Unit - 3

Plaster of Paris

It is formulated as hemi-hydride of calcium sulphate

$$CaSO_4 \cdot \frac{1}{2} H_2O \; / \; 2CaSO_4 \cdot H_2O$$

consists of a series of hydrates ranging from (0 - 2)

Preparation :

$$\underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O} \xrightarrow[150-200^\circ C]{\Delta} CaSO_4 \cdot \frac{1}{2} H_2O + \frac{3}{2} H_2O$$

POP is mixed with water to make (Plaster of Paris) thick paste liberating heat of crystall (Exothermic)

$$\downarrow 1\tfrac{1}{2} H_2O$$

$CaSO_4 \cdot 2H_2O$ (hardening)

Setting of unmodified POP starts in 10 mins after mixing water. It completes in 25-40 mins, but is fully set and hardened in 75 mins.

Properties :

1. white coloured powder, light weight.
2. when mixed with water, it gains gypsum form.
3. Easy to work with for forming cast and moulds due to quick binding property.
4. The set material is not strong.
5. cannot be used for load bearing.

Applications :

1. Decorative plaster of wall and ceilings.
2. Orthopaedic cast for protection of limbs with broken bones, surgical bandages.
3. Used as quick sealing material, structural tiles

It slightly expands while setting

→ $CaSO_4$ and $NaSO_4$ are used to accelerate the setting of POP

→ used in dental chemistry for making dental cast

66
77
72
78

Electrochemistry

The branch of science which deals with the production of energy from energy released during spontaneous chemical reactions and the use of chemical energy to bring about non-spontaneous chemical transformations.

Energy

- Converted to Electric Energy
  - ↓ Galvanic cell
- Converted to chemical energy
  - ↓ Electrolytic cell

Cells

- Electrochemical
  - Galvanic cell
  - Concentration cells
    - without transference
    - with transference
- Electrolytic

Electrode:

It is a metallic or non-metallic charged terminal of a cell. An electrode and electrolyte solution in contact makes a half cell. These are of two types:

- Cathode
- Anode

Cathode:

Cathode is a +vely charged electrode in a electrochemical cell at which reduction takes place. It is deficient of electrons

Anode:

Anode is a -vely charged electrode/terminal in a cell at which oxidation takes place.

Galvanic Cells

In this cell, the two electrodes are different

E.g. Daniel cell - Zn and Cu electrodes.

Dry cell - Graphite and Zn electrodes

The two electrodes may be in contact with a common electrolyte, i.e., without transference or the two electrodes may be seperated by a liquid junction section or a porous section known as salt bridge.

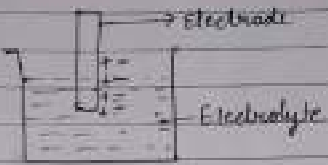
Concentration Cell:

In this type of cell, two electrodes which

SHE ✓

are similar but they are in contact with soln of different concentration. They may also be with or without transference.

Electrode Potential:

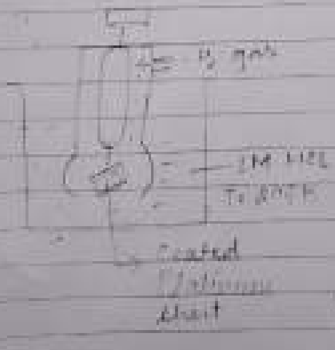


Electrode potential = potential difference b/w electrode and electrolyte

Emf:

$E_{cell} = E_{cathode} - E_{anode}$

Standard Hydrogen Electrode:



At anode:
$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

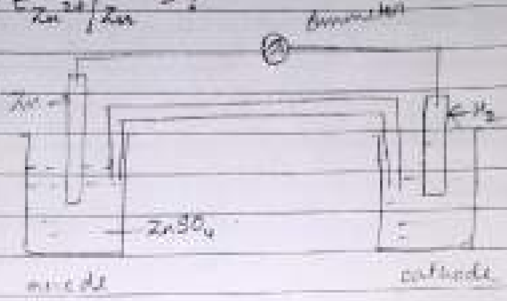
At cathode
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$

Net reaction:
$H_2(g) \rightleftharpoons 2H^+ + 2e^-$

$E^\circ = 0$

Standard Electrode Potential :

→ $E^{\circ}_{Zn^{2+}/Zn} = ?$



At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$

at cathode : $2H^+ + 2e^- \longrightarrow H_2(g)$

Cell Representation :

