CEMENT

Cement: Cement may be defined as the powdered substances which initially have [illegible] flow when mixed with water or other liquid, but has the property of setting to a hard, solid structure in several hours with varying degree of strength and [illegible] properties.

□ **Portland cement:** Portland cement is physically may be defined as the strongly heated mixture of limestone and clay, when mixed with a small amount of water, set in a few hours to a hard stone like substances.

Portland cement chemically may be defined as the finely ground mixture of calcium aluminates and silicates of varying compositions, which hydrate when mixed with water to form a rigid, solid structure in few hours with superior compressive strength and better durability.

The portland cement is called portland cement because of the resemblance of this hardened cement to the natural stone occurring at Portland in England.

□ **Raw materials:** The essential raw materials for the manufacture of cement are lime-stone and clay, which supply all the four principal ingredients viz, CaO (calcium oxide), SiO_2 (silica), Fe_2O_3 (Iron Oxide) and Al_2O_3 (alumina). CaO and Fe_2O_3 are obtained from limestone, while SiO_2 and Al_2O_3 are obtained from clay.

There are two kinds of raw materials for the manufacture of portland cement. They are

(i) Calcareous materials and
(ii) Argillaceous materials

Calcareous materials: They supply lime. The following calcareous materials are used: Lime stone, chalk, Marl, Alkali waste. Calcareous materials should be such that they contain not less than 33% CaO and 3-4% SiO_2, Al_2O_3 and Fe_2O_3 combined.

Argillaceous materials: They supply silica, alumina and iron oxide. The following kinds of argillaceous materials are used – clay, shale, slate, Marl [illegible]. Argillaceous materials should be such that they have [illegible] Alumina.

II **Principle of production:** The raw materials required for the manufacture of Portland cement are calcareous materials, such as limestone, chalk, marl, alkali waste and argillaceous materials such as clay, shale, slate, blast furnace slag. In the process of manufacture of cement at first the raw materials are ground separately, then mixed with each other intimately in certain proportions depending upon their purity and composition and then burn in a kiln at a temperature of about 1300°-1500°C. At this temperature the raw materials partially fuses to form nodular shaped clinker (3-20mm). Then the clinker is cooled and ground in a ball mill to a fine powder after the addition of about 2-3% of gypsum. The powder obtained by using this process is known as portland cement.

II **Raw meal:** In the dry process, the raw materials are separately crushed and ground in suitable machine and dried. These are then mixed in proper proportions, pulverised in ball mills and finally homogenised by means of a compressed air mixing arrangement. The resultant mass is known as raw meal.

II **Raw slurry:** In the wet process, the limestone is crushed in a suitable mill to particles of suitable size and clay is washed with water in wash mills to remove foreign materials, and a slurry containing about 60% water is obtained. Crushed limestone and clay slurry are mixed in requisite proportions and then pulverised in a special type of ball mill. The resulting slurry containing about 40% water is called raw slurry.

II **Clinker:** It is the intermediate product in the process of manufacture of cement. In wet process, after crushing and then washing the raw materials, the resulting slurry is grinded first by ball mill and then by tube mill. Then the slurry is passed through a rotary kiln. Then finally the greenish black or grey coloured mass that is obtained is called clinker.

Composition / oxide composition of portland cement:

The approximate oxide composition of ordinary portland cement is as follows

- lime (CaO) — 60-67%
- Silica (SiO_2) — 17-25%
- Alumina (Al_2O_3) — 3-8%
- Iron oxide (Fe_2O_3) — 0.5-6%
- Magnesia (MgO) — 0.1-4%
- Alkalies (Na_2O, K_2O) — 0.4-1.3%
- Sulphuric anhydride (SO_3) — 1-3%

Clinker constituent

The principle constituent of portland cement's clinker are as follows—

(I) Dicalcium silicate ($2CaO.SiO_2$ — C_2S)

(II) Tricalcium silicate ($3CaO \cdot SiO_2$ — C_3S)

(III) Tricalcium aluminate ($3CaO \cdot Al_2O_3$ — C_3A)

(IV) Tetracalcium alumino ferrite ($4CaO.Al_2O_3 \cdot Fe_2O_3$) — C_4AF

(V) Some excess magnesia (MgO)

(VI) Some excess lime (CaO)

Use of Gypsum

Generally 2-3% gypsum is added to the clinker before grinding. The function of gypsum in cement is to slow down the initial setting time of the cement, so that it gets sufficiently hardened in less time.

