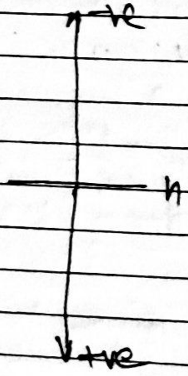
Unit-5

Electrochemistry

Q. Write diff between electrochemical & electrolysis.

Electrochemical	Electrolytic
Chemical energy to electrical energy	Electrical energy to chemical energy
Galvanic cell	
Salt bridge is required.	No salt bridge ~~not~~ required.
Two different solution for anode & cathode	Two electrode in same electrolyte.
Anode (-ve) Cathode (+ve).	Cathode (-ve) Anode (+ve).

* Electrochemical series



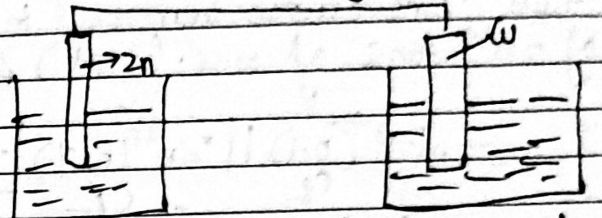
High (oxidation value), oxidizing power, greater reducing agent.

High ~~reducing~~ reduction, reducing power, greater O.A.

Q. Give examples, give the increasing order of their oxidizing power.
X (-2.5V), Y (-1.08)V, Z (1.54)V

Ans Higher oxidizing power - X > Y > Z.

* Construction & working of Galvanic cell



→ Electropotential - The tendency of cation & element to loose or gain e^- is called e^- potential.

Anode (-ve) $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode (+ve) $Cu^{2+} + 2e^- \rightarrow Cu$

$Zn | Zn^{2+} (1M) || Cu^{2+} (2M) | Cu$

Q. Why salt bridge is required?

Ans
- It maintains electrical neutrality conductivity
- Its maintains movement of ions.

Q. Calculate Emf of the cell -

$Zn(s) | Zn^{2+} (0.2M) || Ag^+ (0.002) | Ag$

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

$2Ag^+ + 2e^- \rightarrow 2Ag$

$\Rightarrow Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

$E^\circ cell = 1.54$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{(0.2)}{(0.002)^2}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \times \log \frac{(1/2 \times 10^{-1})}{2/4 \times 10^{-6}}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \left(\frac{1 \times 10^{5}}{2}\right)$$

$= 1.599$

$C_1 > C_2$ always

Q. Calculate Emf of a conc. cell at 25°C consisting of two Zinc electrode immersed in the solution of Zn^{+2} ions of conc. (0.1M) & (0.01)M.

$$Zn | \underset{C_2}{Zn^{2+}(0.1)} || \underset{C_1}{Zn^{2+}(0.01)} | Zn$$

$Zn + Zn^{2+} \rightarrow Zn^{2+} + Zn$

$$E_{cell} = \frac{0.0591}{2} \log \frac{(\cancel{0.01})(0.01)}{(\cancel{0.01})(0.1)}$$

$$E_{cell} = \frac{0.0591}{2} \log \frac{(0.1)}{(0.01)}$$

$$E_{cell} = \frac{0.0591}{2} \log 10 = \frac{0.059}{2}$$

$$E_{cell} = 0.02952$$

Q. Determine the conc. of Cd^{2+} ion in a e$^-$ chemical cell

$$Fe | Fe^{2+}(0.1 M) || Cd^{2+}(x) | Cd$$

Assuming, activity will continue till equal conc. The Emf of the cell = −0.02V at 25°C. E°_{cell} = 0.04V

$Fe + Cd^{2+} \rightarrow Fe^{2+} + Cd$ $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{(x)}{(0.1)}$

$$-0.02 = 0.04 - \frac{0.0591}{2} \log (10x)$$

$$\frac{0.0591}{2} (\log 10x) = 0.04 + 0.02$$

$$\log (10x) = \frac{0.12}{0.0591} = 0.06$$

$$\log (10x) = 0.307$$

$$10x = 2.027$$

$$x = \frac{2.027}{10} = 0.2$$

* **Nernst Equation** –

For a reversible reaction, the free energy & equilibrium constant are related as –

$$M^{n+} + ne \rightleftharpoons M(s)$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[Products]}{[Reactants]} \quad -(1)$$

(Van't Hoff)

For a reversible reaction, the electrical energy is produced at the expenses of free energy.

[$\Delta G = -nFE_{cell}$, $\Delta G^\circ = -nFE^\circ_{cell}$]

now place the value of ΔG & ΔG° in eq(1)

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln \frac{[M]}{[M^{n+}]}$$

Dividing by nF on both sides.

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303 RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

This is nernst equation.

