hydrated which have less solubility. Hence they are precipitated as insoluble gels or crystals. These have the ability to surround sand, crushed stones (in mortars on concretes) on other inert materials and bind them very strongly.

The physical changes occurring in the setting and hardening of cement may be summarized diagrammatically as follows :

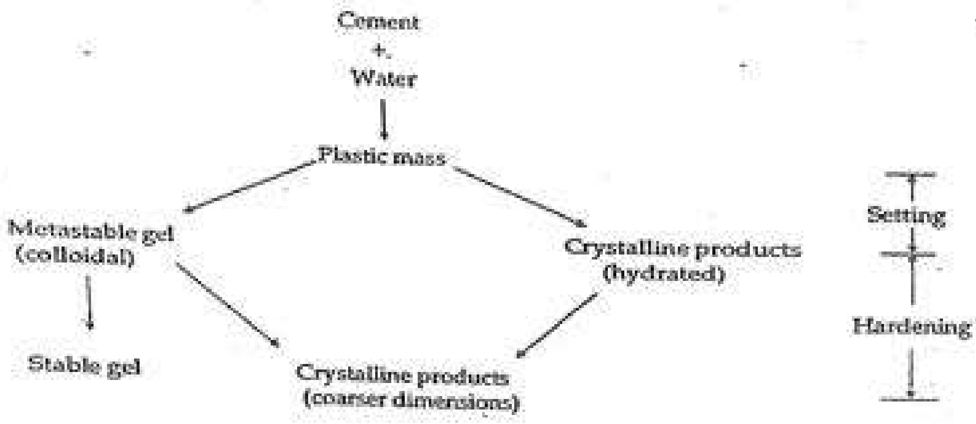


Fig. 3. Schematic diagram of setting and hardening of cement.

Hardening of cement can be explained on the basis of two theories :

(*i*) ***Colloidal theory*** (*by Michaelis*). According to this theory, during hydration silicate gels are formed which undergo hardening and are responsible for the hardening of cement.

(*ii*) ***Crystalline theory*** (*by Lechatlier*). According to this theory, constitutional compounds after hydration form crystalline products. These crystalline products undergo interlocking which is responsible for hardening of cement.

Thus, it can be concluded that setting and hardening of cement is due to the formation of interlocking crystals reinforced by the rigid gels formed by the hydration and hydrolysis of the constitutional compounds.

Stiffening of a concrete mixture with little evidence of significant heat generation is known as *false set*. Further mixing without additional water can restore plasticity in such cases.

In some cases, cement also exhibits a *flash set*. In these cases the cement has hydrated and further remixing will do no good.

Most portland cements exhibit initial set in about 3 hours and final set in about 7 hours. If the cement sets too slowly valuable construction time would be lost. A cement used in concrete must not set too fast as it requires some time to be placed and finished. The rapid set makes the material unworkable.

The main constituents of cement, their percentage composition and characteristic property they impart to cement are summarized in Table 2 :

The behaviour of the cement can be altered by *modifying the relative percentages* of these compounds, as each of the components *exhibits a particular behaviour.*

Tricalcium silicate (C_3S). It is largely *responsible for initial set and early strength* as it hardens rapidly as per the reaction shown below :

$$3\,CaO\,.\,SiO_2 + xH_2O \longrightarrow \underset{\text{Crystals}}{Ca(OH)_2} + \underset{\textit{Hydral gel}}{2CaO\,.\,SiO_2\,(x-1)\,H_2O} + \textit{Heat}$$

The hydral gel thus formed is responsible for the binding action between the aggregates.

Dicalcium silicate (C_2S) hardens slowly, and its *effect on strength occurs at ages* beyond one week. This is due to its *slower rate of reaction with water*

$$2CaO\,.\,SiO_2 + xH_2O \longrightarrow \underset{\textit{tobermorite gel (with high surface area)}}{2CaO\,.\,SiO_2\,.\,xH_2O}$$

However, if moist curing is continued, the later strength *after about 6 months* will be greater for cements with a higher percentage of C_2S.