Difference between Dry and Wet Process

Dry process	Wet process
① This process can only be used when raw materials are quite hard.	① This process can be used for hard as well as soft raw materials.
② In this process no water is added to the materials in grinding and thus no slurry is made.	② In this process water is added to the materials in grinding and thus slurry is made.
③ Mixture of crushed and ground raw materials is pulverised in ball mill.	③ Slurry is pulverised in ball mill.
④ This process is slow	④ This process is comparatively faster
⑤ This process is costly.	⑤ This process is comparatively cheaper.
⑥ cement produced is of low quality.	⑥ cement produced is of superior quality.
⑦ The fuel consumption is low	⑦ The fuel consumption is higher.
⑧ It is a modern process	⑧ It is an older process.
⑨ Heat is saved, more accurate in controlling and mixing	⑨ More heat is needed, controlling is not so accurate.

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Hydration of cement

Anhydrous cement compounds when mixed with water react with each other to form hydrated compound of very low solubility. The hydration of cement can be visulized in two ways

(i) Through solution mechanism

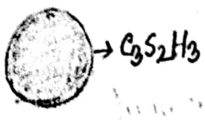
(ii) Solid state mechanism

(i) Through solution mechanism

It is happened the initial stage of hydration when large amount of hydration water is present. In this cement compounds dissolve and produce a supersaturated solution from which hydrated products get precipitated.

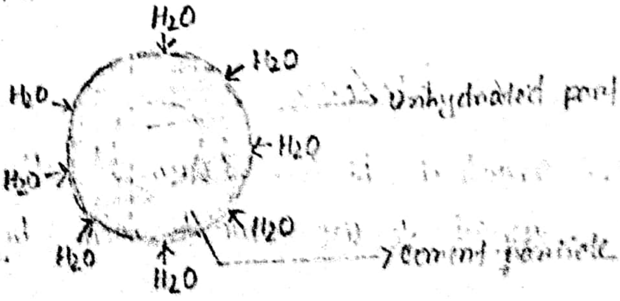
$$C_3S + H_2O \longrightarrow C_3S_2H_3 + Ca(OH)_2$$

The reaction of cement with water is exothermic. The reaction liberates a considerable quantity of heat which is called heat of hydration.



(ii). Through solid state mechanism

It is happened at the final stage of hydration, when the amount of water is quite low. In this, water attacks cement compounds in the solid state converting the compound into hydrated products starting from the surface and proceeding to the interior of the compounds with time.



II Hydration of calcium silicates of cement:

During hydration of cement, C_2S and C_3S hydrate and calcium hydroxides are formed.

Reactions

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3Ca(OH)_2$$

The corresponding weights involved are

$$100 + 24 \longrightarrow 75 + 49$$

Similarly,

$$2C_2S + 4H \longrightarrow C_3S_2H_2 + Ca(OH)_2$$

The corresponding weights involved are

$$100 + 21 \longrightarrow 99 + 22$$

In the above reactions $Ca(OH)_2$ is a undesirable product. It is seen that later reaction C_2S produce less $Ca(OH)_2$. So, it is useful to use cement with higher percentage of C_2S content.

☐ Hydration of calcium Aluminate of cement

Reactions,

$$C_3A + 6H \longrightarrow C_3AH_6$$

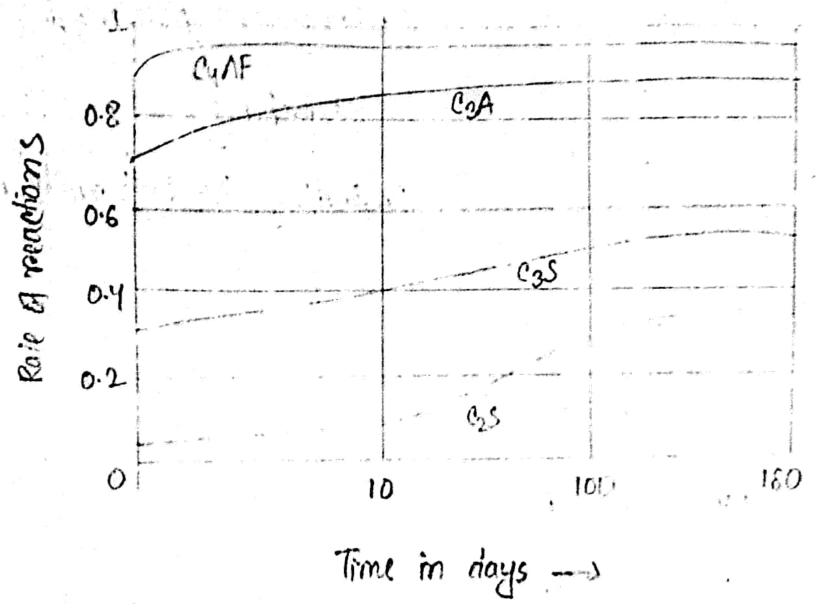
The product of hydration of C_3A i.e. C_3AH_6 is highly stable and may contribute to initial strength of concrete mass to small extent. But it is harmful. But it is harmful as it may be attacked by sulphates.

