CHAPTER:- CEMENT

Manufacture of Portland cement, vertical shaft kiln technology, Chemistry of setting & hardening.

Cement may be described as "a material possessing adhesive, cohesive properties and capable of bonding material like stones, bricks, building block etc."

The cements have property of setting and hardening under water by virtue of certain chemical reaction with it and are therefore called 'hydraulic cements.'

PORTLAND CEMENT:-

Portland cement is the most important & widely used cementing materials used for construction works. It was discovered in 1824 by Joseph Aspidin. It is so named, because a paste of cement with water on setting and hardening resembles in colour & hardness to Portland stone, a lime stone quarried in Dorset.

Portland cement is a type of cement, not a brand name. A number of special Portland cements are manufactured for specific uses. The most important of these are (i) White portland cement (ii) Rapid hardening cement (iii) Low-heat cement (iv) High alumina cement (v) Coloured cement (vi) Sulphate-resisting cement. etc.

Portland cement is also known as "magic powder." It consists primarily of compounds of lime, silica, alumina and iron. It forms a paste when mixed with water. This paste subsequently hardens and binds the aggregates (crushed rock, sand, gravels etc.) together to form a hard durable mass called concrete.

Manufacture of Portland Cement:-

Raw Material for Cement Manufacture:-

followings raw materials are required for manufacturing the cements

(1.) calcareous material (CaO) such as lime stone, chalk, marl etc.

(2.) Argillaceous material (Al_2O_3 and SiO_2) such as clay, shales, slate etc.

(3.) Powdered coal or fuel oil

(4.) Gypsum ($CaSO_4 \cdot 2H_2O$)

S. No.	Cement Constituent	% range by mass	Functions
[1.]	Lime (CaO)	60-69%.	Excess of lime reduces the strength of cement because it makes the cement to expand & disintegrate. Presence of lesser amount of lime than required also reduces the strength of cement & makes it quick setting.
[2.]	Silica (SiO_2)	17-25%.	Its higher % increases the strength & usually prolongs the setting time. High silica cement donot attain their full strength for a considerable period.
[3.]	Alumina (Al_2O_3)	3-8%.	Its higher % increases the strength and reduces the setting time.
[4.]	Iron oxide (Fe_2O_3)	2-4%.	It imparts characteristic grey colour, strength & hardness to the Portland Cement
[5.]	Magnesium oxide (MgO)	1-5%.	

[6.]	Sulphur trioxide (SO_3)	1-3 %.	It imparts soundness to cement when present in small amount.
[7.]	Alkali oxide ($Na_2O + K_2O$)	0.3-1.5 %.	It present in excess, causes the cement efforescent.
[8.]	Gypsum		It helps to retard the setting action of cement. It actually enhances the initial setting time of cement.

Manufacturing Process:-

It involves following steps - Crushing, mixing, burning, grinding and packing.

[1] Crushing:- It is done in primary crusher (which reduces the size of lime stone to an approximately 5-inch) & in secondary crusher (it further reduces the size to 3/4 inches).

[2.] Mixing:- Mixing of raw materials can be done either by (a) dry process or (b) wet process.

(a) Dry process:- The raw materials [lime stone (or chalk) and clay (or shale)] are crushed in gyratory crusher into roughly 2.5 cm. size pieces. Then, these are ground to fine powder in ball mills / tube mills. Each separate powdered ingredient is stored in seperate hopper. Then, the powdered materials are mixed in the required proportions to get dry raw mixture, which is stored in storage bins (called silos) and kept ready to be fed in a rotary kiln.

b) Wet process:- The calcareous raw materials [illegible] powdered & stored in big storage tanks, called silos. The argillaceous material (clay) is thoroughly mixed with water in wash mills, to remove any adhering organic matter etc. Powdered lime stone (from silos) and washed wet clay (stored in basins) are allowed to flow in a channel, in the right proportions. From channel, the two raw materials are led to 'grinding mills' where they are mixed intimately to form a paste called slurry. [Grinding operation is carried out either in tube mill or ball mill or both]. This slurry contains about 38 to 40% water. The slurry is finally stored in storage tanks & kept ready for feeding it to a rotary kiln.

