

BATTERIES AND CORROSION

batteries

1) Primary & Lithium

2) Secondary Lithium Ion

⇒ Rechargeable 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) & 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 (Li):

* 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.

Eg:- Lithium cells.

2. Secondary battery:

→ These are the batteries which are reversible in which ~~the~~ redox reaction takes place in both the directions. Therefore, the cell can be discharged & reused again.

Eg:- Lithium ion cells.

→ Reverse batteries are batteries which have it is a type of primary batteries which has the capacity to store large amount of electrical energy.

Eg:- Zinc air battery.

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 cells & solid oxide fuel cells (SOFC).

Primary Battery :-

Lithium cells:-

* It is due to the lighter weight of lithium.

This is classified into three types:-

i) liquid cathode lithium cell.

ii) solid cathode lithium cell.

iii) solid Electrolyte lithium cell.

i) liquid cathode lithium cell:-

The cell consists of liquid cathode, solid anode & the anode material is made up of lithium

in presence of lithium aluminium chloride LiAlCl_4 .

acting as electrolyte. The redox reaction can be written as:-

Anode - Lithium, $\text{Li} \rightarrow \text{Li}^+ + 2e^-$

Cathode - SOCl_2 .

Electrolyte - LiAlCl_4 .

Anode/Oxidation:-



Cathode/Reduction:-



Redox reaction:-



Properties of lithium cells:-

Advantages & Disadvantages of lithium cells:-

iii) solid cathode lithium cell

It consists of MnO₂ as solid cathode & lithium anode.

Manganese anode + mixture of 1,2 dimethoxy ethane & propylene carbonate is used as electrolyte.

Cathode - MnO₂ + propylene carbonate

Anode - Lithium anode

Electrolyte - 1,2 dimethoxy ethane & Propylene carbonate

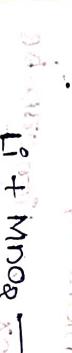
Anode / oxidation:-



Cathode / Reduction:-



Redox Reaction:-



iii) solid electrolyte lithium cell :-

It consists of lithium acting as anode.

PvP ac cathode in presence of iodine (I₂)

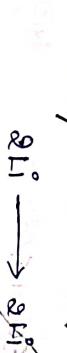
where LiI - lithium iodide is used as solid electrolyte.

Anode - Li

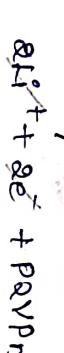
Cathode - Poly-2-vinyl pyridine - PvP/I₂

Electrolyte - LiI.

Anode / oxidation:-



Cathode / reduction:-



* Secondary Battery

Lithium ion cell :-

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 vice

cathode to anode.

* The cell consists of several layers of carbon

graphite acting as anode & several layers of

lithium metal oxide LiCoO₂

e.g:- lithium cobalt oxide acting as cathode

The anode & cathode is separated by an

organic solvent consisting of polymer gelatin

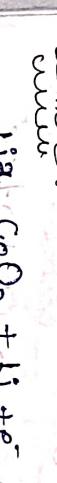
Anode = layers of carbon graphite & metal

cathode = layers of metal oxide LiCoO₂

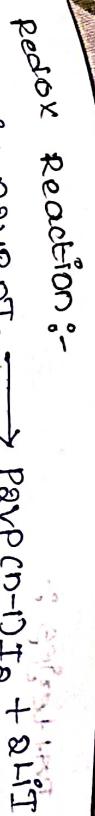
Anode :-



Cathode :-



Overall :-



Reserve Batteries :-

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

Eq:- Zinc Air Battery & Zn-Air

The battery consists of zinc dust (zn) zinc granules (zn) zinc powder acting as anode oxygen (O₂) act as cathode. Both the electrodes are separated by a KOH - Potassium hydroxide as electrode, no insulation from each other.