Again,

$$C_4AF + 6H \longrightarrow C_3AH_6 + Fe(OH)_3$$

The product of above reaction is less harmful than that of C_3AH_6 by sulphate. So it is useful to use cement with high amount of C_4AF content.

Effect of particle size on the rate of hydration

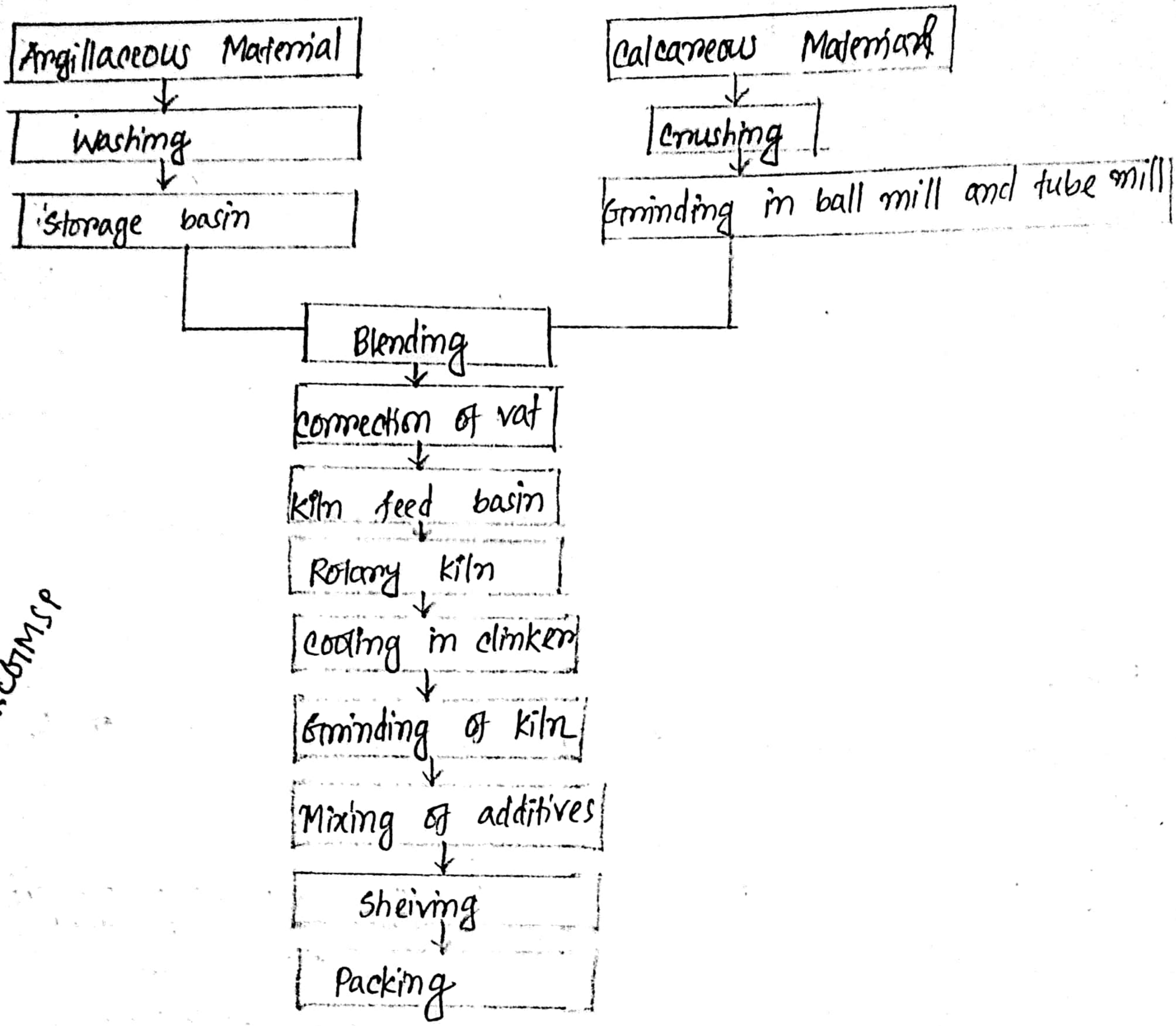


Relation

Effect of relative percentage of oxides in the raw material on the quality of cement :

Oxide composition percent	Calculated compound composition using Bogus equation per cent
$CaO \rightarrow 63$	$C_3S \rightarrow 54.1$
$SiO_2 \rightarrow 20$	$C_2S \rightarrow 16.6$
$Al_2O_3 \rightarrow 6$	$C_3A \rightarrow 10.8$
$Fe_2O_3 \rightarrow 3$	$C_4AF \rightarrow 9.1$
$MgO \rightarrow 1.5$	
$SO_3 \rightarrow 2$	
$K_2O + Na_2O \rightarrow 1$	

Industrial production of portland cement



Types of cement and testing of cement

Classification : Portland cement & Non portland cement.