Dry Process	Wet Process
[1.] It is adopted when the raw materials are quite hard.	[1.] It can be used for any type of raw materials.
[2.] Fuel consumption is low	[2.] fuel consumption is higher
[3.] Process is slow	[3.] Process is comparatively faster.
[4.] cement produced is of inferior quality.	[4.] cement produced is of superior quality.
[5.] cost of production of cement is less	[5.] cost of production of cement is somewhat higher.
[6.] On the whole, the process is costly.	[6.] On the whole the process is cheaper.
(7.) This process is not suitable when the principal raw material has an inherent moisture content 15% or above	[7.] This process has to be adopted in this case.

Burning:- Burning is done in rotary kiln, which is a steel tube about 2.5 to 3.0 m in diameter and 90 to 120 m in length, lined inside with refractory bricks. The kiln is laid in slightly inclined position. This rests on roller bearing, which are supported on columns of concrete. The kiln is capable of rotating at 1 r.p.m. about its longitudinal axis. A long hot flame is produced on burning of coal, which heats the interior of the kiln up to 1750°c temperature.

Process:- The corrected slurry is injected into the kiln at its upper end; while hot flames is forced into the kiln from the lower end. Due to slope & slow rotation of the kiln the materials move towards the hottest end at a speed of about 15 m per hour.

Chemistry:- (i) In the upper part of kiln, where the temp. is around 400°c, most of the water is the slurry gets evaporated. (DRYING ZONE)

(ii) In the central part of kiln, where the temp. is around 1000°c, lime stone of dry mix or slurry undergoes decomposition to form quick lime & CO_2; & later escapes out. The material forms small lumps called nodules. [CALCINATION ZONE]

$$CaCO_3 \rightleftharpoons CaO + CO_2 \uparrow$$

Lime stone Quick lime

(iii) In the lower part of the kiln, the temp. is between 1500°c to 1700°c. Here lime and clay of nodules undergo chemical interaction or fusion, yielding calcium aluminates and silicates. [CLINKERING ZONE]

$2CaO + SiO_2 \longrightarrow Ca_2SiO_4$

Dicalcium silicates (C_2S)

$3CaO + SiO_2 \longrightarrow Ca_3SiO_5$

Tricalcium silicates (C_3S)

$3CaO + Al_2O_3 \longrightarrow Ca_3Al_2O_6$

Tricalcium aluminate (C_3A)

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

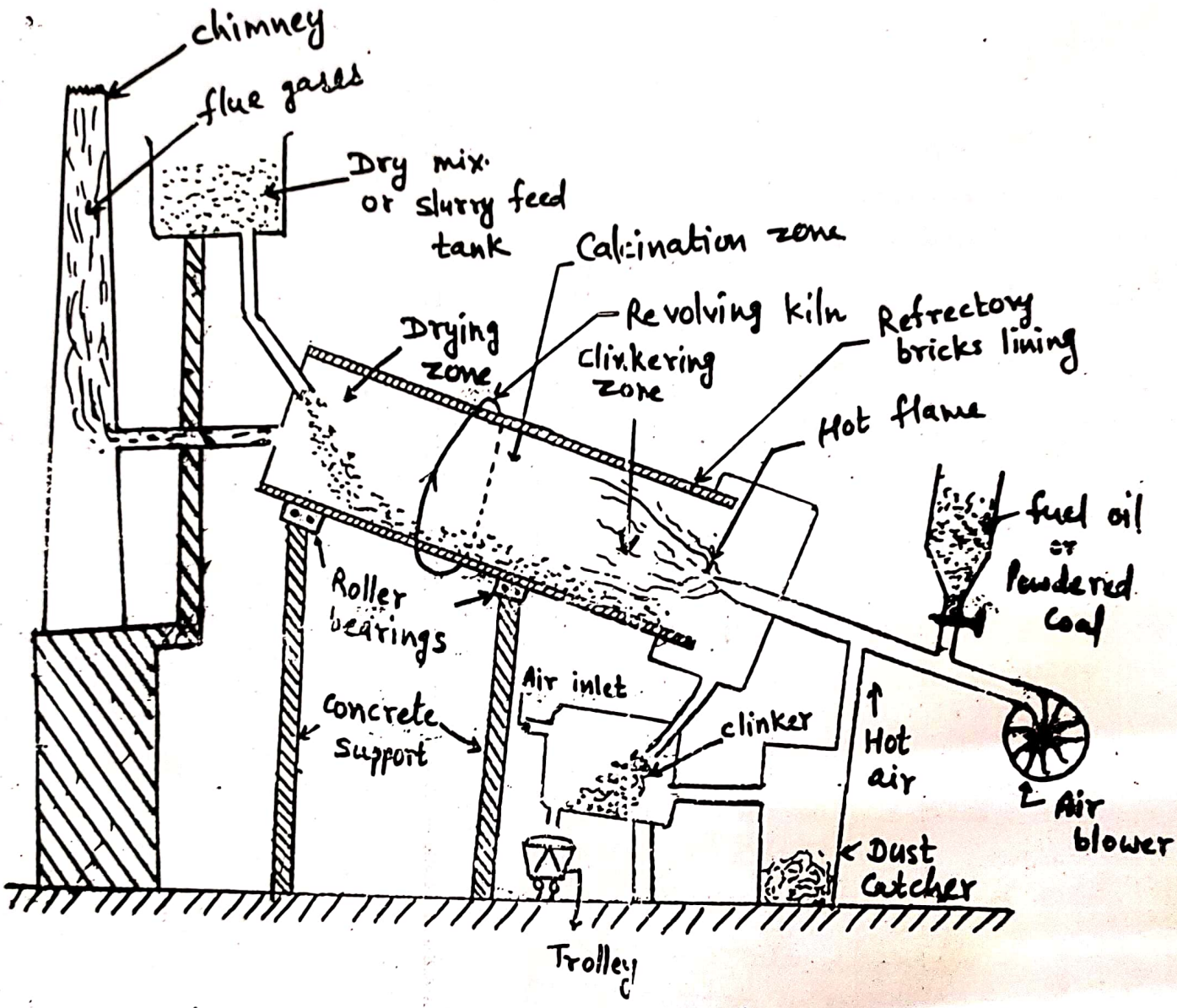
Tetracalcium aluminoferrite (C_4AF)