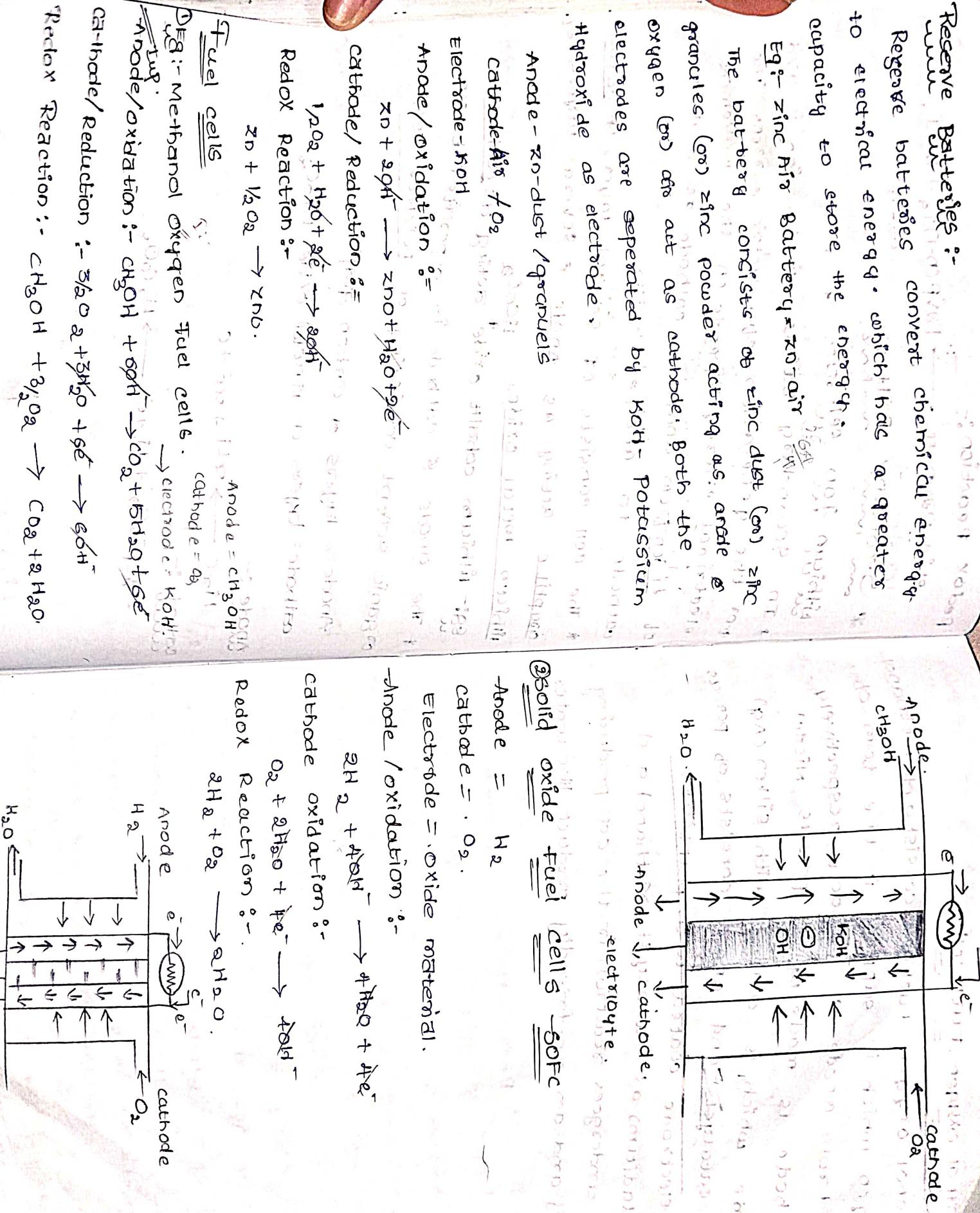
Anode - Zn-dust / granules
cathode - Air + O₂

Electrode - KOH
Anode - Zn + 2OH⁻ → Zn(OH)₄²⁻
cathode / reduction : -

O₂ + 2H₂O + 4e⁻ → 4OH⁻
Redox Reaction :-
Zn + 1/2O₂ → ZnO.

Fuel Cells
Eq:- Methanol Oxidation Fuel Cells :-
Anode / Oxidation :- CH₃OH + 5OH⁻ → CO₂ + 5H₂O + 5e⁻

Cathode / Reduction :- 3/2O₂ + 3H₂O + 6e⁻ → 6OH⁻
Redox Reaction :- CH₃OH + 3/2O₂ → CO₂ + 2H₂O



1) Methanol oxygen fuel cell

Methanol oxygen fuel cell consists of methanol 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 undergoes reaction in the cell producing electricity and an eco-friendly product like water.

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

Description:-
SOFC converts chemical energy of fuel directly by oxidation of hydrogen through anode & cathode. The electrolyte is a solid oxide material which has the high capacity to bear high temperatures. It separates the anode through which oxygen is passed & cathode through which hydrogen flows through anode. This hydrogen flows 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 factors for its storage applications.

3. The electrode materials are environment friendly which posses high performance and electrical vehicles.
4. They are used in plug-in in few 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.

* Advantages or applications of Methanol oxygen fuel cell :

1. Methanol oxygen fuel cell are highly stable at all operating conditions.
2. It is easy to transport as they are used for portable applications.
3. 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 possess poses less fire risk because it has low flammability limit.

* It possess poses less fire risk because Methanol have low flammability limit.

CORROSION

22/04/24.

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 earth's crust which are obtained from stable form & occurs 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 there are highly unstable & thus have greater tendency to revert back to nature in stable form.

a) oxidation corrosion

b) (oxidation) 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



Metal ions

The electrons combine with oxygen forming oxide anions



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

Therefore

Metal + oxygen \rightarrow Metal oxide (M.O)

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.

