Eng. chemistry (BAS-102) UNIT-3

Lecture NO. 54

(Corrosion and its Causes)

Corrosion is the deterioration of a substance due to its reaction with its environment."
eg. Rusting of Iron, Formation of green layer of basic Carbonate etc.

Causes of Corrosion - Metals exist in nature in the form of Carbonates, Sulphides, sulphates etc. These combined state of metal (ore) has a low energy and is thus thermodynamically stable state of metal. A Considerable amount of energy is required during metallurgy. The extracted metals has higher energy and thus it is thermodyna-mically unstable state. Thus metal have a natural tendency to convert back to its natural thermodynamically stable state.

Effects of corrosion -

→ Destruction of Material
→ Metal losses its efficiency
→ Purity of products get affected
→ Maintenance & cost of material increases.

Electrochemical (or Wet) theory of Corrosion

It is also known as immersed corrosion. It takes place under moist or wet conditions. through the formation of short circuited galvanic cell. In this corrosion following steps involved -

Step-1 - (Separate Area) - Separate anodic and cathodic areas between which current flows through the conducting medium.

Step 2 oxidation- occurrence of oxidation at anodic area which generates metallic ions.

Step 3 Reduction- occurrence of reduction at cathodic area which generates non metallic ions like OH^-, O^{2-}.

step 4 Corrosive Product - Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosion product somewhere between anodic area and cathodic area. for ex. Rusting of iron

At anode

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

At Cathode: The electrons released at anode are responsible for various cathodic reactions and on the basis of cathodic reaction corrosion is of two types-

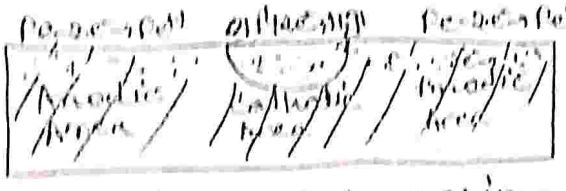
(A) Hydrogen Evolution - In absence of O_2

(I) In acidic medium:

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

$Fe - 2e^- \longrightarrow Fe^{++}$ (at Anode)

At Cathode



In this type of corrosion Anodic areas are large than cathodic areas.

(B) Absorption of oxygen type corrosion-

This type of corrosion takes place in Neutral medium or slightly alkaline medium.

Reaction Involved-

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

$H_2O + \frac{1}{2}O_2 + 2e^- \longrightarrow 2OH^-$ (At Cathode)

Net reaction.

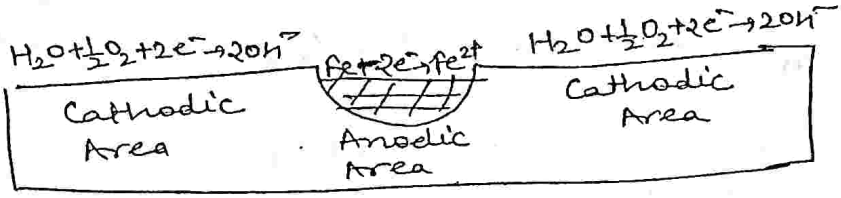
$$Fe + H_2O + \frac{1}{2}O_2 \longrightarrow Fe(OH)_2$$

(Corrosive product)

→ If oxygen is present in sufficient amount $Fe_2O_3 \cdot H_2O$ is formed as a corrosive product, which is yellow in colour

→ If oxygen is limited than Fe_3O_4 is formed, which is black in colour.

In this type of corrosion cathodic area are large than anodic area.



* Questions asked in university examinations.

* Explain the electrochemical theory of corrosion.

Eng. chemistry (RAS-102)

Lecture No- 55

(Corrosion and its Prevention)

Corrosion is started from Anode. By protecting Cathod Corrosion can be prevented. Corrosion Can be prevent by following methods -

(1) Sacrificial anodic protection Method - This is a cathodic protection method. In this method metal is coated or connected with metal which comes above the metal, which we want to protects in electro-chemical series. so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly, while the parent structure (Cathodic) is protected. The more active metal so employed is called "sacrificial anode". The Corroded sacrificial anode block is replaced by a fresh one, when consumed completely.
Eg. Galvenization (Coating of Zn on Fe).