⇒ ASTM classification based on composition and uses:-

Type I → for use in general concrete construction at the special properties specified for types II, III are not required. [ordinary portland cement

Type II : For use in general concrete construction to moderate sulphate action or where moderate heat of hydration is required. [Moderate heat of hardening cement]

Type III : For use when high early strength is required [Rapid hardening cement]

Type IV: For use when low heat of hydration is required [low heat cement]

Type V: For use when high sulphate resistance is required [sulphate resisting cement]

I **Rapid Hardening Cement:**

Rapid hardening cement is an ordinary portland cement with higher percentage of C_3S and lower percentage of C_2S. It's specific surface is not less than 3250 sq.cm. per gram.

Recommended application:

① In - Prefabricated concrete construction.

② where formwork is required to be removed early for re-use elsewhere.

③ cold weather construction.

II **Extra rapid hardening cement** is a rapid hardening cement intergrinding $CaCl_2$ which should not exceed 2% by weight of the rapid hardening cement. It's specific surface is obtained between 4000 to 5000 sq.cm/gm. The size of most of the particles are generally less than 3 microns.

Application:

Extra rapid hardening cement is used in cold weather construction.

Quick setting cement is an ordinary portland cement with higher percentage of C_3A and reduced percentage of $CaSO_4$. It is used in under water construction where pumping is involved.

Sulphate attack: The calcium hydroxide also reacts with sulphates present in soils or water to form calcium sulphate which further reacts with C_3A and cause deterioration of concrete, which is known as sulphate attack.

How sulphate attack occurs in concrete ~~cement~~ structure?

Ordinary portland cement is susceptible to the attack of sulphates, in particular to the action of $MgSO_4$. Sulphates react both with the free $Ca(OH)_2$ in set cement to form $CaSO_4$ and with hydrate of calcium alluminate which is approximately 227% of the volume of the original alluminates. Solid sulphate donot attack the cement components. Sulphates in solution permeate into hardened concrete and attack $Ca(OH)_2$, hydrated calcium aluminate and even hydrated silicates.

This above is known as sulphate attack. It is greatly accelerated if accompanied by alternate wetting and drying which normally takes place in marine structures in the zone of tidal variations.

Sulphate resisting cement:

To remedy the sulphate action the use of cement with low C_3A content is found to be effective. Such cement with low C_3A and comparatively low C_4AF content is known as sulphate resisting cement. In other words, this cement has a high silicates content. The specification generally limits the C_3A content to 5 percent. IS code limits the total content of C_4AF and C_3A as follows.

Recommended application:

(i) concrete to be used in marine construction.

(ii) concrete to be used in foundation and basement

(iii) concrete to be used in fabrication of pipelines to be buried in marshy region or soil containing SO_4^{2-}

(iv) concrete to be used in sewage water treatment plant.

□ **Bound water:** 23% by weight of water is required to combine with cement compound is known as bound water.

□ **Gel water:** Beyond chemical reaction 15% of water by weight of cement is also required to occupy the gel pores within the hydratent products is known as gel water.

Mortars and concrete

Cement can not be used alone for construction work as it is very sensitive to moisture and many internal stresses are depeloped in it. These stresses cause cracking and reduction in strength. In order to avoid these defects in cement, it is mixed with sand and stone and in this way it is diluted and stabilized. Two forms of such a construction material are here given

(i) **Mortars:** These are mixture of cement and sand and occasionally other fine aggregates below 3/16 in mesh size. They are used for bonding in masonary and as surface covering also.

(ii) **Concrete:** It is a mixture of cement, sand (below 3/16 in mesh size) and coarse aggregates (above $\frac{3}{16}$ in mesh size). The mixture is made into a solid mass.

The common proportions for cement, sand and coarse aggregate are –

ⓐ 1 : $1\frac{1}{2}$: 3

ⓑ 1 : 2 : 4

ⓒ 1 : 3 : 6

Reinforced concrete : Concrete has high compressive strength and relatively low tensile strength. Concrete can resist load which tend to crush it, However it is relatively low in strength to forces which tend to bend it or pull it apart. that is concrete has low tensile strength. so in order to impart tensile strength to concrete another form of concrete is called reinforced concrete.

Reinforced concrete is ordinary concrete reinforced with steel rods or heavy wire mesh. On setting, the concrete adheres very strongly to the reinforcements. The reinforced concrete can withstand not only high tensile strength but also high compressive stresses.

Testing of cement :

(i) Field Test

(ii) Laboratory Test

Following test are conducted in Laboratory

(i) Fineness Test

(ii) Setting time Test

(iii) Strength Test

(iv) Soundness Test

(v) Heat of Hydration test

(vi) Chemical composition Test.