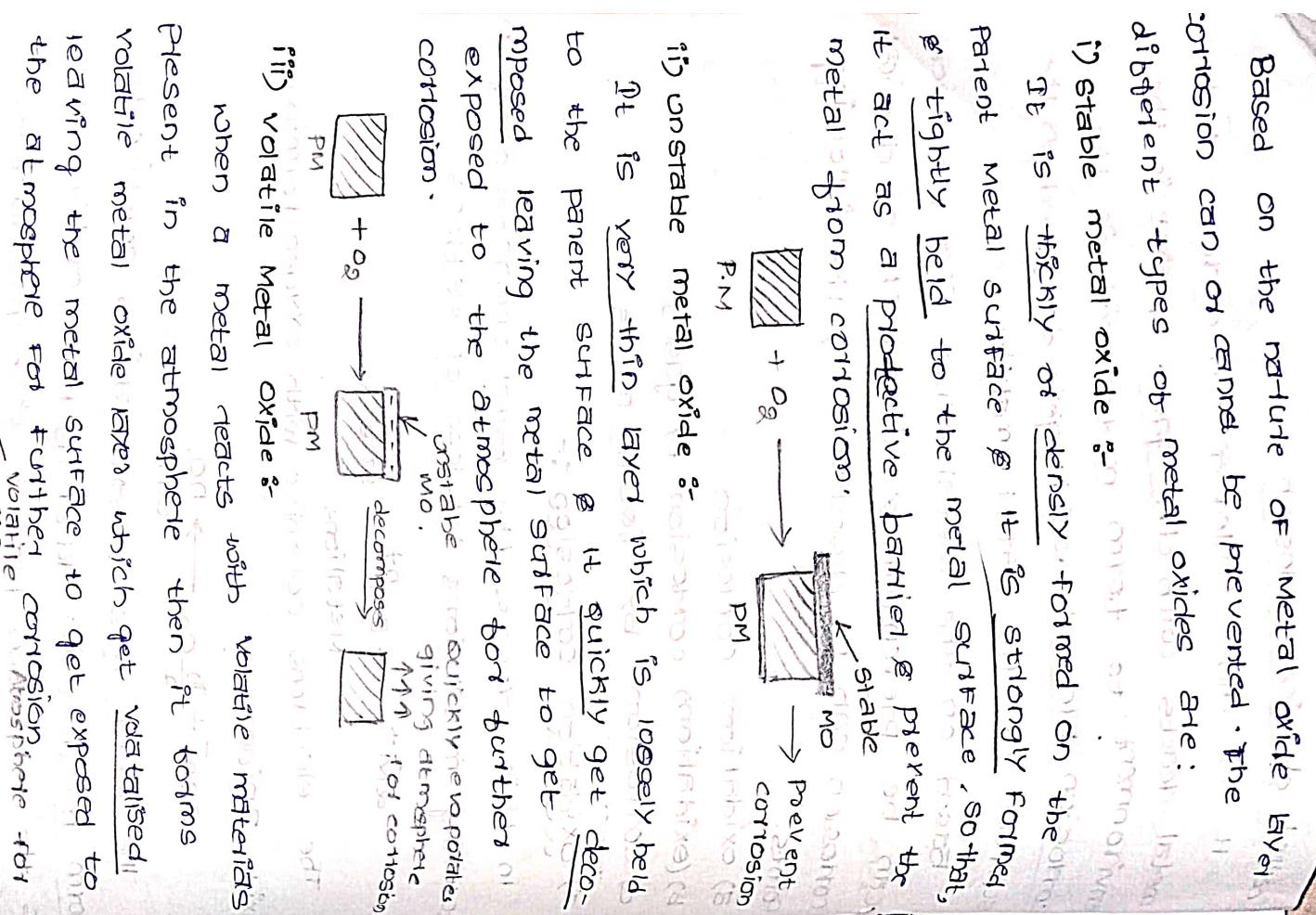
- a) oxidation corrosion
 - b) (oxidation) corrosion by gases.
 - c) corrosion by liquid metals.
 - d) oxidation corrosion :
- In this process the metal undergoes oxidation forming metal ions by loss of electrons
- $$2M \rightarrow 2M^{n+} + n e^-$$
- Metal ions
- The electrons combine with oxygen forming oxide anions
- $$e^- + \frac{1}{2} O_2 \rightarrow O^{2-}$$
- The metal ions & oxide anions combine to form metal oxide layer as thick or thin film at the corrosion product which gets deposited on the surface of the parent metal.