The aluminates & silicates of calcium then fuse together to form small (0.5 to 1 cm.) hard, greyish stones called clinkers.

These clinkers are very hot (1000°C) so cool air is admitted from opposite direction. Air counter blast cools the clinkers. Hot air so produced is used for burning powdered coal/oil. The cooled clinkers are collected in small trolleys.

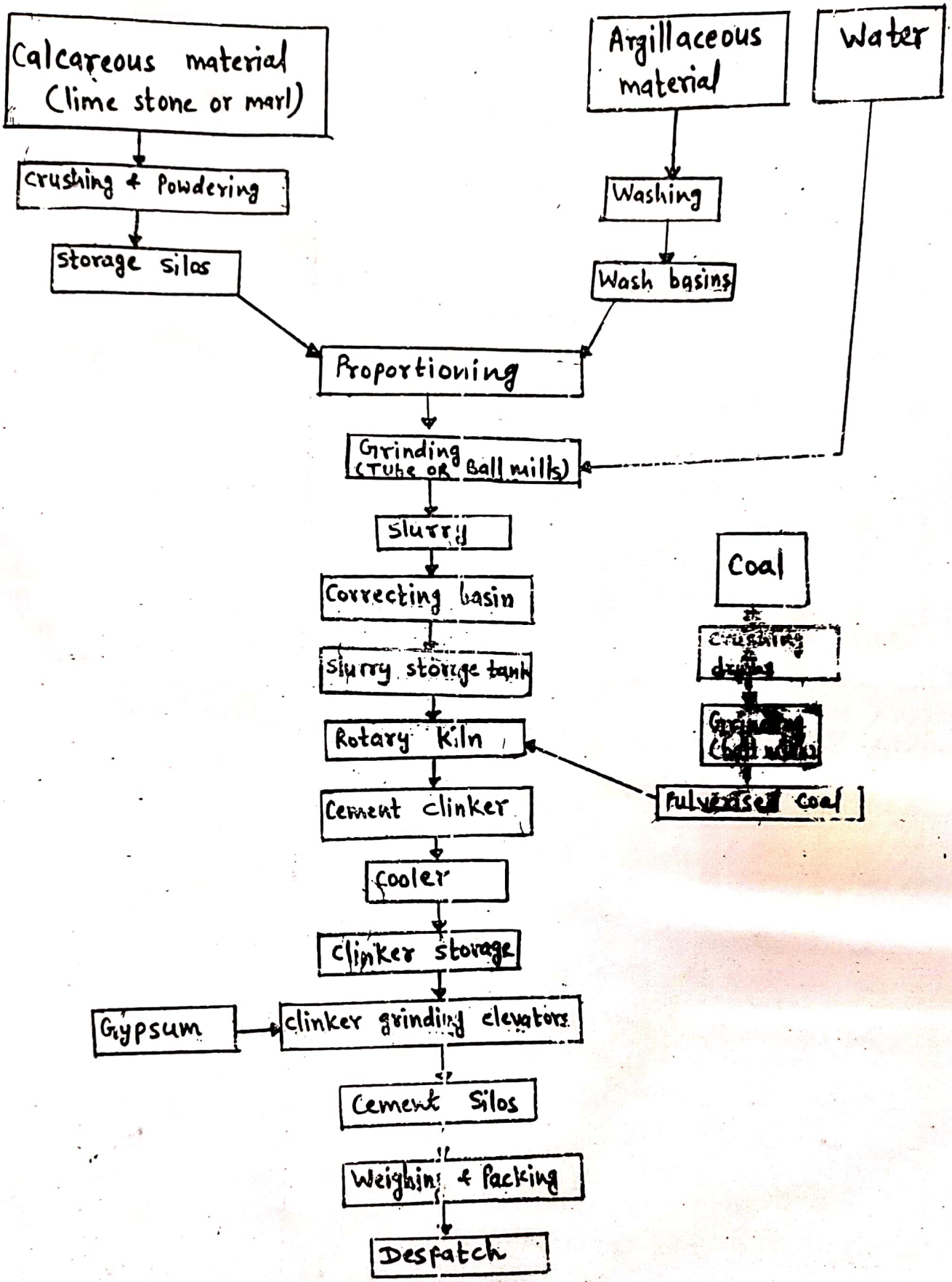
[4.] Grinding:- The cooled clinkers are ground to a fine powder in ball mills or tube mills. During final grinding, a small quantity (2-3%) of powdered gypsum is added so that the resulting cement does not set very quickly, when it comes in contact with water. Gypsum thus acts as a retarding agent for early setting of cement.