Tricalcium aluminate (C_3A) is the first compound *to hydrate and it contributes* to strength development in the first few days.

$$3CaO\,.\,Al_2O_3 + 6H_2O \longrightarrow \underset{\text{Hydrated Tricalcium aluminate}}{3CaO\,.\,Al_2O_3\,.\,6H_2O} + 880\ kJ/kg$$

The above reaction is highly exothermic. Cements made with *low* C_3A contents usually generate less heat, develop higher strengths, and *show greater resistance* to sulphate attacks. In general, C_3A is least desirable component because of (*a*) its high heat generation and (*b*) its reactiveness with soil and water *containing* moderate to high sulfate concentrations.

The presence of gypsum in the cement helps to retard the speed of the initial set. This is due to the formation of calcium sulphoaluminate (by the reaction between gypsum and C_3A) which does not show any tendency to rapid hydration.

$$\underset{C_3A}{3CaO\,.\,Al_2O_3} + \underset{\text{Gypsum}}{x\,CaSO_4\,.\,2\,H_2O} \longrightarrow \underset{\substack{\text{Tricalcium sulphoaluminate}\\ \text{where } x\,=\,32}}{3CaO\,.\,Al_2O_3\,.\,x\,CaSO_4\,.\,2H_2O}$$

The tetracalcium alumino ferrite (C_4AF) *compound* assists in the manufacture of portland cement by allowing lower clinkering temperature. Even though it hydrates very rapidly, it contributes very little to the strength of concrete.

$$4CaO\,.\,Al_2O_3\,.\,Fe_2O_3 + 7H_2O \longrightarrow 3CaO\,.\,Al_2O_3\,.\,6H_2O + CaO\,.\,Fe_2O_3\,.\,H_2O$$

3.3 Setting and Hardening of Cement

When water is mixed with cement paste to form a fluid paste, hydration of cement takes place. The mixture eventually becomes stiff and then hard. This process is known as *setting*. After hydration, anhydrated compounds become