(2) Impressed current Cathodic protection - In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to Cathode.

(3) Coatings - There are two metallic Coating -
(i) Anodic Coating - Eg. Galvanization.
(ii) Cathodic Coating - Eg - Tinning.
In this method parent metal is coated with non-reactive metal. Due to corrosion resistance (non-reactive) property, metal is

protected. But if any crack is develop on the coating, then corrosion speed up. This is due to the fact that exposed metal (parent metal) act as anode & coating becomes cathode.

(4) Proper Designing - The design of metal should be of that type, that corrosion if occurs, is uniform & does not result in intense & localized corrosion.
→ Avoid the contact of dissimilar metals. If they are to be in contact, the anodic material should have large area & it should not be painted or coated.

(5) Using Pure Metal - Corrosion resistance of metal can be improved by increasing purity.

(6) Using Metal alloys - Corrosion can be minimized by using metal alloys. Rate of corrosion decreases by alloying metal.

(7) Modifing environment - Corrosion can be minimized by improving or modifing the environment. For eg - Removal of harmful chemical constituent.

(8) By Corrosion Inhibitor - These are the chemical substance which reduce the corrosion rate when added in small quantity to the corrosion environment

Types - Corrosion inhibiters are of two types -

(i) Anodic inhibitor
(ii) Cathodic inhibitor

(i) Anodic inhibitors – The substance which reduce the rate of Anodic reaction are known as Anodic inhibitor. eg. alkalies, phosphates, molybdates, phosphates and chromates etc.

These inhibitors react with the ions of metal (anode) and produce insoluble precipitate, which is absorbed by metal surface.

(ii) Cathodic inhibitors – The substance which reduce the rate of Cathodic reaction are known as Cathodic inhibitors. They are used in acidic as well as neutral medium.

For eg. Na_2SO_3, Mg, Zn ~~etc~~. Ni salts etc.

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* Questions asked in University examination.

* What is corrosion. Give five methods to protect metal from corrosion.

* Write a short note on Sacrificial anodic protection method.

Corrosion Issues in Pulp and Paper industries

Corrosive contaminants are produced in Pulp and paper industry. In this industry major cause of concern is TRS (Total reduced Sulphur) gases which include, H_2S, ~~mercaptan~~ Mercaptans, dimethyl sulphides etc.

Prevention

⇒ Proper material selection in production.

⇒ Better ventilation and proper drainage system.

⇒ Routine protective coating of structure, pipelines and equipments.

Corrosion Issues in Oil and Gas Industries

The basic process of gas ~~corrosion involves~~ Oil and gas industry involves extracting the resource from underground using high pressure ~~boreholes~~ pipes and the refining. This industry uses high performance ~~steel~~ stainless steel which is a robust material. The major type of corrosion occuring in this industry are -

⇒ Sweet corrosion (CO_2 corrosion)

CO_2 dissolved in aqueous phase promotes electrochemical corrosion.

⇒ At high temp Iron Carbide scales are formed in pipes.

⇒ Sour corrosion (H_2S Corrosion)

This is due to H_2S and moisture (Acidic) which causes pipeline embrittlement, due to formation of iron sulphide.

⇒ Oxidative corrosion and erosion corrosion are other common corrosion in this Industry.

Prevention

⇒ Choosing appropriate material.

⇒ Using Inhibitors such as aldehydes, amines.

⇒ Using protective coating.

Corrosion Issues in Chemical process Industry.

⇒ During manufacturing process this industry use specialised equipments.

⇒ As a result of extreme condition such as contact with chemicals and process related stress, the metal must able to withstand corrosion, heat and other stress.

⇒ The most common cause of concern in chemical industry is piping system.

Prevention

⇒ stainless steel is mostly used to store chemicals.

⇒ CPVC is used in pipes and fittings which provide high mechanical strength and chemical resistance.

⇒ CPVC reduces internal and external corrosion.

Corrosion issues in Power Generation Industry.

Hot corrosion may be defined as corrosion resulting from salt components present in boiler metal ~~corrosion~~ at high temp. Na_2SO_4, NaCl + V_2O_5 combined to form molten deposits which damage protective coating.