Therefore

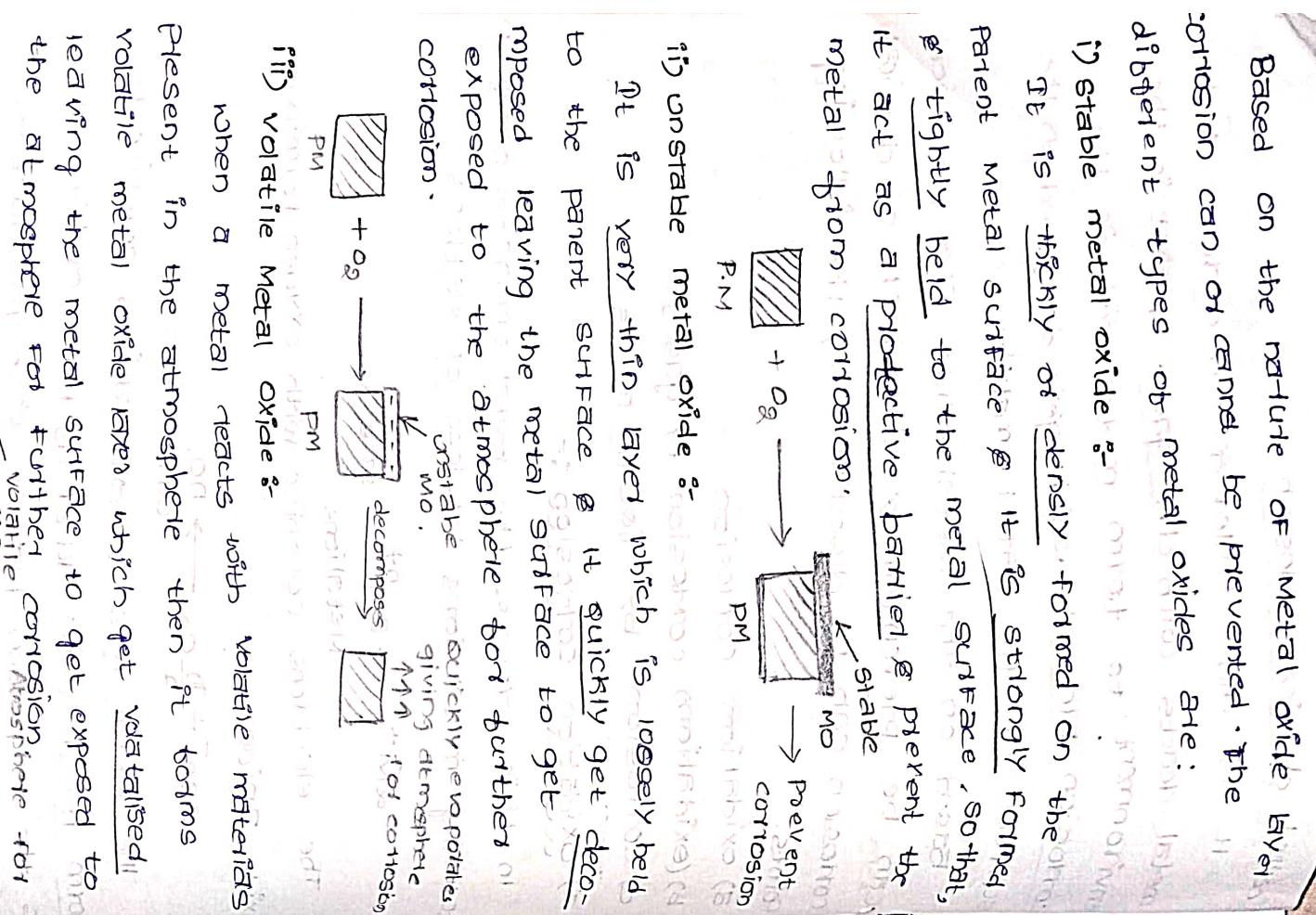
Metal + oxygen \rightarrow Metal oxide (M.O)

Based on the nature of metal oxide layer corrosion cannot be prevented. The different types of metal oxides being:

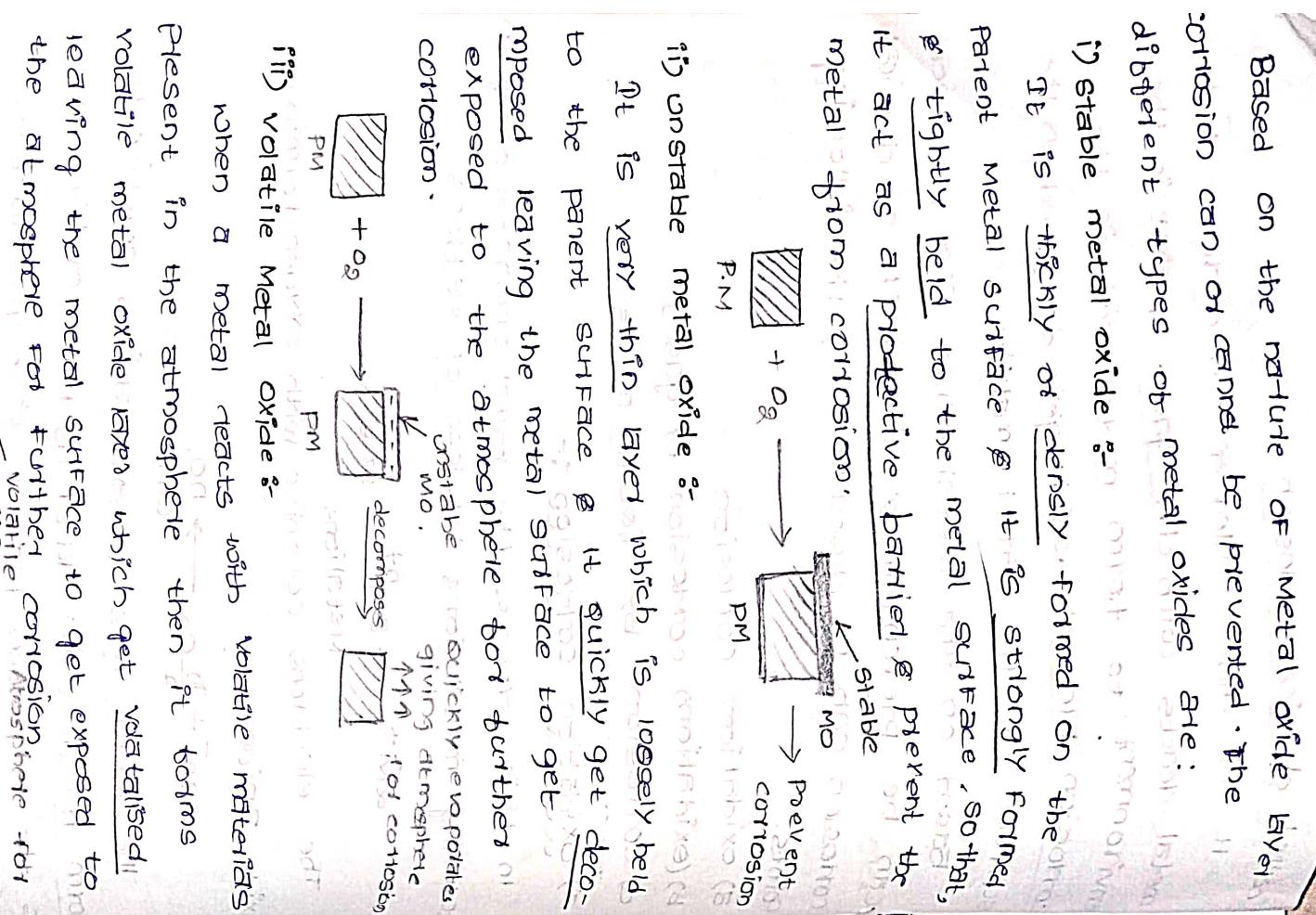
- stable metal oxide & It is thickly or densely formed on the surface.
- parent metal surface & It is strongly formed & tightly held to the metal surface, so that it acts as a protective barrier to prevent the metal from corrosion.
- unstable metal oxide or transient which is loosely held to the parent surface & it quickly gets decomposed leaving the metal surface to get exposed to the atmosphere to further corrosion.



i) unstable metal oxide or transient which is loosely held to the parent surface & it quickly gets decomposed leaving the metal surface to get exposed to the atmosphere to further corrosion.