For pure solid –

$$E_{cell} = E^\circ_{cell} - \frac{2.303 RT}{nF} \log \frac{1}{[M^{n+}]}$$

At T = 25°C,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[1]}{[M^{n+}]}$$

Q. What is primary battery? Describe [illegible] -ruction & working of dry cell or Leclanche's [illegible]

Imp Q. what are the secondary batteries describe [illegible] -uction & working of lead-acid battery?

Imp Q. Discuss charging & discharging reactions of lead acid battery.

* **Battery** —

Batteries are storage devices used for storage of chemical energy & its transformation into electrical energy.

Battery/cell

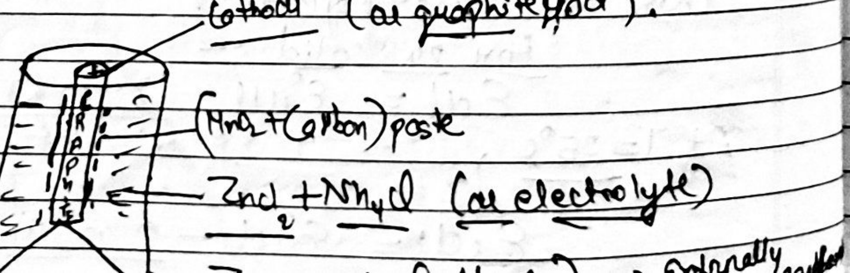
- Primary (Non-chargeable batteries)
- Secondary (Rechargable batteries)
- Reserve battery (Active components in reserve)
- Fuel cell (Byproduct H_2O) (H_2–O_2) fuel

* **Primary Battery** —

The batteries which can be used once only. Primary batteries are a source of energy till chemicals are available. Once chemical becomes exhaust that cell is of no use. The net cell reaction ~~is~~ of these batteries are irreversible.

Example —

1. Dry cell or Leclanche's cell. — (Zn–MnO_2 cell)



Anode : $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode : $2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$

Secondary reactions —

$$2OH^- + 2NH_4Cl \rightarrow 2NH_3\uparrow + 2H_2O + 2Cl^-$$

$$Zn^{+2} + 2NH_3 + 2Cl^- \rightarrow [Zn(NH_3)_2]Cl_2$$

Overall reaction : $Zn + 2MnO_2 + 2NH_4Cl \rightarrow [Zn(NH_3)_2]Cl_2 + Mn_2O_3 + H_2O$

→ NH_3 disturbs the cell reactions, thus Zn^{+2} added.

$E_{cell} = 1.5V$

Cell voltage.

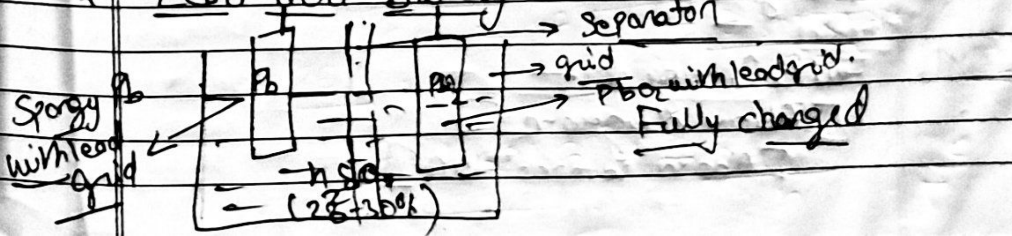
* Advantages —
- Low prices

* Disadvantages —
- Non rechargeable
- Power lost over time
- Issue of disposal.

* Rechargeable cell (Secondary battery) —

These batteries can recharged once discharged hence are known as rechargeable batteries. Net cell reactions are reversible.

* **Lead acid Battery** —



~~During discharging —~~

~~Anode —~~

~~$Pb \rightleftharpoons Pb^{2+} + 2e^-$~~

~~$Pb^{2+} + SO_4^{2-} \rightarrow$~~

In a Lead acid battery following composition is present —

- Spongy lead with lead grid — Anode.
- Cathode — PbO_2 with lead grid
- Electrolyte — (28-30%) H_2SO_4.

The specific gravity at 25°c is 1.2. The setup of a number of cells enclosed in ebonite case. The cell voltage is 1.86-2.15V.

* ~~For~~ General Reaction —

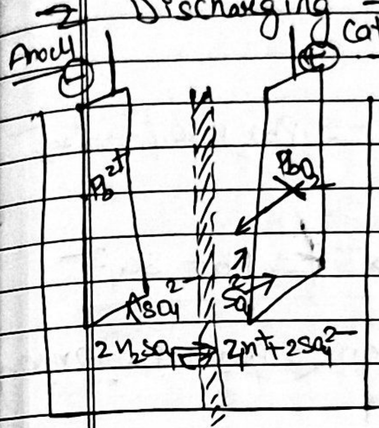
$$Pb + PbO_2 + 2H_2SO_4 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} PbSO_4 + 2H_2O$$

The working of lead acid battery can be explained in four cycle these are known as discharging - charging cycle.