Hot corrosion and erosion are serious problems in in power generation equipments. Further oxidative corrosion Galvanic corrosion ~~acid~~ ~~ash~~ accelerates the corrosion rate.

⇒ The boiler feed water ~~is~~ contamination is also responcible for boiler problems such as scale & formation and caustic embrittlements.

Prevention :-

⇒ Regular inspection and use of protective coating.

⇒ Hot corrosion can be reduced by using super alloy and inhibitors.

⇒ By ~~or~~ using uncontaiminated coal these corrosion can be prevented.

UNIT-3

Eng. Chemistry (RAS-102)

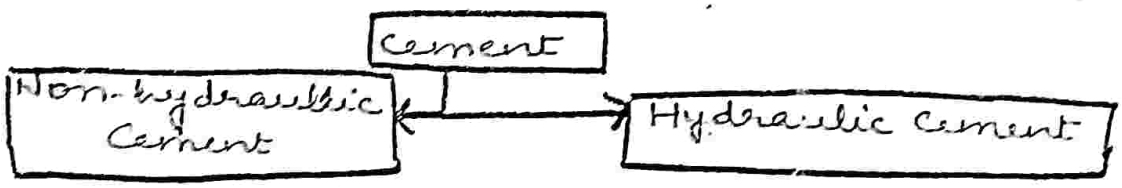
Lecture NO-36

(Cement)

A Cement is a binding material which sets and hardens independently and can bind other material together. These have adhesive and cohesive properties.

Work of cement - The most important use of cement is the production of mortar and concrete, the bonding of natural or artificial aggregates to form a strong building material, which is durable in the face of normal environment effects.

Types of cement -



Which cannot harden while in contact with water or opposed by hydraulic cement.

→ Gain strength very slowly
→ Rarely utilized in modern time

That sets or develop strength by chemical reaction with water by formation of hydrates.

Eg. Portland cement.

Portland cement

Portland cement is a type of hydraulic cement made by heating limestone and clay mixture in a kiln and pulverizing the materials.

Raw materials of Portland Cement - The raw materials used in the manufacture of portland cement are -

(i) Calcareous material
(ii) Argillaceous material.
(iii) Gypsum.

Raw materials of cement

- **Calcareous Material** (which supply lime)
  eg. Limestone, chalk, Cement rock, shells & Waste $CaCO_3$
- **Argillaceous Material** (which supply silica, alumina & iron oxide)
  eg. clay – sedimentary rock Composed of clay materials quartz & calcite.
  Slag – Mixture of metal oxide, glass, SiO_2, silica sand etc.
- **Gypsum** $CaSO_4 \cdot 2H_2O$

Manufacture of Portland cement · Manufacture of portland Cement takes place in following five steps.

(1) Mixing of Raw material < Dry Process / Wet process

(2) Burning — Drying zone (400°C) / Calcination zone (1000°C) / Clinkering zone. (1400-1600°C)

(3) cooling

(4) Grinding

(5) Packaging.