[5.] Packing:- The ground cement is stored in silos, from which it is fed to automatic packing machine. Each bag, usually, contains about 50 kg. of cement.



Rotary Cement kiln

FLOW DIAGRAM FOR WET PROCESS

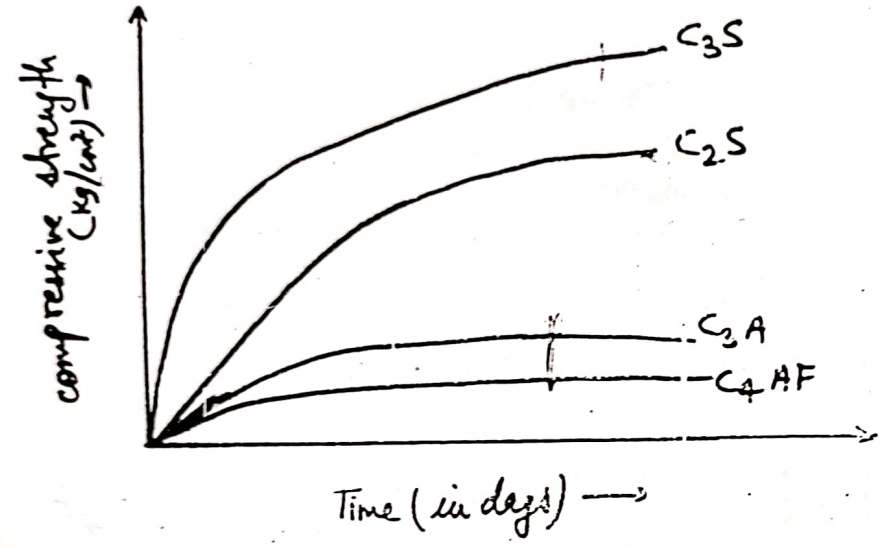


CHEMICAL CONSTITUTION OF PORTLAND CEMENT:-

The ingredients of Portland cement are not present in free state in the final products, but actually in the form of complex chemical compounds. Average compound composition of portland cement is:

Name of compounds	Average %	Setting time	Characteristics
[1] Tricalcium silicate $3CaO \cdot SiO_2$ [C_3S]	45 %	7 days	→ Medium Rate of hydration → Heat of hydration ≃ 500 KJ/kg. → Ultimate strength is highest
[2] Dicalcium silicate $2CaO \cdot SiO_2$ [C_2S]	25 %	28 days	→ Hydration is very slowly. → Lowest heat of hydration ≃ 250 KJ/kg. → Has quite low early strength but develops ultimate strength of slightly less than that of C_3S.
[3] Tricalcium aluminate (C_3A) $3CaO \cdot Al_2O_3$ [C_3A]	1 %	1 day	→ Undergoes hydration very quickly. → Heat of hydration is highest ≃ 880 KJ/kg. → Its early strength is good, but ultimate strength is quite low. So it is responsible for 'initial set' or 'flash set'
[4] Tetracalcium aluminoferrite $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ [C_4AF]	9%	1 day	→ Hydrates slowly. → Heat of hydration ≃ 420 KJ/kg. → Early strength & ultimate strength are poorest amongst all the constituents so does not contribute much to the strength of cement.

calcium sulphate ($CaSO_4$)	5%	–	–
calcium oxide (CaO)	2%	–	–
Magnesium oxide (MgO)	4%	–	–



SETTING AND HARDENING OF PORTLAND CEMENT :-

Setting is defined as stiffening of the original plastic mass while hardening is development of strength.

Cement when mixed with water gives soft plastic mass called "cement paste" & when this cement paste is allowed to stand, its sets to a hard rigid mass by a series of complex reactions involving hydration & hydrolysis. The first setting occurs with in 24 hours but the subsequent setting, hardening requires 15-20 days.

According to crystalline theory proposed by Le chatelier, the setting or hardening of cement is due to the interlocking of crystals formed during hydration.

According to colloidal theory of Michaelis, the hydration products of silicates form rigid cells & strength is developed because of hardening of gel.

The process of setting & hardening is now believed to be partly chemical change and partly physical. The chemical changes involve hydrolysis of constituents with heat changes, while physical change is gel formation followed by seperation of crystalline products.

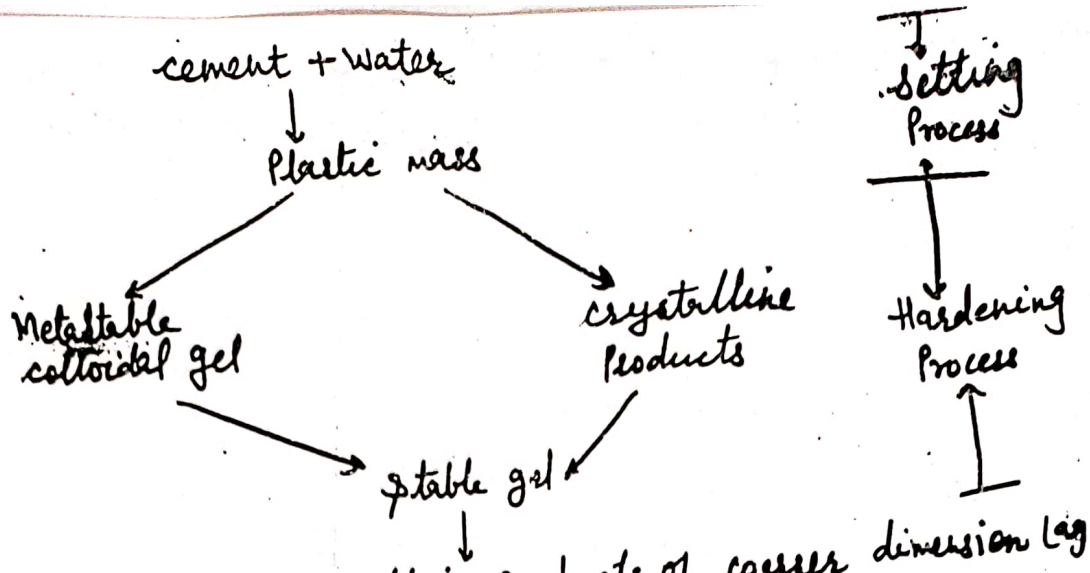
The process of solidification comprises three stages:

(1) Initial set [2.] Final set [3.] Hardening.

[1.] Initial set:- When cement is mixed with water a plastic mixture is formed which can moulded as desired as the action of setting take place gradually in 60 minutes or so. But with the time mixture begins to lose its plasticity marked by slight jelly like of cement paste. In this condition a standard needle may penetrate to a certain depth.