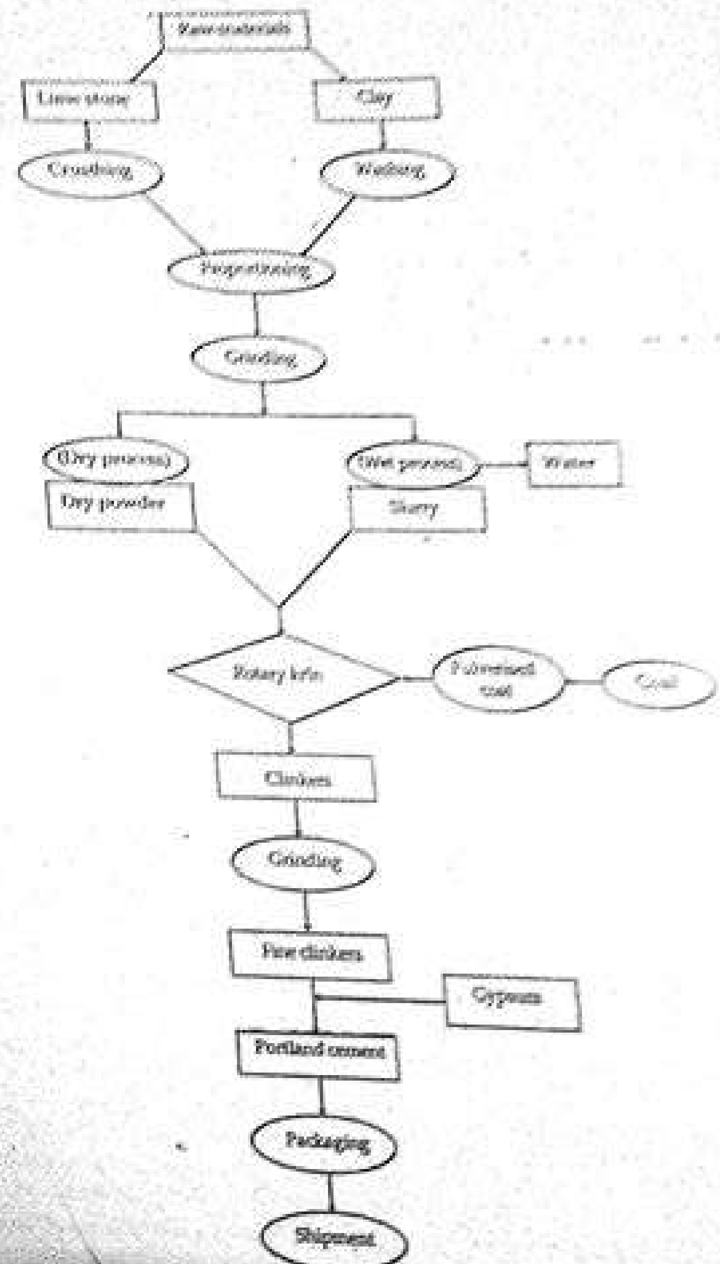


Fig. 2. Flow diagram for the manufacture of portland cement.

(a) *The drying zone.* Here the temperature is moderate (100–500 °C) and this zone is located at upper one-fourth of the length of the kiln. This zone is known as drying zone, because the moisture is driven out and the materials get heated.

(b) *Calcination zone.* Its temperature is about 1000 °C and it is the middle portion of the kiln. In this zone, CO_2 is expelled from lime-stone, quick-lime (CaO) is formed in the form of small lumps, called nodules.

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

(c) *Burning Zone.* Its temperature is about 1400 – 1500 °C and is the bottom and hottest portion of the kiln. In this zone, mixture melts and forms little rounded pasty masses of about the size of the peas which are called *clinkers*. The clinker produced is greenish black or black in colour and has rough textured. Its size makes it relatively inert in the presence of moisture. In this zone, lime and clay undergo fusion yielding calcium aluminates and silicates *viz* :

$$2CaO + SiO_2 \longrightarrow 2CaO\,.\,SiO_2 \qquad (C_2S);$$

$$3CaO + SiO_2 \longrightarrow 3CaO\,.\,SiO_2 \qquad (C_3S);$$

$$3CaO + Al_2O_3 \longrightarrow 3CaO\,.\,Al_2O_3 \qquad (C_3A);$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow 4CaO\,.\,Al_2O_3\,.\,Fe_2O_3 \qquad (C_4AFe).$$

(iv) *Grinding.* From clinker storage the material is transported to final grinding where it is ground to the requisite fineness according to the class of the product. Finely ground clinker sets very fast by absorption of moisture from the atmosphere. To control the setting time of the portland cement (when it is mixed with water) approximately, 2 to 3% gypsum ($CaSO_4 . 2H_2O$) is added.

The mixture of clinker and gypsum powder is known as portland cement. It is stored in silos from which it is bagged or loaded for shipment.

The flow diagram for the manufacture of portland cement is shown in Fig. 2.

Notes :

- The portland cement will retain its cementing quality until it comes in contact with moisture. Hence, it should be stored in a dry and airtight location.
- When bagged cement is in storage for long durations it sometimes acquires a *'warehouse pack'*. This can usually be corrected by rolling the bag on the floor.
- Portland cement should be free of lumps and free flowing when used. It is advisable not to use a cement which contains lumps that cannot be easily broken up.

3.2 Chemical Composition of Portland Cement

Portland cements are composed of following four basic chemical compounds :

S. No.	Name	Chemical formula	Abbreviation
1.	Tricalcium silicate	$3\,CaO\,SiO_2$	C_3S
2.	Dicalcium silicate	$2\,CaO\,SiO_2$	C_2S
3.	Tricalcium aluminate	$3\,CaO\,Al_2O_3$	C_3A
4.	Tetracalcium aluminoferrite	$4\,CaO\,Al_2O_3\,Fe_2O_3$	C_4AFe