1. Fully Charged.
2. Discharging
3. Fully Discharged
4. Charging

1. Fully Charged —
   [Above diagram]
   [Above composition]

2. Discharging —



During discharging

Anode —

$$Pb \rightleftharpoons Pb^{2+} + 2e^-$$
$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4$$
$$\overline{Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^-}$$

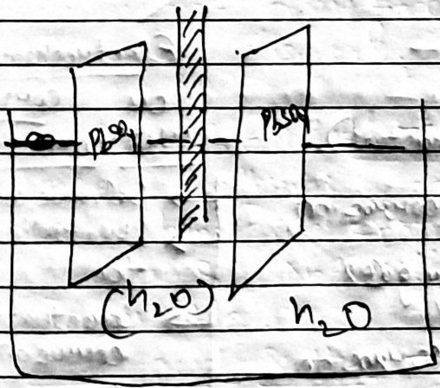
Cathode —

$$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$$
$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4$$
$$\overline{PbO_2 + 4H^+ + 2e^- + SO_4^{-} \rightleftharpoons PbSO_4 + 2H_2O}$$

Net cell reaction —

$$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O.$$

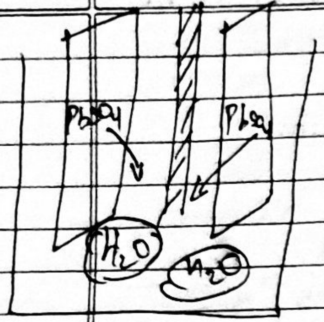
3. Fully Discharged — (No reaction).



4. Charging —

Q1. What is corrosion?

2. Describe ~~two~~ the e⁻ chemical theory of corrosion by suitable examples.
(Reverse)



Cathode:

Pb^{2+}

$PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$

Anode:

$PbSO_4 + 2e^- \rightleftharpoons Pb + SO_4^{2-}$

Net cell reaction – $2PbSO_4 + 2H_2O \rightleftharpoons Pb + PbO_2 + 2H_2SO_4$

* Corrosion –
It is the degradation or deteriotation of metals by surrounding environment through chemical or e⁻ chemical changes.

Corrosion

- dry corrosion (In absence of moisture).
  - Oxidative corrosion
  - Corrosion by gases
  - Liquid-Liquid corrosion
- Electrochemical corrosion or Wet corrosion
  - Galvanic corrosion
  - Waterline corrosion
  - Concentration cell corrosion (Crevice corrosion) (Gasket corrosion)
  - Pitting corrosion
  - Stress corrosion
  - Fatigue corrosion
  - Intergranular corrosion

Examples –

- Oxidative corrosion –

$Mg \rightleftharpoons Mg^{2+} + 2e$

$\frac{1}{2}O_2 + 2e^- \rightleftharpoons O^{2-}$

$Mg + \frac{1}{2}O_2 \rightleftharpoons MgO$

3. Describe the e⁻ chemical theory of corrosion by rusting of iron.

4. Describe the e⁻ chemical theory of corrosion when H_2 get evolved → in absence of O_2 or presence of O_2.

In presence of oxygen, metals form their respective metal oxides, In the form of oxide film or layer. It may be porous or non-porous.

* Corrosion by the gases –
Gases like H_2S, Cl_2 can cause corrosion.

Example – $Fe + H_2S \rightarrow FeS + H_2\uparrow$

$Fe + Cl_2 \rightarrow FeCl_2$

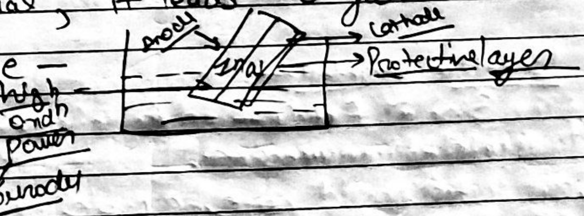
$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$

* Liquid-Liquid Corrosion –
Example – alloys.
When different metals are used and one of them is in liquid form, then it leads to liquid-liquid or liquid-metal corrosion.

* Electrochemical Corrosion (wet corrosion) –

1. Galvanic Corrosion – If two dissimilar metals are in direct contact having difference in their electrode potential, it leads to galvanic corrosion.

Example –



2. Waterline Corrosion –

5. Now can corrosion can be minimized by proper selection and designing of machine.
6. Explain Saacrificial, anodic protection & impressed current / cathodic current.

Q. What are metallic coating explain anodic & cathodic Coating by suitable example.
Q. What are the factors which affect the rate of corrosion.

Imp * Electrochemical Theory of Corrosion –

It takes place when –

(i) When a metal is in contact with moist air or any liquid.

(ii) When two different metals or an alloy is in contact with a solution.

Following conditions must be fulfilled for the formation of an electrochemical cell. –

1. Presence of anode & cathode
2. There must be an electrode potential difference between anode & cathode.
3. Anode & Cathode must be immersed in an electrically conducted medium.
4. There must be an metallic path electrically connecting anode & cathode.