$Zn(s) \mid Zn^{+2}(aq) \parallel H^+(aq) \mid H_2(g)$

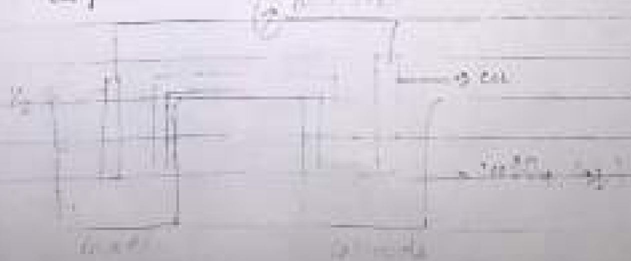
(anode) (cathode)

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$0.76 = 0 - E^{\circ}_{Zn}$

$\boxed{E^{\circ}_{Zn} = -0.76\,V}$

→ $E^{\circ}_{Cu^{2+}/Cu} = ?$



at anode: when E_{cell} +ve —

$H_2(g) \longrightarrow 2H^+ + 2e^-$

at cathode

$Cu^{2+} + 2e^- \longrightarrow Cu(s)$

Representation:

$H_2 \mid H^+(aq) \parallel Cu^{2+} \mid Cu(s)$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$0.34 = E^\circ_{cathode} - 0$

Electrochemical Series:

At 298 K

Electrode	Reaction	E°
$Li \mid Li^+$	$Li \rightarrow Li^+ + e^-$	−3.05
K / K^+	$K^+ + e^- \rightarrow K$	−2.93
$Ba \mid Ba^{+2}$	$Ba^{+2} + 2e^- \rightarrow Ba$	−2.9
$Ca \mid Ca^{2+}$	$Ca^{+2} + 2e^- \rightarrow Ca$	−2.87
$Na \mid Na^+$	$Na^+ + e^- \rightarrow Na$	−2.71
$Mg \mid Mg^{2+}$	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.31
$Al \mid Al^{+3}$	$Al^{+3} + 3e^- \rightarrow Al$	−1.66
$Zn \mid Zn^{2+}$	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76

$Fe \mid Fe^{2+}$	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Pb \mid Pb^{2+}$	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Co \mid Co^{+2}$	$Co^{+2} + 2e^- \rightarrow Co$	−0.28
$Ni \mid Ni^{+2}$	$Ni^{+2} + 2e^- \rightarrow Ni$	−0.25
$H \mid H^+$	$2H^+ + 2e^- \rightarrow H_2$	0.00
$Cu \mid Cu^{2+}$	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Ag \mid Ag^{+}$	$Ag^+ + e^- \rightarrow Ag$	0.80
$Cl \mid Cl^-$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Au \mid Au^{+3}$	$Au^{+3} + 3e^- \rightarrow Au$	1.50

Ques What are the differences between electrochemical and electrolytic cell?

Ans

Electrochemical	Electrolytic
• It converts chemical energy (via redox) into electrical energy.	It converts electrical energy into a chemical energy.
• At the electrodes spontaneous redox reaction takes place	At the electrodes, non-spontaneous redox reacⁿ occurs only when energy is supplied.

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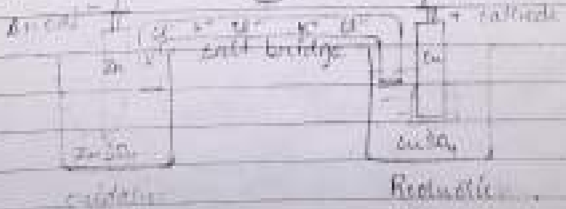
• Electrodes are dissimilar	Electrodes may be same or different
• Each electrode is dipped in electrolytic solution of its own ions.	Both the electrodes are fitted in the same electro-lyte solution.
• Salt bridge is used in electrochemical cell.	Salt bridge is not needed.
• Anode is negative and cathode is positive electrode	Anode is positive and cathode is -ve electrode
•	

Galvanic Cell

Daniel Cell :-



Anode : $Zn \longrightarrow Zn^{+2} + 2e^-$ (oxidation half)

Cathode : $Cu^{+2} + 2e^- \longrightarrow Cu\,(s)$ (Reduction half)

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Cement :

Cement is the material possessing adhesive and cohesive properties which make it capable of binding mineral fragments like bricks and stones into a compact coherent structure. Cement has a characteristic property to form a paste with water and setting into a hard solid mass within a few hours

Types of Cement
There are four types

1. Natural Cement:
 Produced by calcining and pulvarising.
 Naturally occuring
 Argillacious limestone at high temperature

2. Puzzolana cement:
 Made from volcanic ash
 containing silicates of calcium, Fe and Al
 mixed with slaked lime

3. Slag cement:
 Mixing hydrated lime, Ca and Al silicates alongwith slag from blast furnace

4. Portland cement:
 Lime, Silica, alumina, Iron oxide, alkali oxide, etc

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Portland Cement :

chemical composition of Portland Cement :

Avg chemical composition

chemical oxides %

1. Lime (CaO) 61 - 67 %

→ If in excess, reduces the strength because it expands.