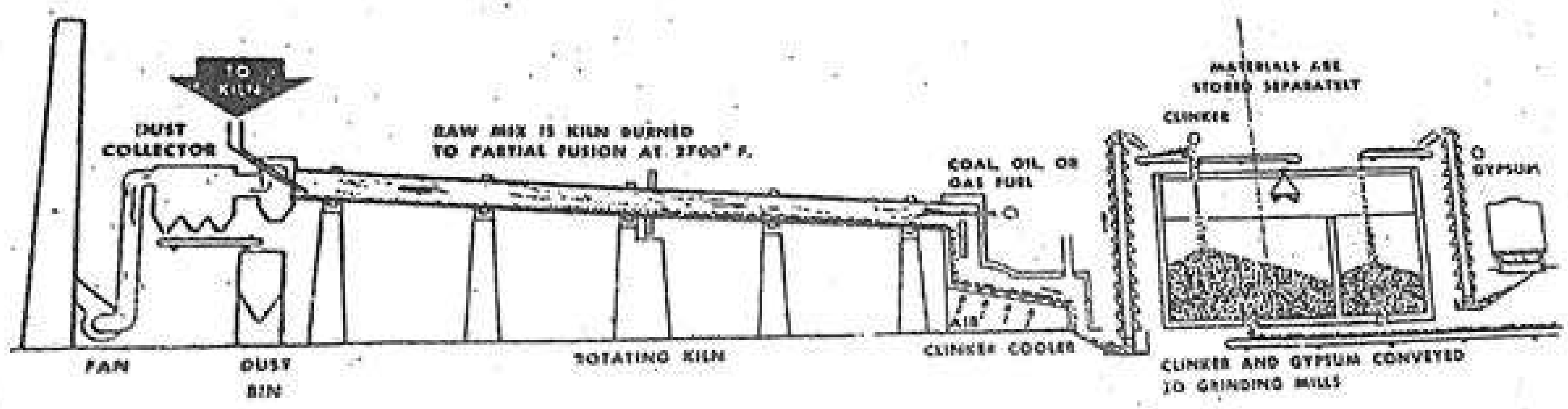


Fig. 1.. (c) Burning : Burning changes raw mix chemically into cement clinker.

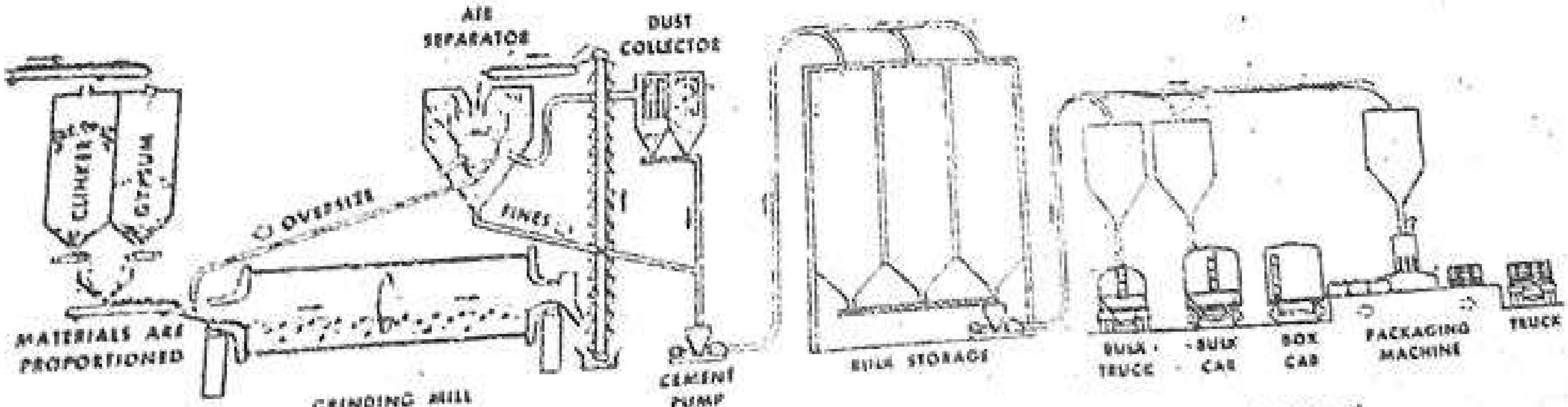


Fig. 1. (d) Grinding : Clinker with gypsum added is ground into portland cement and shipped.
Manufacture of portland cement.