Example – Rusting of Iron.

→ Anodic Reaction –

The metal having higher position in e⁻chemical series behaves like an anode & get oxidised.

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

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

→ Cathodic Reaction –

It depends upon the medium and can be divided into two category –

(i) In absence of oxygen / In acidic medium / When evolution of hydrogen takes place.

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$

Q. What is corrosion? Discuss its classification with suitable examples.
Q. What are corrosion inhibitors.
Q. Explain anodic & cathodic inhibitors

2. In presence of Oxygen / In basic medium or Neutral / Absorption of oxygen.

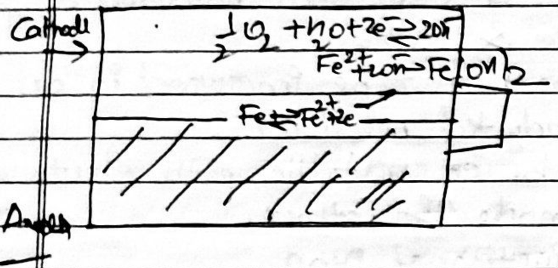
$$\frac{1}{2}O_2 + H_2O + 2e^- \rightleftharpoons 2OH^-$$

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

$$Fe(OH)_2 \xrightarrow{H_2O / O_2} Fe(OH)_3$$

Rust.

$$Fe_2O_3 \cdot nH_2O \leftarrow Fe(OH)_3$$



Q.* Factors Affecting Rate of Corrosion—
1. Metallic factor
2. Environmental factor.

1. Metallic factor—
(i) Size of Anode— inversely related to rate of corrosion.
(ii) Metal should ~~have~~ be noble or less reactive.
(iii) If two different metals are in contact combination, then difference in their electrode potential should be minimum.
Q. (iv) Grone size $\propto \frac{1}{\text{rate of corrosion}}$.
(v) Stressed metallic part ∝ rate of corrosion.
(vi) Purity of metal is inversely related to rate of corrosion

2. Environmental factor—

Temp, Moisture content.

→ (i) Humidity is directly related proposional to rate of corrosion.
(ii) PH is inversely proportional to rate of corrosion.
(iii) Conducting medium is directly proposional to rate of corrosion.
(iv) Nature of Product—

Oxide film
- Porous → harmful
- Non-porous → Protective.

* Prevention of Corrosion—
- It can be prevented by following ways—
1. Proper Selection & Designing—
2. Protective coating
3. Cathodic & Anodic Protection
4. Corrosion Inhibitors

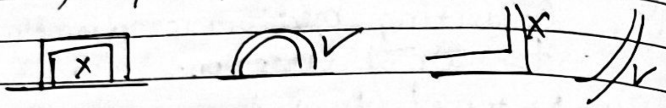
5.

* Proper Selection & Designing—

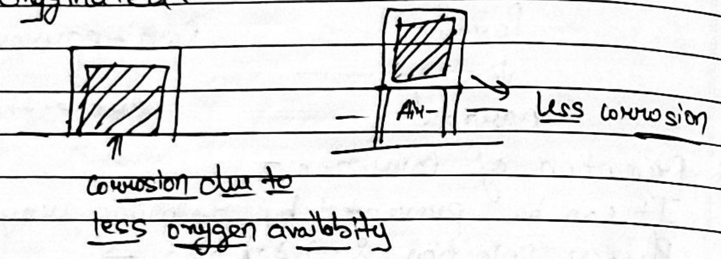
1. Design an equipment by avoiding contact between two dissimilar metals.
2. Always select pure metal.
3. Metallic grain size should be large.
4. Always design an equipment by keeping larger anodic area.
5. The metal part as far as possible should be stress or strain free.
6. If dissimilar metals are used, difference in their electrode potential should be less.
7. During designing avoid ~~stop~~ sharp edges and joints.

8. Avoid following shapes —

A, L, I, V, M, N,

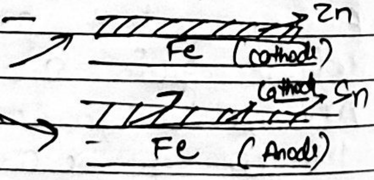


9. Metallic part of machine should be properly originated.



* Protective Coating —
It is of three types —
(i) Metallic coating
(ii) Inorganic coating
(iii) Organic coating.