If less than ratio, reduces the strength bcoz it causes quick setting.

2. Silica (SiO_2) 17 - 25%

→ It provides strength

If in excess, slow hardening

3. Alumina (Al_2O_3) 3 - 8%

→ helps in quick setting

If in excess, weakens the cement

4. Calcium sulphate (Gypsum) 1.5 - 4.5 %

→ Speeds up ~~increase~~ initial setting time

5. Fe_2O_3 0.5 - 6%

→ Strength, hardness and colour

6. Sulphur Trioxide (SO_3) 1-3%
→ provides soundness to cement

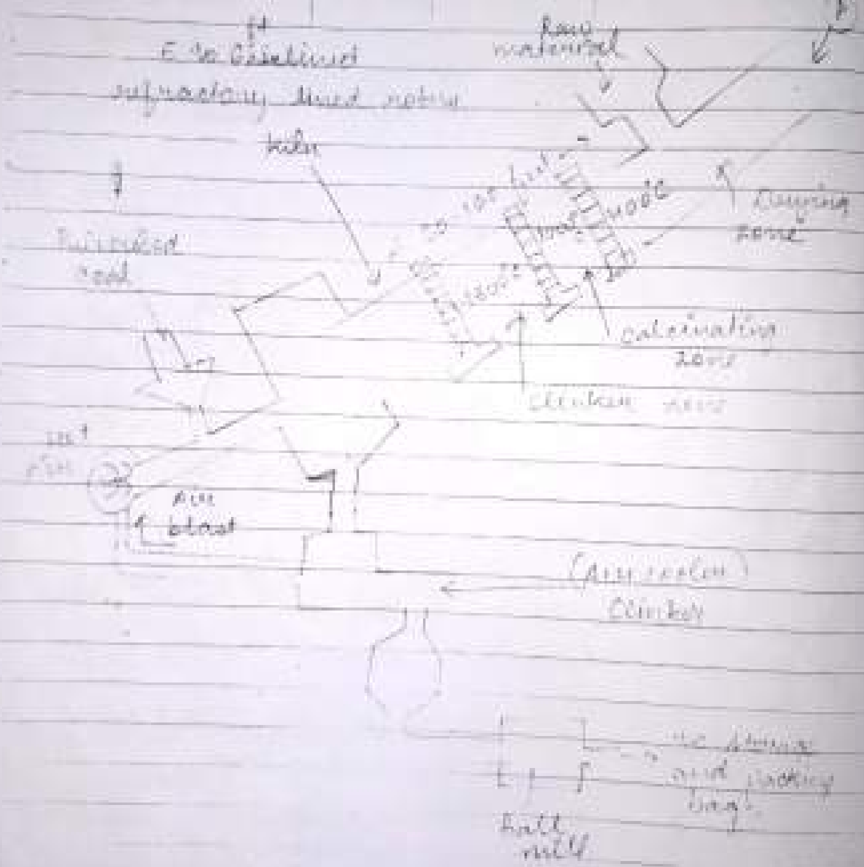
7. Alkali oxides (Na_2O, K_2O) 0.3 – 1.5%
→ Soda and Potash
provides efflorescence to cement

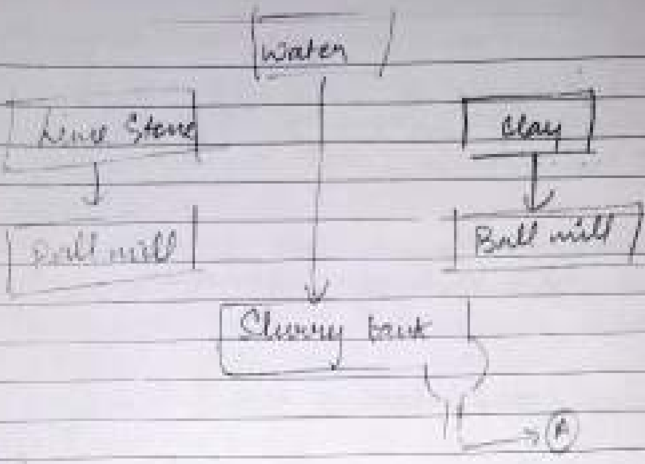
8. Magnesium oxide (MgO) 0.1% – 5%
→ provides hardness and colour to cement