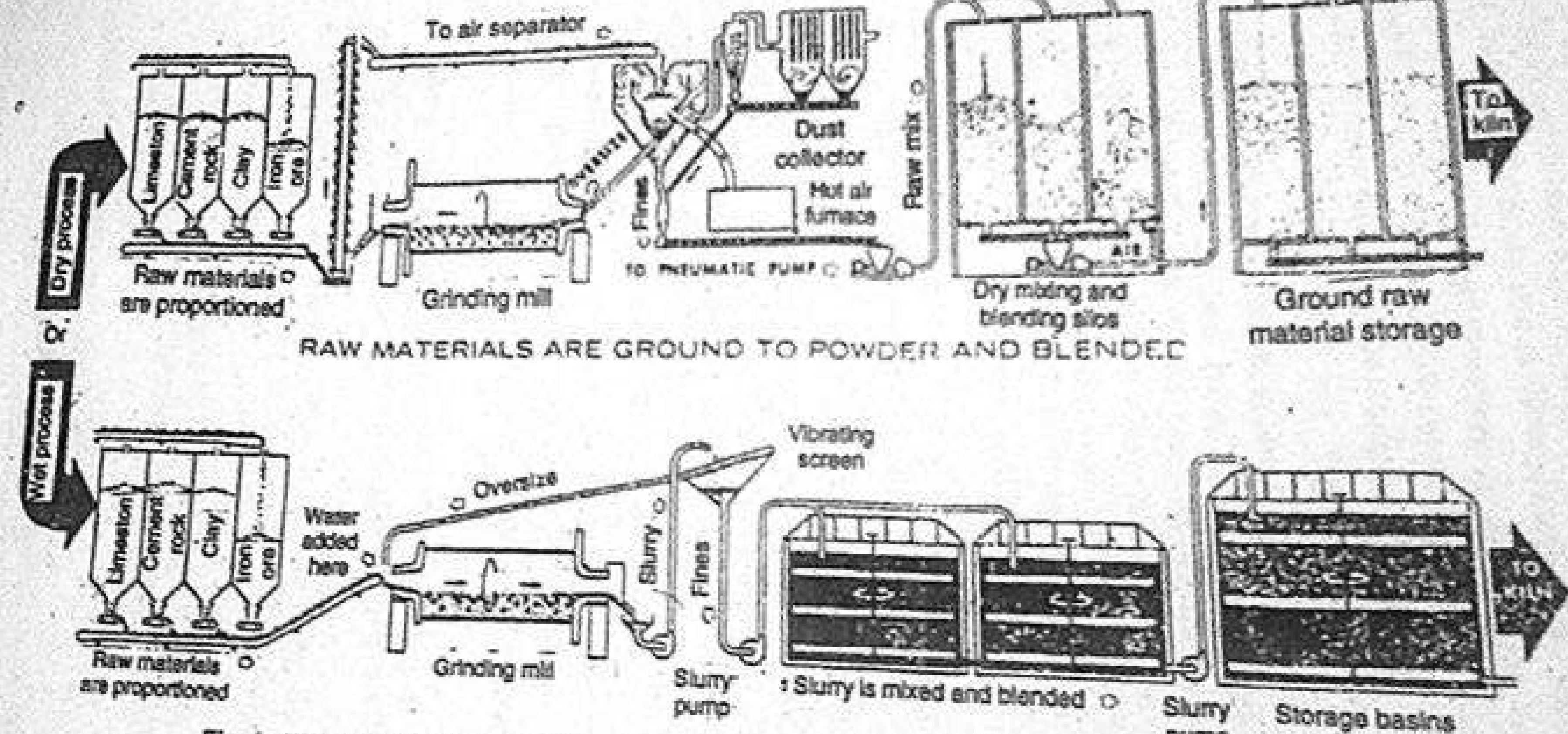


Fig. 1. (b) Mixing : (Raw material are ground, mixed with water to form slurry and blended).