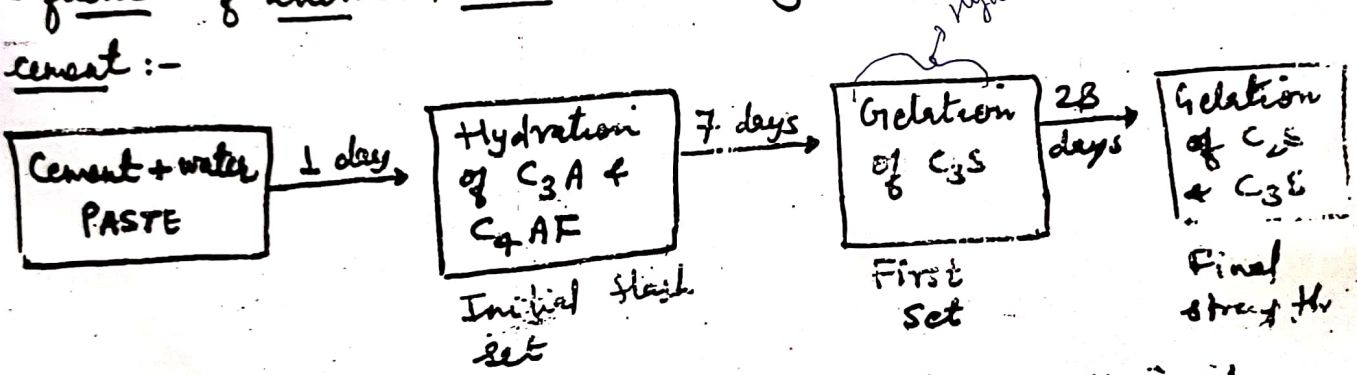
[2.] Final set:- It take place after few hours of mixing. Here concrete mixture can neither be moulded into any shape nor it can be remixed. In this condition standard needle can not penetrate in the cement mass at all due to high stiffness.

[3.] Hardening:- After final setting of the solid cement material begins to gain strength & it is this increase in strength which is known as 'hardening'. The hardening or development of strength depends on chemical combination of cement & water. The hardening of concrete stops as it is dried out.



Flow diagram for setting & hardening

Sequence of chemical reactions during setting & hardening of cement :-



Initial set of cement is due to the gel formation of aluminate. The development of early strength between 1 to 7 days is due to the hydration of tricalcium silicate & the further hydration of aluminate. The increase of strength between 7 to 28 days is due to hydration of dicalcium silicate & continued hydration of tricalcium silicates. (hydration and hydrolysis)

The reactions involves are :

(a) Hydration - gelling :-

(1) $3CaO \cdot Al_2O_3 + 6H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O$ [hydrated C_3A]

(C_3A)

(2) $2CaO \cdot SiO_2 + H_2O \longrightarrow 2CaO \cdot SiO_2 \cdot H_2O$

hydrated C_2S & C_3A are crystalline in nature.

(3) $4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 7H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + CaO \cdot Fe_2O_3 \cdot H_2O$

(C_4AF)

Hydrolysis :- chemical reaction with water.

(1) $3CaO \cdot SiO_2 + H_2O \longrightarrow 2\,CaO \cdot SiO_2 (aq.) + Ca(OH)_2 + heat\uparrow$

less water

(c) Role of Gypsum :-

As a result of hydration of C_3A, after the initial set, the paste becomes some what stiff. However, the added gypsum retards the dissolution of C_3A by forming insoluble calcium sulphoaluminate.

$$3CaO \cdot Al_2O_3 + y\,CaSO_4 \cdot 2H_2O + x\,H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot y CaSO_4 \cdot zH_2O \quad (z = 10\text{-}33)$$

(C_3A) Gypsum

This reaction prevents a high concentration of alumina in the cement solution thereby retarding the early initial set of the cement.

(d) final setting & hardening of cement is mainly due to formation of tobermorite gel - ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) & crystallization of $Ca(OH)_2$ & hydrated C_3A.

S No.	Dry Process	Wet Process
1.	It is costly and slow process.	It is relatively cheaper and faster process.
2.	Productions cost of cement is low, because fuel consumption low and shorten kiln is sufficient.	Productions cost is higher because relatively greater amount of fuel required to get kiln is required to expell at the excess of water.
3.	Cement produced is of inferior quality.	Cement produced is of superior quality, as more accurate control of consumption can be attained.
4.	This process is not suitable when the principal raw material has an inherent moisture content 15% or above.	This process has to be adopted in this case.