Compound Composition of Portland Cement:

Name	Formula	Abb.	% & function
1. Tricalcium Silicate	$3CaO.SiO_2$ or Ca_3SiO_5	C_3S	45%. final setting 10 hrs & final hardening in 7 days
2. Dicalcium Silicate	$2CaO.SiO_2$ or Ca_2SiO_4	C_2S	25%. final hardening 28 days
3. Tricalcium Aluminate	$3CaO.Al_2O_3$ or $Ca_3Al_2O_6$	C_3A	10%. initial setting 30 minutes
4. Tetracalcium Alumino Ferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	9%. initial setting 1 hour
5. Gypsum	$CaSO_4.2H_2O$	-	4% Retards the process (initial setting)

6.	Magnesium oxide	MgO		4% provides plasticity to cement paste
7	Free calcium oxide	CaO		2%.





Process:
It is of two types
- Dry
- Wet

Dry
used for hard and bulky raw material

1. Mixing of raw material
done by dry and wet process

2. Grinding
Separate grinding in dry process
Mixing of water in wet process

3. Burning
Slurry in kilns is burned from one end

→ a) Drying zone - upper part 200-400°C evaporates water

b) Pre-heating zone - temp 400-700°C

$MgCO_3 \longrightarrow MgO + CO_2$

→ calcination zone:

700° - 1100°C - limestone decomposes.

$CaCO_3 \longrightarrow CaO + CO_2$

→ Deburning zone / clinkering zone:

1400° - 1450°C

$2CaO + SiO_2 \longrightarrow Ca_2SiO_4$ (C_2S)

$3CaO + SiO_2 \longrightarrow Ca_3Si_2O_5$ (C_2S)

$3CaO + Al_2O_3 \longrightarrow Ca_3Al_2O_6$ (C_3A)

$4CaO + Fe_2O_3 + Al_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10}$ C_4AF

→ cooling of clinkers:

$C_2S + C_3S + C_3A + C_4AF$

→ Grinding:

cooled clinker is ground into fine particles (powder) and 2-4% gypsum is added while grinding.

→ Packaging:

The cement powder is immediately packed.

Imp. What is portland cement? write the chemical reactions involved during setting and hardening of cement.

Setting :
process of solidification of cement paste with some early strength and takes the cast/ shape

Hardening :
Development of high strength in the set mass of cement is known as hardening.
3 stages :
- Initial / flash setting (24 hrs)
- final / Initial hardening (1-7 days)
- final hardening (28 days)

→ Initial / Flash Setting :
Hydration of C_3A (15 mins) and hydration of C_4AF (one hr.)

$C_3A + 6H_2O \longrightarrow C_3A.6H_2O + 880\ KJ/kg.$

$C_4AF + 7H_2O \longrightarrow C_3A.6H_2O + CF.H_2O + 420\ KJ/kg$

Hydration of C_3A and C_4AF do not result in the development of appreciable strength

→ what is the role of gypsum?

→ Final Setting or Initial hardening :
(24 hrs - 7 days)
Hydrolysis of C_3S

$C_3S + (n+1)H_2O \longrightarrow C_3S.nH_2O + Ca(OH)_2 + 120\ kJ/kg$
(gel)
(Tobermorite Gel)

Tobermorite Gel is formed which it has strong binding character.

Final hardening / curing:

C_2S and C_3S react with water

$C_3S + (n+1) H_2O \longrightarrow C_2S.nH_2O + Ca(OH)_2 \downarrow$

$C_2S.nH_2O \longrightarrow C_2S.nH_2O$ (gel)

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$ (weakly binding)

A total strength of 99% is properly cured up in 28 days.

Role of Gypsum:
Gypsum reacts with C_3A to form an insoluble calcium sulphoaluminate complex which do not hydrate rapidly. Therefore, no sudden heat is liberated prolonged time is about half an hour.

$C_3A + xCaSO_4.2H_2O + 7H_2O \longrightarrow C_3A.xCaSO_4.7H_2O$
Gypsum

Application:
Portland cement is used in construction of buildings, walls, foundations, roads bridges, plasters, underwater construction and reinforced construction.

Drawback:

Cement mass has very high compressive strength but it has less or inadequate tensile strength. Therefore, reinforcing materials like steel bars, steel network, etc. are embodied in it.