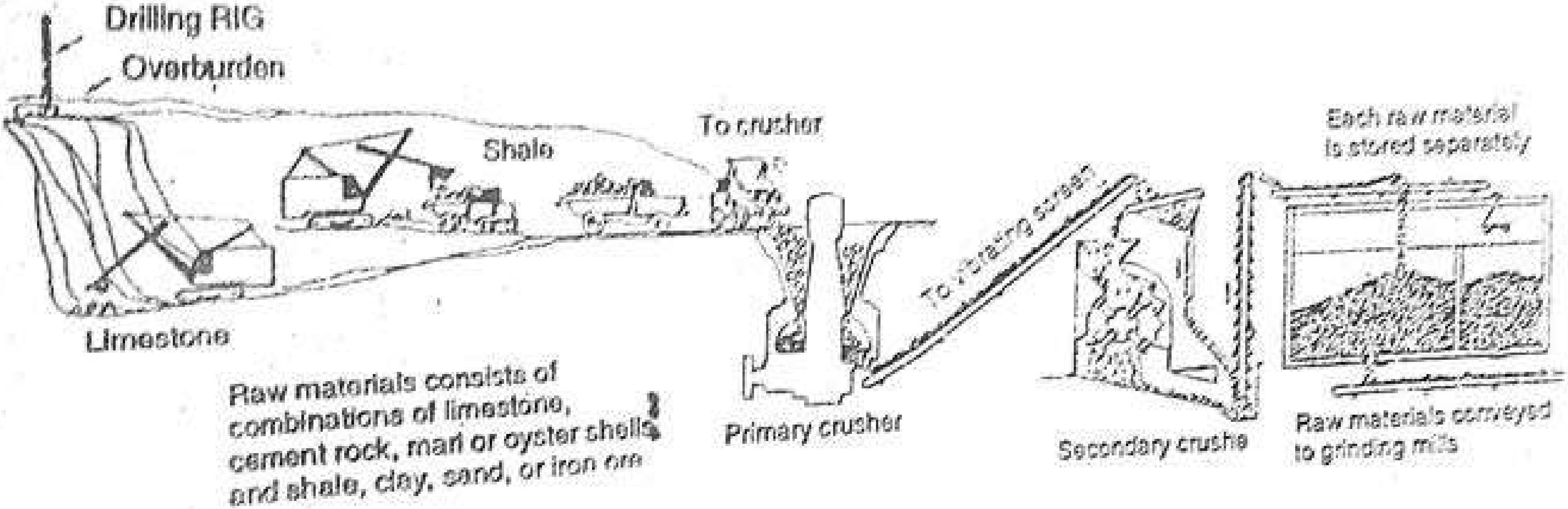


Fig. 1. (*a*) Crushing : stone is first reduced to 5-in. size, then 3/4-in. and stored.

(*a*) *The lime* (CaO) *component* (*i.e.* calcareous materials such as Aragonite, Calcite, Marl, Shale and limestone) ; (*b*) *The silica* (SiO_2) *component* (*i.e.*, siliceous materials such as clay, marl, shale and sand) ; (*c*) *The alumina* (Al_2O_3) *component* (*i.e.*, Argillaceous materials such as alumiri-um-ore refuse, caly, fly ash and shale) ; (*d*) *The iron* (Fe_2O_3) *component* (*i.e.* Ferriferous materials such as clay, iron ore, mill scale etc.)

Manufacturing process. The manufacture of portland cement involves the use of skills of engineers, chemists and technicians to ensure a uniform product. The actual manufacturing involves the following operations :

(*i*) ***Crushing***. It is done in primary crusher (which reduces the size of limestone to an approximately 5-in) and in secondary crusher (it further reduces the size to 3/4-in).

(*ii*) ***Mixing***. It begins with the acquisition of raw materials such as limestone, sand and clay. These are mixed either by the dry process or by the wet process. The raw materials which are stored in the bins are first proportioned and then delivered to the grinding mill. The *dry process* produces a fine ground powder. It is stored in bins. The *wet process* (in the presence of water) results in a slurry, which is mixed and pumped to storage basins.

(*iii*) ***Burning***. Both dry and wet processes feed rotary kilns where burning results in actual chemical changes. The rotary kiln is a long steel cylinder with length 30-160 metres and diameter 2-4 metres. Its inside surface is lined with fire brick refractory. It is slightly inclined downwards towards the exist end. It can be rotated at desired speeds as it is mounted on rollers. The material is fed in the rotary kiln from the upper end. As the kiln rotates, the material passes slowly from the upper to the lower end at a rate controlled by the slope and speed of rotation of the kiln. The kiln is heated (using solid, liquid or gaseous fuel) from the lower end. The upper end is cooler. As the material passes through the kiln, its temperature is raised to the point of clinkering temperature where the actual chemical reactions take place. In fact, there are different zones in the rotary kiln, viz.