8.3 Vertical Shaft Kiln (V.S.K.)

Rotary kiln process (for wet as well dry method) is adaptable for large cement plants involving large capital investment, whereas vertical shaft kiln can be successfully adopted in mini cement plants which are being encouraged presently in the country. Such kilns are already working satisfactorily in many parts of the country and many such plants are under construction. The capacity of a mini cement plant may range from 40,000 to 150,000 tonnes per annum. The vertical shaft kiln technology (VSK technology) was used up to 1920 before the advent of rotary kiln technology. In 1950 again, the technology of VSK was revived with the inventions of pan noduliser (pelletiser). The uniform pellets so formed can be fed into the vertical shaft kiln and the cement can be produced of comparable quality. In order to obtain good quality clinkers, it is necessary to proportion the raw materials correctly. Presently, two methods of VSK technology are in use, *i.e.*, *(i)* 'black meal' process and *(ii)* 'fuel slurry' process.

(i) **Black Meal process :** In black meal process, the raw materials (limestone, clay, and other materials) are ground along with coal in the desired proportion and since the ground material is black in colour, the process in known as 'black meal' process. This ground material is then converted into pellets with about 15% water.

(ii) **Fuel slurry process :** In 'fuel slurry' process, the raw material is dry ground separately in a tube mill or roller mill and coal is ground wet separately with equal amount of water in another tube mill. The dry ground material and coal slurry are then made into pellets on a pelletiser.

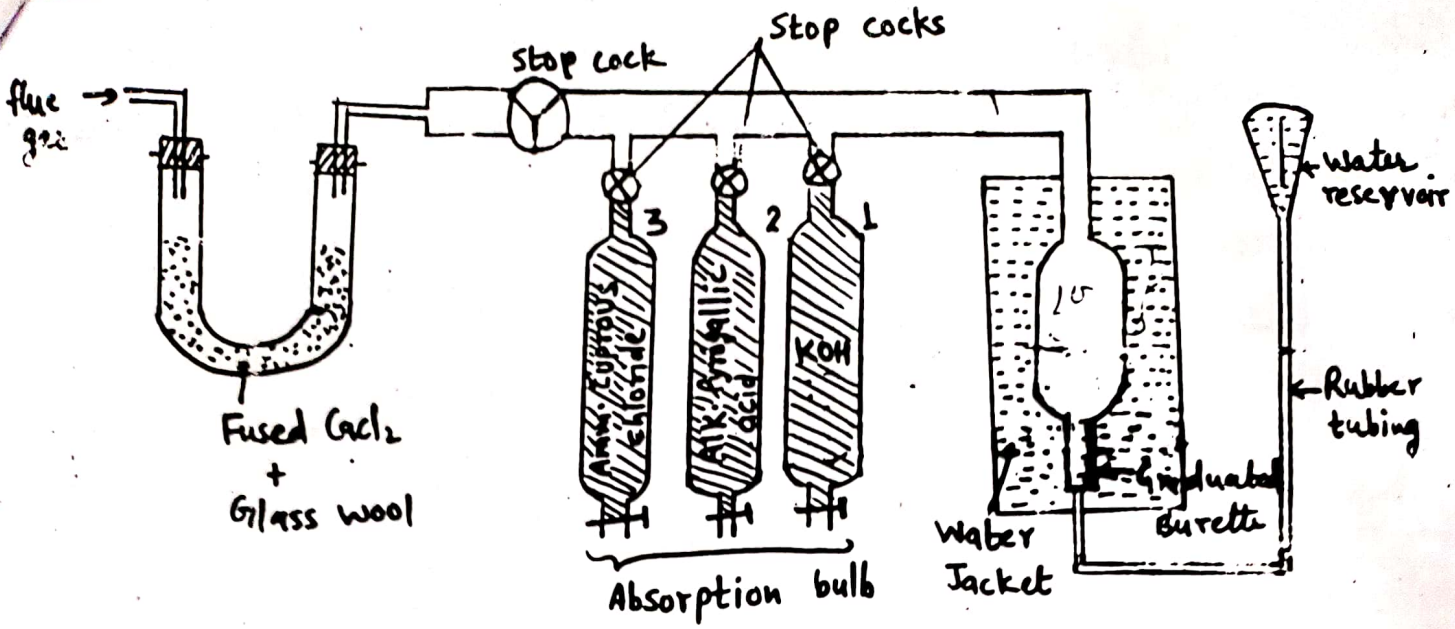
The pellets made by any of the processes (black meal or fuel slurry process) are then fed into the shaft kiln lined with refractory through a rotating feeder. The pellets pass through the kiln from the top downwords and get heated and sintered by the ascending hot gases. The sintered pellets are discharged from the bottom through a slowly rotating grate and cold air is blown through the discharge unit to cool the clinkers. The air gets heated in cooling the clinkers which is then utilized in combustion of coal present in the pellets. The clinkers are ground with 4-5% gypsum as in other cases. Vertical shaft kiln technology is believed to possess following advantges