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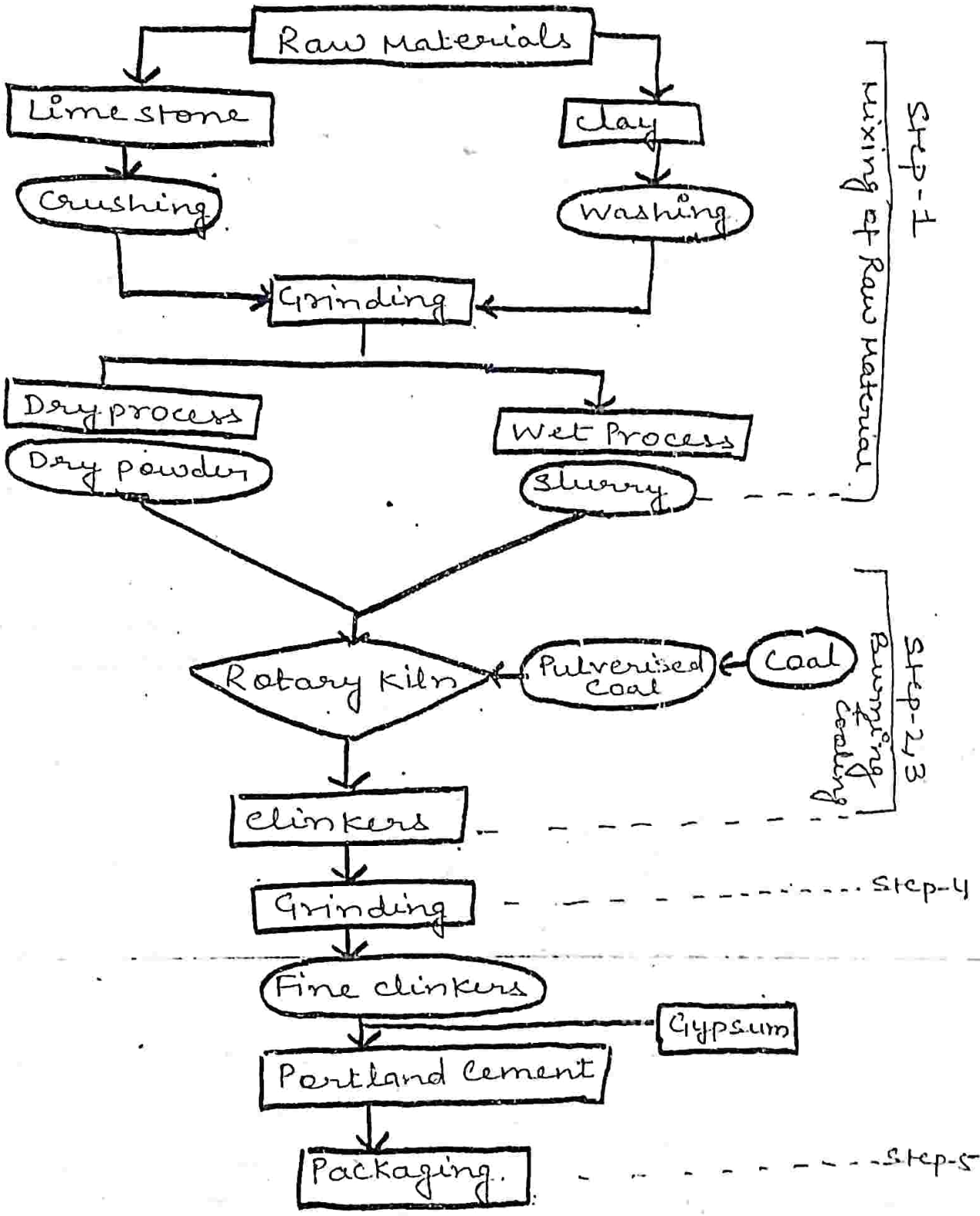
(1) **Mixing of Raw Materials** – Raw materials Can be mixed by two methods.

(i) Dry process (ii) Wet process

	Dry Process	Wet process.
1.	It is a slow process	1. It is relatively faster process
2.	cost of production Cement is less	2. cost of production is somewhat higher as there is fuel consumption.
3.	The quality of cement Produced is inferior	The quality of cement produced is somewhat superior since more accurate Control of composition can be attained.
4.	This process is adapted when raw materials are quite hard & they donot have any inharent moisture content of 15%.	4. This is adopted when raw materials are soft.



Flow diagram for the manufacture of Cement

(2) Burning - Burning process takes place in the kiln in three different zones.

(i) Drying zone - In this zone moisture and slurry get evaporated. This is the upper part of kiln where the temperature is about 400°C.

(ii) Calcination zone - This the central part of kiln where the temperature is around 1000°C. The dry material reaching this point undergo decomposition of limestone

$$\underset{\text{limestone.}}{CaCO_3} \rightleftharpoons \underset{\text{Quick lime}}{CaO} + CO_2\uparrow$$

(iii) Clinkering zone - This is the hottest zone having temperature 1400–1600°C. Here the main reaction between lime & clay takes place to form clinkers.