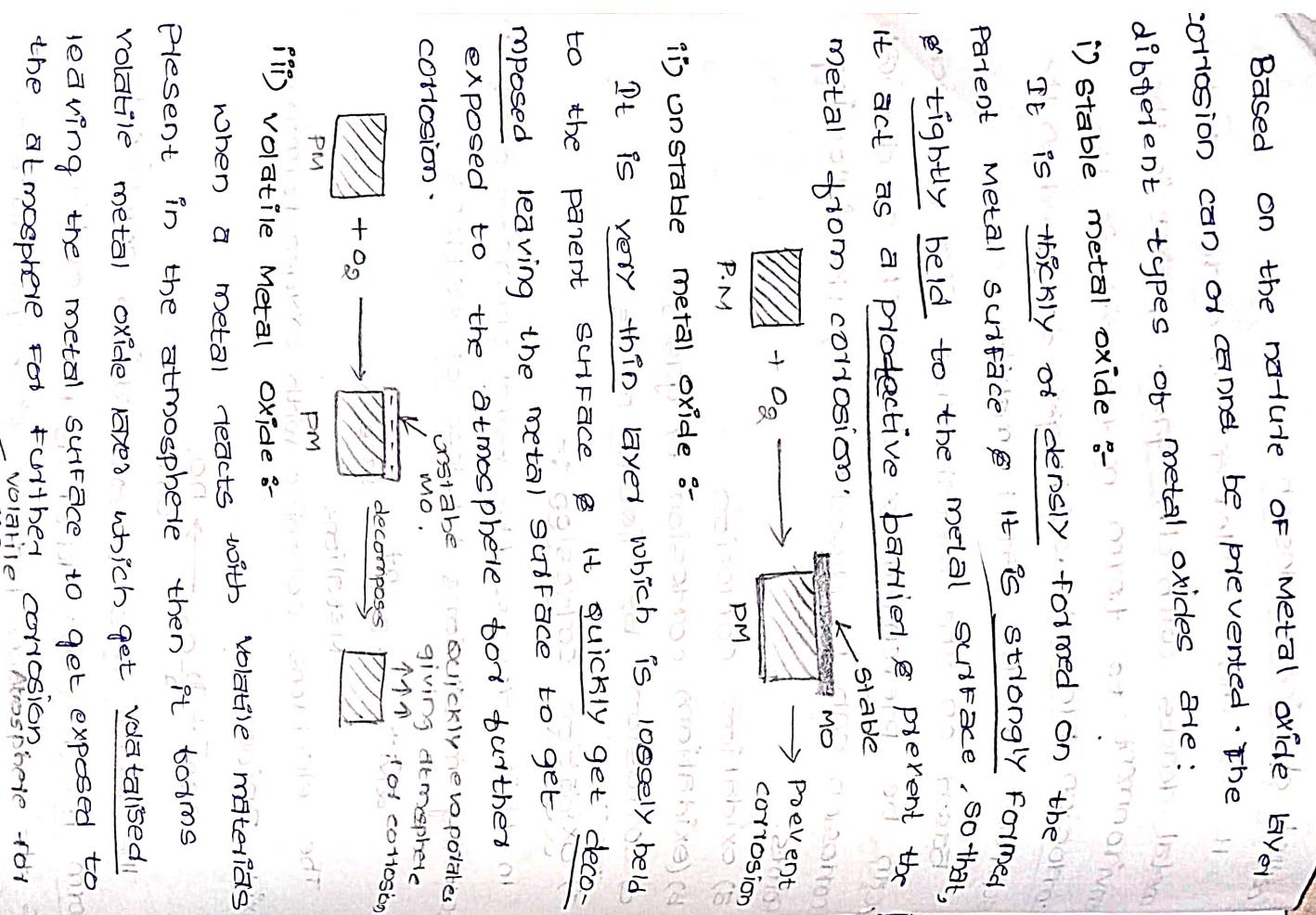


ii) volatile metal oxide & when a metal reacts with volatile materials present in the atmosphere then it forms volatile metal oxide layer which get volatilised leaving the metal surface to get exposed to the atmosphere for further corrosion.



iii) porous metal oxide :-

Porous metal oxide layer consists of cracks or 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 Bed worth Rule.

* Piling Bed worth 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

$$R \propto \frac{M}{D} \quad (\text{M} = \text{Molecular weight of metal oxide}, D = \text{Density of metal oxide})$$

where $M = \text{Molecular weight of metal oxide}$ and $m = \text{atomic weight of metal oxide}$ & D & $d = \text{Density of metal oxide respectively}$.

parent metal formed is greater than the volume

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

When R_d , the volume of metal oxide formed is less than the volume of the parent metal which results in wave further corrosion.

b) corrosion by gases:

When the metal react with the gases like H₂ 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".

Hydrogen reacts with the metal forming the metal hydride.

c) corrosion by liquid metals:
Liquid metals like mercury (Hg) reacts with metals resulting in the formation of "alloys (or) amalgams". This deactivates the metal surface causing corrosion or in some cases. If the concentration of alloy is high then it makes the metal-metal bonds weaker causing damage to the metal.

Electro chemical attack theory (or)
Electro chemical corrosion / wet corrosion
⇒ corrosion in presence of wet medium / environment is called wet corrosion.
⇒ It is also called as electrochemical 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 pair of us never gains the
hy and e it to me.

electrons, loss of thus the metal, the corrosion products being electrons.

part act as cathodes during chemical corrosion a

thus, in electric cells the metal act as anode & another part of the metal act as cathode. At some which are formed

anode the metal ions in the liquid medium undergo dissolution.

due to the smaller anode area, therefore the anode part of the meter undergoes

Factors responsible for the formation of anode & cathode regions are as follows :-

In wet corrosion when metal is placed

In the liquid medium there is a normal
gradient of temperature regions. The various

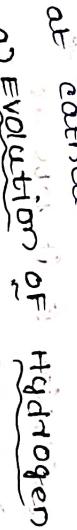
ob cathode & anode regions are.
factors responsible for the formation of
cathode & anode regions are.

(ii) presence of impurities.

3) cracks on the surface floor

(*Presen^{ce}* *is* *impossibl^e*) *and* *not* *nothing*)

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



Absorption of oxygen:-
The cathode gains electrons.

The cathode gains electrons & oxygen is torn into $\frac{20H^-}{10H_2O}$ ions.

2OH⁻ ions formed combine with Fe²⁺ ions, forming (Fe(OH)₂)²⁻ hydroxide.

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

3 Diccion

卷之三



When the concentration of oxygen is less, then Fe_3O_4 -magnetite (yellow rust) is formed which occurs due to the formation of oxygen concentration cell it is called as differential

(d) Presence of impurities:

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 acts 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.

