electroplating.

Important questions

- 1) Define Battery & explain its classification with suitable example.
- 2) What is a fuel cell. How it differs from battery.
- 3) Define Recharge battery with example.
- 4) Define Dry & wet corrosion.
- 5) State & explain pilling bed worth rule.
- 6) What is meant is hot dipping method.
- 7) What is electroplating.
- 8) What are primary batteries? Explain Lithium cells in detail.
9. What are secondary batteries? Explain Lithium ion cells & its application.
10. What are reserve batteries? Explain zinc air battery.
11. Explain Methanol oxygen & gold oxide fuel cell (SOFC) with suitable diagram.

5. explain oxidation corrosion in detail.
6. explain the mechanism of electrochemical corrosion with suitable reactions.
7. Describe cathodic protection in detail.
8. Explain the following in detail.
 - a. Galvanic corrosion.
 - b. water line corrosion.
 - c. Pitting corrosion.
 - d. Galvanising
 - e. tinning
 - f. electroplating.