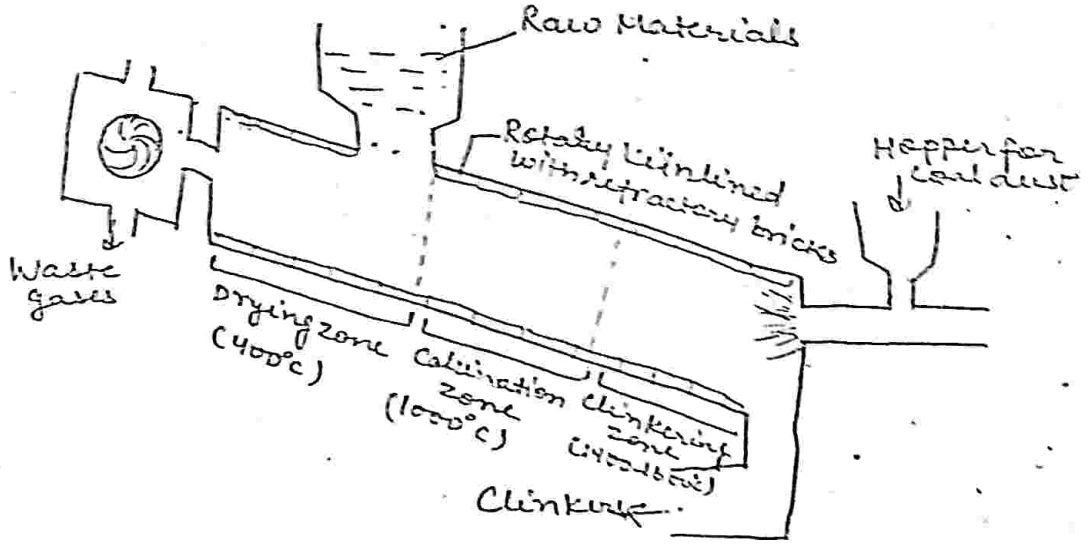
$$2CaO + SiO_2 \longrightarrow 2CaO \cdot SiO_2$$ (Dicalcium silicate)

$$3CaO + SiO_2 \longrightarrow 3CaO \cdot SiO_2$$ (Tricalcium silicate)

$$3CaO + Al_2O_3 \longrightarrow 3CaO \cdot Al_2O_3$$ Tricalcium aluminate

$$4CaO + Fe_2O_3 + Al_2O_3 \longrightarrow 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$$ Tetra calcium alumino ferrite

Clinkers.



Manufacture of Portland cement by Rotary kiln.

3. Cooling - The clinkers are cooled by a stream of air. The rate of cooling should not be slow, if it is slow then $2CaO \cdot SiO_2$ converts into powder form, which does not have binding property.

4. Grinding - The fired clinker is finely ground with about 2-5% of gypsum. Gypsum retard or delay the setting of cement when it comes in contact with water.

(5) Storage & Packaging - It requires special care The cement retains its property until it comes in contact with the moist air or water.

Composition of cement -

Clinker + Gypsum ⟶ Portland Cement

[$2CaO \cdot SiO_2$ (C_2S)
$3CaO \cdot SiO_2$ (C_3S)
$3CaO \cdot Al_2O_3$ (C_3A)
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (C_4AF)] + $CuSO_4 \cdot 2H_2O$ ⟶ Portland Cement

(Retard the setting of cement)

Characteristics of main constituents -

(C_2S) — Provide ultimate strength comparable to C_3S
(C_3S) — Provide ultimate strength.
(C_3A) - Undergo hydration at very fast rate.
(C_4AF) - has slow rate of hydration.
Gypsum - Retard the setting of cement.

Questions asked in University examinations

* Explain manufacture of Portland Cement
* Explain the composition of cement with their characteristics.

Eng. Chemistry (RAS-1.02)

Lecture NO-57

(Setting and Hardening of Cement)

It is due to the formation of interlocking crystals reinforced by the rigid gels formed by the hydration & hydrolysis of the constitutional compounds.