(e) Galvanic corrosion:

For when zinc & copper are connected in series then zinc having higher oxidation potential act as anode undergoing corrosion

Chemical series:

(g) Difference in oxygen concentration:

When the metal surface is unevenly exposed

to oxygen supply then it acts as anode. "Oxygen concentration cell" where the part of the metal which is well exposed to oxygen supply, it act as cathode

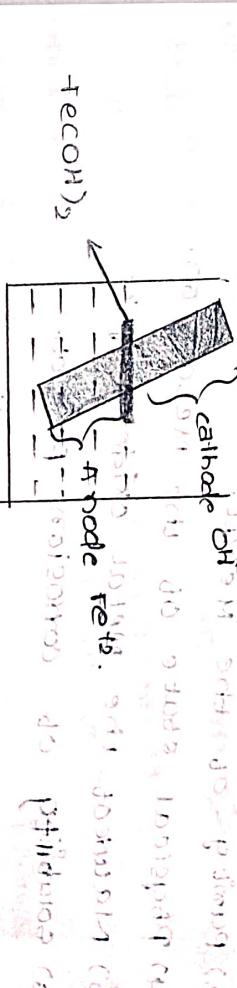
metals which is not exposed less exposed to oxygen supply then it acts as anode. Such a type of corrosion undergoing corrosion which occurs due to the formation of oxygen concentration cell it is called as aeration corrosion.

Water line corrosion:

When a metal is partially submerged water then the part of the metal which is well above the "water line" is exposed to sufficient oxygen supply thus it act as cathode whereas the part not the metal which is more submerged in water have less oxygen supply to act as anode undergoing corrosion. There

it act as anode undergoing corrosion. From cathode to Fe^{2+} from anode $\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe(OH)}_2$ combine to form rust or ions of ferrous

Hydroxide. Along the water line called as "waterline corrosion".



3) 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 intense 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 where corrosion takes place

act as anode

in the pit & it is called as "pitting".

"The cracked part causes a small area

of 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

the metal surface having larger area act as

cathode thus a small anode region is formed

nearby large cathode region result in intense

dangerous corrosion.

Factors Affecting corrosion

A) Nature of the Metal

B) Position of Metal in galvanic series.

C) Position of cathode & anode region

D) Relative areas of cathode & anode

E) Purifying of the metal.

F) Physical state of the metal ion.

G) Nature of the metal oxide layer.

H) Solubility of corrosion product.

I) Nature of corroding Medium (e.g. H₂O)

J) Effect of pH on metal surface

K) Effect of temperature on metal surface

L) Effect of Humidity

M) Nature of ions present in solution

N) Presence of impurities in atmos.

O) Difference in oxygen concentration

FACTORS AFFECTING CORROSION

Induce 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 tip

position of galvanic series undergoes intense

corrosion.

2) Relative areas of cathode & anode :-

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) Pitting other metal :-

When two dissimilar metals are in

electrical contact leading to irregularities of

their metals then the metal having higher

oxidation potential according to electrochemical

Sources will act as anodes that undergoes corrosion.

- (d) Physical state of the metal ion :-
 - when the grain size of the metal is too large then it readily undergoes dissolution leading to corrosion.
 - smaller than it readily undergoes dissolution leading to corrosion.
- (e) Nature of metal oxide layer formed :-
 - 5) Nature of metal oxide layer formed is when the metal oxide layer formed is continuous when the parent metal surface is porous in nature then the pores in atmosphere can expose to oxygen which reacts with the metal surface to form a protective metal oxide layer which is exposed to oxygen which reacts with the metal surface to form a protective metal oxide layer.
 - 6) Therefore porous metal oxide leads to dangerous corrosion compared to unstable or volatile metal oxide.

- (f) Effect of pH :-
 - when pH is less than 4 then it refers to acidic medium in which corrosion is faster.
 - when pH is more than 7 then it refers to basic medium. In basic medium the rate of corrosion increases.
- (g) Effect of temperature :-
 - at higher temperatures the rate of corrosion reaction increases.
- (h) Effect of humidity :-
 - The rate of corrosion increases when humidity (or) moisture increases.
 - 5) Nature of ions present in the atmosphere depends on the nature of metal oxide formed 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 due to which the metal is reacting with unstable volatile materials present in the atmosphere.
 - 6) Volatile materials present in the atmosphere then it leads to the formation of unstable volatile metal oxide layer which enhances the corrosion.
 - 7) 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 there 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 to oxygen supply exposed less exposed undergoing then it is act as anode undergoing corrosion.

→ Corrosion control methods
Corrosion control method refers to inhibit or minimize the corrosion rather than preventing the corrosion completely.
What is cathodic protection method? In this method corrosion is prevented by protecting the anode part of an 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.

i) Sacrificial anodic protection

ii) Impressed current cathodic protection

1) SACRIFICIAL ANODIC PROTECTION

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

This can be done by connecting the actual anode to a more active anode 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 active

anode through an external circuit & it undergoes corrosion. Then 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. But getting anode itself.

e.g. If the metal iron acting as anode can be protected by connecting to zinc metal to have through an external circuit where zinc having higher oxidation potential than iron act as anode & the zinc undergoes corrosion sacrificially called as sacrificial anode.