Table 1. *Pros and Cons of dry and wet Processes*

	Dry Process	*Wet Process*
1.	It is a slow and costly process.	It is comparatively faster and cheaper process.
2.	Cost of production of cement is less, as the fuel consumption is low. Shorter kiln is sufficient.	Cost of production is somewhat higher because of the higher fuel consumption. As longer kiln is needed to drive off the excess water.
3.	The quality of cement produced is inferior.	The quality of cement produced is somewhat superior, as more accurate control of composition can be attained.
4.	This process is adopted when the raw materials are quite hard.	This process is preferred when the raw materials are soft.
5.	This process is not suitable when the principal raw material has an inherent moisture content of 15% or more, as it is uneconomical to drive away the excessive quantity of moisture.	This process has to be adopted in this case.

(x) Compressive strength :
After three days : ≥ 1600 lb/sq. inch
After seven days : ≥ 2500 lb/sq. inch

(xi) Tensile strength :
After three days : ≥ 300 lb/sq. inch
After seven days : ≥ 375 lb/sq. inch

3.5 Physical Properties of Portland Cement

(i) ***Fineness.*** It affects the hydration of cement. For a given weight of cement, the surface area of the grains of a fine-ground cement is greater than for a coarse-ground cement. Hence, hydration process occurs more rapidly in a fine-ground cement as water is in contact with more surface area. The cement should not be ground too finely because there is a possibility of prehydration due to accidental contact with moisture vapour during manufacturing and storage. This results in loss in cementing properties of the material.

In general, the finer a cement is ground, the higher the heat of hydration and resulting accelerated strength gain.

(ii) ***Soundness.*** It is the ability of a cement to maintain a stable volume after setting. A sound cement resists cracking, disruption and eventual disintegration of the material mass. An unsound cement has excessive amounts of free lime which is enclosed in cement particles. After the cement has set, when the moisture reaches the lime, lime expands with considerable force, disrupting the set cement.

Table 2 : *The main constituents, their percentage composition and their Influence on the properties of portland cement*

S. No.	Cement Constituent	% range by mass	Functions
1.	Lime (CaO)	60–69	Too little lime reduces strength of cement if its content is high. It gives high early strength but generally increases the setting time. Too high a % of lime produces cement of unsound quality and makes it liable for disintegration.
2.	Silica (SiO_2)	17–25	Its higher % increases the strength and usually prolongs the setting time. High silica cement do not 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 and 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 Oxides ($Na_2O + K_2O$)	0.3–1.5	If present in excess, causes the cement efforescent.

3.4 I.S.I. Specifications of Portland Cement

Specifications for ordinary portland cement as per Indian standard : 269-1975, are given below :

(*i*) Lime saturation factor $\left[\dfrac{CaO - 0.7\, SO_3}{2.8\, SiO_2 + 1.2\, Al_2O_3 + 0.65\, Fe_2O_3}\right] = 0.66 \text{ to } 1.02$

(*ii*) The ratio $\dfrac{Al_2O_3}{Fe_2O_3}$ shall not be less than 0.66

(*iii*) Insoluble residue should not exceed 2%

(*iv*) The weight of magnesia (MgO) : should not exceed 6%

(*v*) Total sulphur contents, calculated as sulphuric anhydride (SO_3) shall not be more than 2.75%

(*vi*) Loss on ignition shall not exceed 4%

(*vii*) Fineness not to exceed 10%, after sieving the residue (by weight) on B.S. 170-mesh test sieve.

(*viii*) Setting times : Initial = 30 minutes
Final = 10 hrs.

(*ix*) Heat of hydration :
After seven days : ≤ 65 cal/gm
After twenty Eight days : ≤ 75 cal/gm

(b) ***Puzzolana Cement***. It is oldest cement invented by Romans. It was used by them in making concrete for the construction of walls and domes.