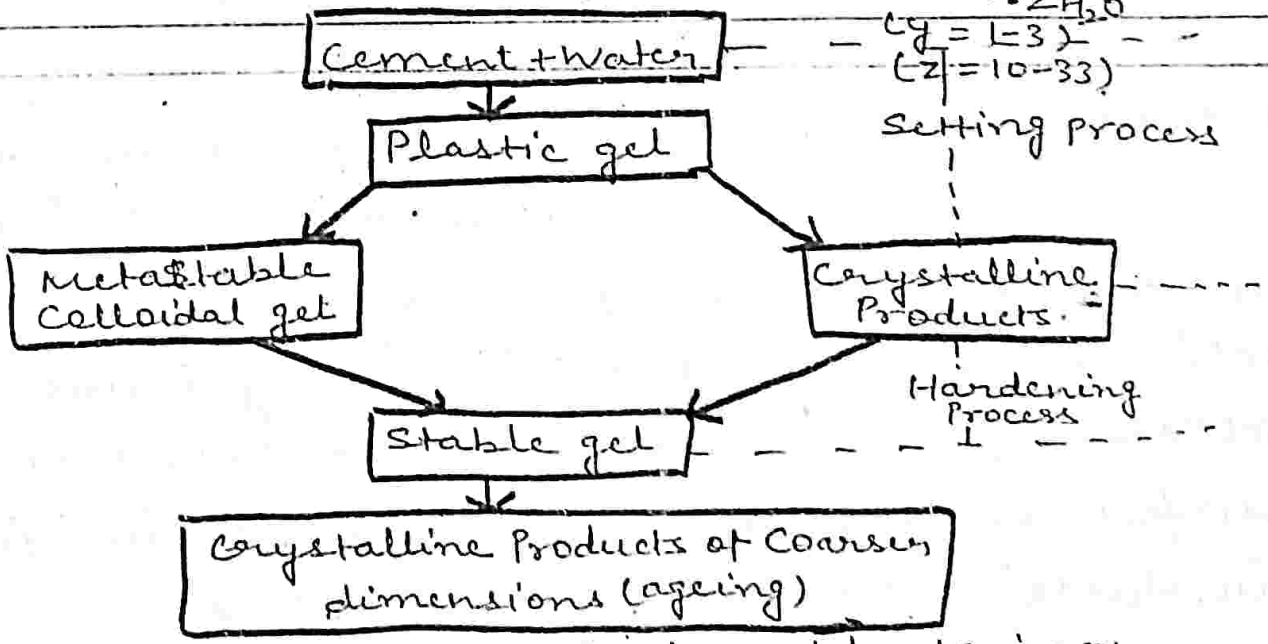
When cement is mixed with water, the paste becomes quite rigid within a short time which is known as initial set or flash set. This is due to C_3A ($3CaO.Al_2O_3$) which hydrates rapidly as follows -

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow \underbrace{3CaO.Al_2O_3.6H_2O}_{\text{Crystals.}}$$

In order to retard this flash set gypsum or POP is added during the pulverisation of cement clinkers. Gypsum interacts with C_3A to form insoluble complex sulfoaluminate which does not have quick hydrating property.

$$3CaO.Al_2O_3 + xH_2O + yCaSO_4.2H_2O \longrightarrow 3CaO.Al_2O_3.yCaSO_4.zH_2O$$

($y = 1-3$)
($z = 10-33$)



Schematic diagram of Setting and hardening of cement

Hardening of cement can be explained by two Theories :-

(i) Colloidal Theory (by Michaelis)

According to this theory during hydration silicates - gels are formed which undergo hardening.

(ii) Crystalline Theory (by Le Chatlier)

According to this theory, constitutional compounds after hydration forms crystalline products, these products undergo interlocking which is responcible for hardening.

* Questions asked in university examination.

* Explain the setting and hardening of cement. Also give reactions involve in it.

Decay of cement :- Cement is susceptible to attack by salty water and acidic solutions.

Decay of cement is due to -

(i) leaching out of free lime from it due to CO_2)

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

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O$$

(ii) hydrolysis of silicates and aluminates which also get dissolved out from cement structure.

Prevention :- Decay of cement can be minimized by coating it with epoxy resin paints.

In case of concrete pipes carrying sewage (which is normally alkaline) decay is due to attack on SiO_2 component. To overcome this surface is treated with SiF_4, which forms insoluble CaF_2 and controls decay.