In this method when the anode gets replaced by a fresh metal having higher

OXIDATION POTENTIAL

2) Impressed current cathodic protection:

In this method impressed current is passed at anode which opposes the anodic current. so that 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 + dip-coat or base

b) Hot dipping method

c) Galvanizing: (or) galvanization

b) Tinning - Coating of tin on iron

d) Electroplating - Coating of zinc on iron

e) Hot dipping method:

This method involves the coating of base metal which is dipped in the molten bath containing zinc.

where coating takes place on the base metal.

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

for flux which prevents oxidation of the base

metal. Anticorrosive bath is also required.

for flux which prevents oxidation of the base

metal. Anticorrosive bath is also required.

o) Galvanizing (or) galvanization

Annealing

Drying chamber

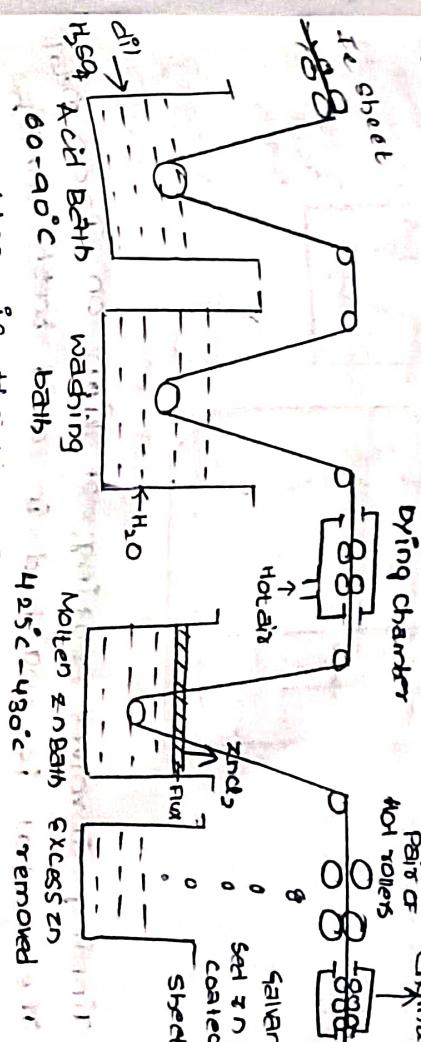
Hot rollers

Sheet

Gallan

Coated

Sheet



Galvanization is the process of coating of zinc on

the iron base metal which is to be coated is immersed in acid bath containing dil. H₂SO₄ 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 maintained at 425°C - 430°C in presence of zinc dusting as 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 coated in a annealing chamber to produce zinc coated galvanized sheet.

This method involves the coating of base metal which is dipped in the molten bath containing zinc.

where coating takes place on the base metal.

This method is applicable for the base metals having higher melting point which are coated with the coating material having lower

melting points. The coating material is kept in a bath in presence of coating material of the base

metal. Anticorrosive bath is also required.

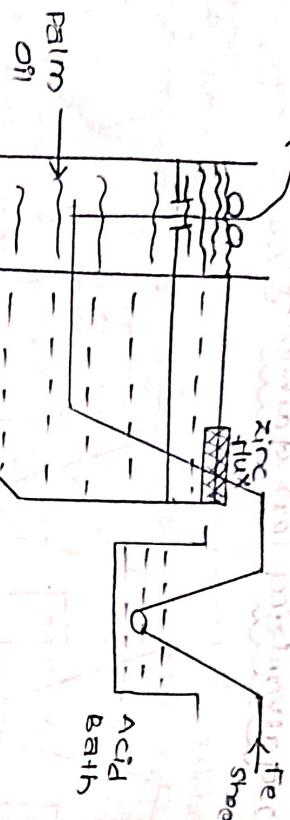
for flux which prevents oxidation of the base

metal. Anticorrosive bath is also required.

for flux which prevents oxidation of the base

metal. Anticorrosive bath is also required.

b) Tinning on 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 smoother by passing the tin coated sheet in between the pair of rollers thorough 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. The coating 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 anion move towards the base material acting as cathode

& thus get deposited on cathode i.e.

Important Questions

- 1) Define battery & explain its classification with suitable example.
- 2) State & Explain Redox rule.
- 3) What is meant by hot dipping method.
- 4) What is Electroplating.

1. What are primary batteries? Explain lithium cells in detail.
2. What are secondary batteries? Explain lithium ion cells & its applications.
3. What are reserve batteries? Explain zinc air battery.
4. Explain Methanol oxygen fuel cell or fuel cell (FC) with suitable diagram

Q) If iron ions get coated on the base material taken as cathode. This process of coating the material through electrolysis is called electroplating.

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.
- Galvanic corrosion.
 - water line corrosion.
 - Pitting corrosion.
 - Galvanising
 - Tinning
 - Electroplating.