* Metallic Coating —
On the basis of applied metal, metallic coating are of two types —
(i) Anodic Coating
(ii) Cathodic Coating

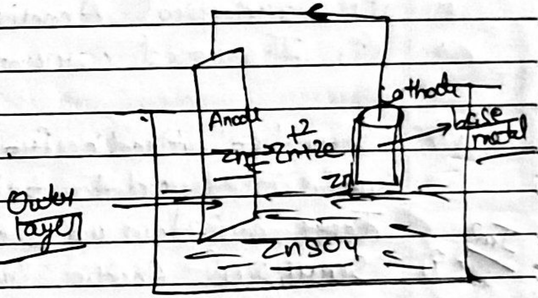


Metal can be protected by applying another metal in form of coating.
If more active metal is applied over the base metal, then it is known as anodic coating, here our base metal remains protected till the last traces of the

anodic coating present.
If less active metal is used for the coating of the base metal, it is known as Cathodic coating. Here, it will provide protection till the layer is continous once it get ruptured or damaged then it lead to faster rate of corrosion.
Example — Galvanization → Anodic coating
Tinning → Cathodic coating

→ Metallic Coating method —

(i) Hot dipping
(ii) Cladding
(iii) Spraying
(iv) Electroplating.



* Inorganic Coating —
Inorganic Coating are non-metallic protective coating. Some of the important inorganic coatings are as follows —
(i) Surface conversion or chemical dip coating.
It can be done by applying material chemically at the surface of base metal.
Example — Phosphate coating, Chromate Coating.
(ii) Anodized ~~Oxidized~~ Oxide coating — These coatings done by anodic oxidation process which leads to formation of Corrosion resistant protective layer. Example — Non-ferrous metals (Aluminium, Silver, Zinc, magnesium) (base metals).

Q. A Mg strip is hanged with ... insulated wire to the domestic steel (water) tank.

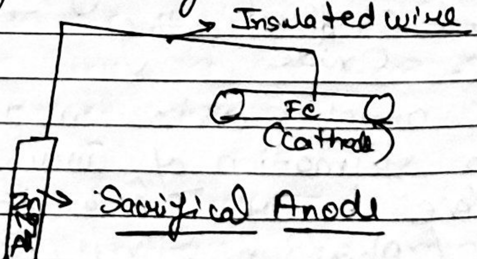
(iii) Porcelein Enamel Coating – These coatings are applied on ferrous material.

* Organic Coating –
The important function of organic coating are –
(i) to give decorative & aesthetic look.
(ii) To protect the metal from corrosion.
Example – Paint, varnishes.

* Cathodic & Anodic Protection –
(i) Sacrificial Anodic Protection
(ii) Impressed current cathodic protection.

(i) ~~Sacrificial Anodic Pro~~ In this method, corroding metal is forced to behave ~~a~~ like a cathode. There are two ways for this type of protection

Imp (i) Sacrificial Anodic Protection –
In this method, the metallic structure which is to be protected from corrosion is connected to a more anodic metal with the help of insulating wire so that the entire corrosion get concentrated on the more active metal. This more active metal get corroded and known as sacrificial anode. The metals commonly used for sacrificial anode are Mg, Zn & Al.

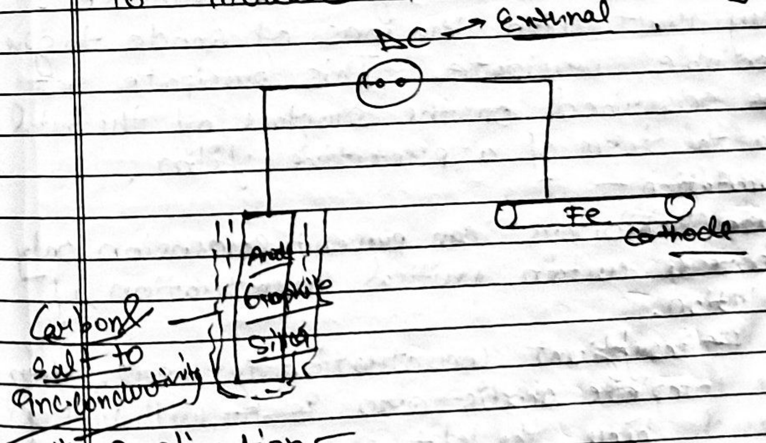


$Mg \rightarrow Mg^{2+} + 2e^-$

Q. Explain why a Mg strip is connected with the help of insulated wire to the underground pipeline?
Q. Explain why Mg strip is attached with the help of insulating wire to the ship hull?

* Application –
- This technique is useful for the protection of underground pipelines, underground cables & marine structure. Example –

(ii) Impressed current Cathodic Protection –
In this technique an impressed current (external) is applied in the opposite direction to the corrosion current so that the corroding metal behaves like a cathode. And this impressed current can be derived from any direct current source like battery. And to complete the circuit an inert electrode is used like graphite. The surrounding of anode should be filled with salt & carbon to increase the ~~core~~ conductivity.



* Application –
* This type of cathodic protection has been applied to water cooler, water tank, underground oil & water distribution tower etc.
It is useful when –
(i) long term protection is needed.

(ii) A large structure to be protected.
(iii) Less costly source of electric power is used.