Preparation : This is made by mixing and grinding of natural puzzolana and slaked lime. Natural puzzolana is deposit of volcanic ash produced by rapid cooling of lava. Lava in turn is a molten mixture of silicates of calcium, iron and aluminium.

Puzzolana cements form hydraulic cementing materials.

Properties. They also possess hydraulic properties.

Applications. They are first mixed with portland cements and then used for different applications.

(c) *Slag Cement*

Preparation. It is made from hydrated lime and blast furnace slag. A mixture of calcium and aluminium silicates (*i.e.*, blast furnace slag) is granulated by pouring it into a stream of cold water. Subsequently, it is dried and mixed with hydrated lime. Then the mixture is pulverized to fine powder. Sometimes, accelerator like clay, salt or caustic soda are added to hasten the hardening process.

Properties :

(*i*) Slag cements are slow setting,

(*ii*) They are poor in abrasion-resistance and

(*iii*) They have lower strength.

Applications. Because of the above shortcomings, slag cements have very limited applications. It is used for making concrete in bulk construction.

(d) ***Portland Cement***. It is made by calcining (at about 1500°C) an intimate and properly proportioned mixture of clay and lime containing raw materials. After calcination, retarder like gypsum is added.

Gypsum

It is discussed in detail in the following sections.

3 PORTLAND CEMENT

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, gravel, etc.) together to form a hard durable mass called concrete. Thus, cement is one ingredient of concrete.

William Aspdin is generally recognized as the father of the modern portland cement industry. Because in 1824, he produced an improved cement by heating a mixture of limestone and clay and crushing the resulting product to a fine powder. *The name portlant cement was used because* this powder, on mixing with water, set to give a hard, stone-like mass which resembled stone quarried on the Isle of Portland, England.

Portland cement is a type of cement, not a brand name. Each cement manufacturer makes portland cement. All portland cements are *hydraulic cements* because they set and harden under water.

3.1 Manufacture of Portland Cement

Raw Materials. Raw materials required for the manufacture of Portland cement may be divided into those supplying

9

Cements

> *"Health is the primary requisite for all activities : physical, intellectual and spiritual".*

1 INTRODUCTION

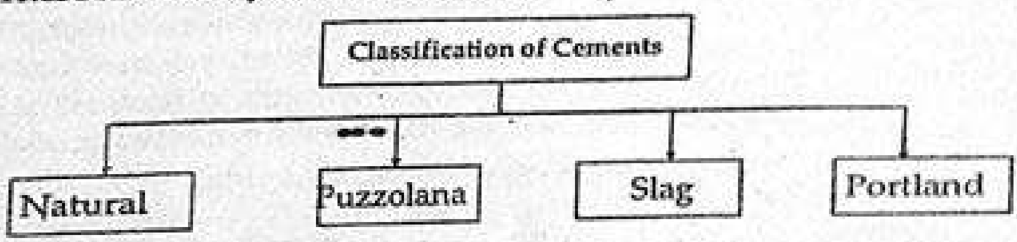
In this industrial age, the concrete is the most widely used non-metallic material of construction. It is used for the construction of buildings, bridges, high ways, dams, run-ways for the aircraft etc. The essential bonding material, which binds sand and rock (when mixed with water) in concrete is cement. In this chapter we will discuss cement (its classification, composition, manufacturing methods and decay), lime, plaster of paris and their setting and hardening.

2 CEMENT AND ITS CLASSIFICATION

Cement is a material which possesses adhesive and cohesive properties and capable of binding materials like bricks, stones, building-blocks etc.

Classification of Cements

There are four types of cements viz. Natural, Puzzolana, Slag andPortland cement. These are briefly discussed below :



(a) Natural Cement

Preparation. It is made by calcining a naturally occurring argillaceous lime-stone at a high temperature and subsequently, pulverizing the calcined mass. Calcium silicates and aluminates are formed by the combination of silica and alumina with calcium oxide during calcination.

Properties :

(*i*) It possesses hydraulic qualities,

(*ii*) It is quite setting cement, and

(*iii*) It possesses relatively low strength.

Applications :

(*i*) Mortars (combination of sand with natural cement) is used in laying bricks and setting stones.

(*ii*) It is also used in large masses of concretes such as dams and foundations.