(a) Since it utilizes pellets, there is no dust discharged into the atmosphere.

The various zones of reaction starting from the top of the kiln are:-

(i) Preheating zone (ii) calcining zone
(iii) Sintering zone (iv) cooling zone

LUE GAS ANALYSIS :-



ORSAT'S APPARATUS

The nature of chemical combustion can be well understood, if the products of combustion are analysed qualitatively & quantitatively. The mixture of gases mostly CO_2, CO & O_2 coming out of combustion chamber is called flue gas.

The analysis of flue gas is essential as it indicate about the efficiency of the combustion process. For instance, if the flue gas contains considerable amount of CO, it indicates that incomplete combustion is occurring which may due to lack of O_2 or air supply. If the flue gas contain considerable amount of O_2, it indicates that there is excess supply of oxygen or the combustion may be incomplete. Large amount of CO_2 indicates complete & efficient combustion of fuel. Any N_2 present in the fuel is not at all takes part in combustion It remain as such after combustion.

The analysis of flue gases is carried out with the help of orsat's apparatus.

It consists of a horizontal tube. At one end of this ... there is a three-way stop-cock & the other end is connected with a burette. The burette is graduated & surrounded by a water-jacket to keep the temperature of the gas constant during the experiment. The burette is connected in series to a set of three absorption bulbs, each through a seperate stop cock. The lower end of the graduated burette is further connected to a water reservoir with the help of rubber tube. The water level in the burette can be raised or lowered by raising or lowering the water reservoir containing water. The other end of horizontal tube which is connected to three-way stop cock is further connected to a U-tube. The U-tube is packed with fused $CaCl_2$ & glass wool for drying flue gas & for avoiding the incoming of any smoke particles respectively.

The first bulb has KOH to absorb CO_2; second bulb is filled with alkaline pyrogallol to absorb O_2; & third bulb is filled with ammonical Cu_2Cl_2 to absorb CO.

WORKING:- The whole apparatus is thoroughly cleaned, stoppers greased & then tested for air tightness. The absorption bulbs are filled with their respective solution. Then their stop cocks are closed. The water reservoir & jacket are filled with water. Air is first excluded from the burette by raising the water reservoir till the burette is completely filled with water. For the exclusion of air the three way stop cock should be opened to the atmosphere. Next, the flue gas to be analysed is drawn in by lowering the water reservoir & connecting the three way stop cock to flue gas supply. For better results, air from the capillary connecting tubes should be expelled by repeating the above process of sucking & expelling the flue gas by lowering & raising the water reservoir.

100 ml. of flue gas is carefully sucked in the burette for analysis. The three-way-stop-cock is then closed. The flue gas is forced in the bulb ① by opening its stop cock & raising the water reservoir. Bulb ① contains KOH solution which absorbs CO_2. For the complete absorption of CO_2, the flue gas is sent 2 or 3 times, again & again in bulb ①.

The unabsorbed gas is finally taken back in the burette & then stop cock for CO_2 absorption bulb is closed. The levels of water in the reservoir & burette are equalised & the volume of residual gas is noted. The decrease in volume gives the volume of CO_2 in 100 ml. of the flue gas sample. The volume of O_2 & CO are similarly determined by passing the flue gas through absorption bulbs ② & ③ respectively. The gas remaining in burette after absorption of CO_2, O_2 & CO is taken as N_2.

Precautions:-

① All the air should be expelled by lifting & lowering the reservoir repeatedly.

② Amount of CO in flue gas would be very small, it should be measured carefully.

③ It is quite necessary to follow the order of absorbing the gases: CO_2 first, O_2 second & CO last. because alkaline Pyrogallic acid can absorb both O_2 & CO_2 & ammonical Cu_2Cl_2 can absorb CO, O_2 & CO_2.