* Corrosion Inhibitors –

Corrosion Inhibitors are chemical substances which reduce the corrosion rate when added in small quantities to the corroshi environment. These are of three types –
(i) Anodic Inhibitors
(ii) Cathodic Inhibitors
(iii) Valatile Inhibitors or Vapour phase Inhibitors

* Anodic Inhibitors –

Alkalies, molibidates, phosphates & chromates are used for this purpose. They react with the ions of anode to give insoluble precipate. This precipate get ~~abs~~ adsorbed on the surface of the metal in the form of a protective film.

- Limitation –

These inhibitors can prevent corrosion only above a certain critical concentration of solution.

- If its insufficent concentration is used, then the complete anodic area ~~is no~~ will not get covered hence, the left exposed part ~~fate~~ for faster rate of corrosion

* Cathodic Inhibitors –

Organic inhibitors like amines, urea, substituted urea, thiourea & mercaptanes are used for this purpose. They get adsorbed at cathodic surface and slow down the diffusion of ions at cathode.
Example

* Valatile Inhibitors –

These inhibitors on sublimation forms a protective layer on the metallic surface especially these inhibitors are used in enclosed splice, and for delicate part of machines.
Ex – Cyclohexyl Amine Carbonate,
~~Dicycle~~ Dicyclohexylamonium nitrate.

* Effect of corrosion in Various Industries –

- In oil & Gas Industry –

There are no. of different type of corrosion in oil & gas industry –

1. CO_2 corrosion – (also known as Sweet corrosion)
It is the main corroding agent which can lead to pitting corrosion. Dry CO_2 is not corrosive but in presence of water, it will be corroding agent.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

2. Sour Corrosion –
H_2S gas is responsible for this type of corrosion & it causes uniform pitting & Step wise corrosion.

3. Oxygen Corrosion –
Dissolved oxygen in drilling fluids may causes corrosion in drill pipes.

4. Microbial Induced Corrosion – Bacterial activity can cause this type of corrosion. Bacterial action results in the production of CO_2, H_2S

& organic acids. which can cause toxicity of the fluid.

5. * Stress Corrosion Cracking – In this type of corrosion, cracking in metals takes place.

- Prevention –

1. Selecting appropriate material.
2. Using inhibitors
3. Using protective coating of FBE (Fusion bonded Epoxy resin) and three layer poly-olephins (LPO) → polythene & polypropylene.
4. ~~In~~ Vapour & Po

* In Paper & Pulp Industry –

The main corrosion contamination in paper & pulp industry is H_2S. which can causes issues in electronic circuits and compressor. Heat & Chemicals are used in these industries for paper production. And the total reduced sulphur gases get produced, during the reaction which includes H_2S, mercaptance, dimethyl sulphide & other organic sulphides.

* Prevention –

- Selection of corrosion resistant material like titanium.
- Better ventilization & proper drainage system & routine coating of structures including pipeline & equipments.
-

* Equipments

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* In chemical processing Industries. (various method –

1. Natural product separation takes place with or without assistance of chemical reactions.
2. Many products synthesize through chemical processing which are useful every day life.
3. Chemical processing also used for the manufacturing of Robber, Ceramics, different flavouring agents and explosive material.
4. During the manufacturing process most chemical processing plants use speciallized equipments. having following operations –
   (i) Air Scrubbing
   (ii) Waste water treatment
   (iii) Demineralization
   (iv) Blending Operation
   (v) Production Unit
   (vi) Reagent processing.
5. Every chemical plant almost contain certain hazardous acids which are harmful to metals. Examples –

(i) Chlorine. – The flow rate of liquid chlorine through steel pipe is restricted ~~pipe~~ to 2m/s to avoid removal of iron in the form of ferric Chloride.

(ii) Bromine – Titanium metal is not suitble for storage of liquid bromine.

(iii) Sulphuric acid – Corrosion protection of steel takes place by the formation of iron sulphate coating.

(iv) Hydrochloric acid – In general all

Q. what is portland cement? Give the chemical reacn involved during setting & hardining of portland cement

Q. what is the chemical composition of portland cement Draw labelled diagram of rotatory portland

metals get corroded with acids, therefore storage ~~tme~~ tank should be coated properly or it should be lined with lead. Copper is most reactive towards Hcl.

(V) Ammonia - Impurities in liquid ammonia, causes stress corrosion. Cu & Zn are very reactive towards ammonia.

(Vi) Oxygen - The material suitable for liquid oxygen are nickel, aluminium alloy & copper whereas PTFE is poly tetra fluoroethane (Teflon) is used as a sealent.

(Vii) Nitrogen - Temp below 120°C is suitable for storage of hydrogen whereas at high temperature it can penetrate steel and leads to formation of methane. which leads to cracking of steel.

* Power Generation Industry -

In power generation industry, generally are two type of corrosion are -

(i) HTCC (High Temp Hot corrosion) if T 900°C

(ii) LTHC (Low Temp Low corrosion) if T- 700 to 750°C

* Hot corrosion & Erosion -

- In Power Generation Equipment, gas turbines and aircraft, it should be completely avoid to avoid failure.
- In Indian Power Generation Industries - the coal used contains high percentage of ash (60%) along with abrassive material (quartz) (30 to 40%) which can cause erosion tendency.

Q. what is the chemical composition of portland cement. Draw labelled diagram of rotatory kiln used for manufacturing of portland cement by wet process & state its working.

Erosion is a type of corrosion which is caused by high fluid surface velocities in aggressive chemical environment.

* Components of powerplants leads to failure due to corrosion -

1. Feed water lines
2. Steel lines.
3. Demineralized water areas.
4. Coal handling areas.

* Prevention - In Power Industry -

1. Regular maintainance
2. Protective coating are useful for the respective linings.
3. We can use inhibitors and super alloys.

* Cement -

Cement is a lime waste product having adhesive & cohesive. It is used as building material. ~~It~~ Dirty greenish in colour & hydrolic (the property of setting & harding with water) in nature.

* Types of Cement -

1. Natural Cement
2. Puzzolana Cement
3. Portland Cement
4. White Cement
5. Water proof cement
6. Acid-resistant Cement.
7. Sulphur-resistant Cement.

The essential Constituents of Cement used for construction purpose are—

(i) Compounds of calcarius
(ii) Compounds of Aluminium with silicate.

Imp ✱ Chemical Composition — (Portland Cement)

- CaO — (60–70%), • SiO_2 — (20–24%) (Silica)
- Alumina — Al_2O_3 — (5–7.5%)
- Magnesia — MgO (2–3%)
- Ferric Oxide — (Fe_2O_3) (1–2%)
- ✱ Sulphur trioxide — (SO_3) (1–1.5%)
- Sodium oxide — (Na_2O) (Around 1%)
- Potassium oxide — (K_2O) (1%).

✱ Sulphur trioxide is mixed to reduce soundness. Soundness is the ability of hardened cement to retain its volume without destructive expansion.

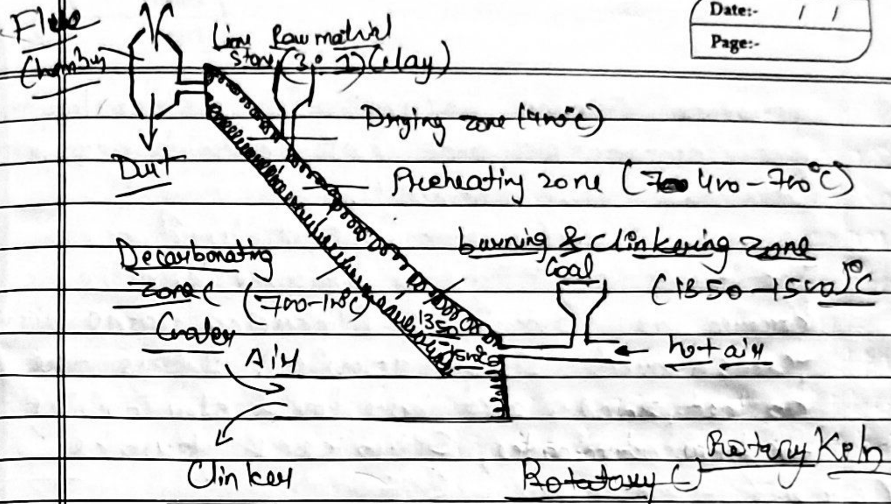
✱ Manufacturing of Portland Cement —

Raw material —

- Lime or Limestone ($CaCO_3$).
- Clay ($Al_2O_3 \cdot SiO_2 \cdot Fe_2O_3 \cdot 2H_2O$)
- Gypsum ($CaSO_4 \cdot 2H_2O$) (to reduce setting time)
- Iron oxide (Fe_2O_3) (it gives strength & hardness to the cement)
- Sulphur trioxide (SO_3).

— It is manufactured by two ways —

- Dry process &
- Wet process.



✱ 1. The mixture of finely grounded limestone & clay (3:1) is made into a thin slurry (wet process) or dry process

2. In dry process the raw material are dried with help of hot air & pulverized whereas in wet process pulverized raw material is mixed with 30 to 40% water and then feeded to rotary kiln.

3. The slurry of raw material enters from the upper end of the rotary kiln. This rotary kiln have different temperature zone because the burning of coal takes place at the lower end of rotary kiln.

(i) The upper part of rotary kiln is drying zone where temperature is around (400°C).

(ii) The upper central part of the kiln is known as preheating zone where temperature is around 400 to 700°C. In this zone, clay & Magnesium carbonate get decomposed.

(iii) The lower central part of the kiln is known as Decarbonating zone having tem

-perature around 700-1000°C. Here limestone get decomposed and carbon dioxide escaped through flue chamber.

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

The lower part of the rotatory kiln is known as Burning & Clinkering zone where temp is around 1350-1500°C. It is the hottest zone and here lime & clay combine to form aluminates, silicates & ferrite.

$$2CaO + Al_2O_3 \rightarrow \underset{(C_2A)}{2CaO\cdot Al_2O_3}$$

$$2CaO + SiO_2 \rightarrow \underset{(C_2S)}{2CaO\cdot SiO_2}$$

$$3CaO + Al_2O_3 \rightarrow \underset{(C_3A)}{3CaO\cdot Al_2O_3}$$

$$2CaO + Fe_2O_3 \rightarrow \underset{(C_2F)}{2CaO\cdot Fe_2O_3}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow \underset{(C_4AF)}{4CaO\cdot Al_2O_3\cdot Fe_2O_3}$$

4.* These compounds combine together to form small hard greyish palletes known as clinker.

5. The hot clinker is cooled down with the help of rotary coolers.

6. Cooled clinker is then grinded with gypsum. Finest the cement, greatest will be its ~~best~~ strength and then packaging can be done.

* **Setting & Hardening of Cement –**

Setting of cement is an exothermic process and involves hydration of calcium aluminate & calcium silicate. When water is mixed with cement, heat is liberated & generally some initial setting takes place which is known as flash set. Setting & hardening of cement takes place due to hydration & hydrolysis.

(i) Hydration – Tricalcium aluminate & Dicalcium silicate on hydration changes into colloidal gel along with the formation of calcium hydroxide & aluminium hydroxide.

$$3CaO\cdot Al_2O_3 + 6H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O + 880\,kJ/kg$$

$$2CaO\cdot SiO_2 + nH_2O \rightarrow 2CaO\cdot SiO_2\cdot nH_2O + 500\,kJ/kg$$

Tricalcium aluminate reacts with gypsum to form crystal of calcium sulphoaluminate.

$$3CaO\cdot Al_2O_3 + CaSO_4\cdot 2H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 2H_2O$$

(ii) Hydrolysis –

Tricalcium silicate & aluminate on hydrolysis results in the formation of precipitate of calcium hydroxide & aluminium hydroxide which fills the interstitial voids to give the hardening to the cement.

$$3CaO\cdot SiO_2 + H_2O \rightarrow Ca(OH)_2\downarrow + 2CaO\cdot SiO_2$$

$$3CaO\cdot Al_2O_3 + 6H_2O \rightarrow 3Ca(OH)_2 + 2Al(OH)_3$$

* **Gypsum ($CaSO_4\cdot 2H_2O$) –**

It is a white crystalline salt which can be prepared with the help of calcium chloride &

or calcium nitrate. On heating, it gives a series of compounds — First it convert into orthorhombic form which on further heating upto 150°c gives Plaster of Paris, which on heating upto 600°c gives anhydride. And above 600°c, it decomposed to give calcium oxide.

$$CaSO_4 + 2H_2O \rightleftharpoons CaSO_4 \cdot 2H_2O \xrightleftharpoons{150°C} CaSO_4 \cdot \tfrac{1}{2}H_2O$$

(Gypsum) (at room temp) (Powder)   Orthombic (Crystaline)   (PoP)

$$CaSO_4 \cdot \tfrac{1}{2}H_2O \xrightarrow{600°C} CaSO_4$$

$$CaO + SO_2 + \tfrac{1}{2}O_2 \xleftarrow{800°C} CaSO_4$$

* Plaster of Paris —

- Preparation —
  (same as above)

- Properties —

1. It is white crystalline which reacts water in an exothermic process.
2. It gets settled and hardened within a short time with slight expansion.

8.* Uses —

1. For plastering
2. For manufacturing of fertilizer (Ammonia sulphate)
3. For manufacturing of chalk.
4. For decorative pieces.
5. Dentist also use it for denturing purpose.

Unit-5

Polymer

- On the basis of arrangement of monomers
  - Alternate polymers
    ABABAB
  - Random polymers
    ABCADEFG
  - Block polymers
    AAA BBB AAA
  - Graft polymers

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AAAAAAA
|  |  |  |
B  B  B  B
B  B  B  B
B  B  B  B
B  B  B  B
B  B  B  B
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- Imp On the basis of synthesis or growth mechanism
  - Step growth polymerization
  - Chain growth polymerization
    - Catalyst
    - Cationic
    - Anionic
    - Catalyst (Zigler-Natta)
    (Coordination polymer)

- Imp On the basis of Environment friendly Behaviour
  - Biodegradable
  - Non-biodegradable

- Imp On the basis of thermal behaviour
  - Thermosetting
    - we cannot reuse, remold.
    - cross linked str.
    Bakelite, Resin, Urea formaldehyde
  - Thermoplastic
    - soft on heating
    - We can reshape, reuse, remold.
    - Linear structure, on heating layer slide over each other
    Ex. Polythene, PVC, Polypropylene

heavy bond. soft the sliding of layer is prevented