CEMENT INDUSTRIES

INTRODUCTION

Cement is broadly described as material having adhesive and cohesive property with capacity to bond the material like stone, bricks, building blocks etc. Cement is a binder, a substance that sets and hardens independently, and can bind other materials together. Cements are inorganic material that shows the cementing properties of setting and hardening when mixed with water. Cement is prepared from calcareous (Ca) material and argillaceous (Al + Si) material.

Cement has property of setting and hardening under water by virtue of chemical reaction of hydrolysis and hydration. Therefore, cements are generally divided into two types hydraulic and non-hydraulic that is on the basis of their setting and hardening pattern. Hydraulic cements harden because of hydration, chemical reactions that occur independently of the mixture's water content; they can harden even underwater or when constantly exposed to wet weather. The chemical reaction that results when the anhydrous cement powder is mixed with water produces hydrates that are not water-soluble. Non-hydraulic cements must be kept dry in order to retain their strength. Portland cement is example of hydraulic cement material while ordinary lime and gypsum plaster are consider as example of non-hydraulic cement.

Cement is used for structural construction like buildings, roads, bridges, dam etc. The most important use is the production of mortar and concrete the bonding of natural or artificial aggregates to form a strong building material that is durable in the face of normal environmental effects.

Both cement and concrete are different, because the term cement refers to the material used to bind the aggregate materials of concrete. Concrete is a combination of a cement and aggregate.

In the last couple of decades of eighteenth century, modern hydraulic cements began to be developed due to fulfill following requirement

- For finishing brick buildings in wet climates
- Development of strong concretes

- Hydraulic mortars for masonry construction of harbor works, etc., in contact with sea water

As the good quality building stone became expensive and construction of prestige buildings from the new industrial bricks, and to finish them with a stucco to imitate stone became the common practice. Hydraulic lime was favored for this, but the need for a fast set time encouraged the development of new cements.

James Parker developed cement from clay minerals and calcium carbonate and patented as Roman cement in 1796. It was made into a mortar with sand, set in 5–15 minutes. The success of "Roman Cement" led other manufacturers to develop competing products by burning artificial mixtures of clay and chalk.

In the first decade of nineteenth century, it was proved that the "hydraulicity" of the lime was directly related to the clay content of the limestone from which it was made first by John Smeaton and then by Louis Vicat. Vicat produce artificial cement by burning of chalk and clay into an intimate mixture in 1817. Also, James Frost produced "British cement" in a similar manner around the same time, and patented in 1822. At the same time Portland cement, was patented by Joseph Aspdin in 1824.

"Setting time" and "early strength" are important characteristics of cements. Hydraulic lime, "natural" cements, and "artificial" cements all rely upon their belite content for strength development. Belite develops strength slowly. Because they were burned at temperatures below 1250°C, they contained no alite, which is responsible for early strength in modern cements. In early 1840s the first cement to consistently contain alite was made by William, who is son of Joseph Aspdin. This was what we call today "modern" Portland cement. Vicat is responsible for establishing the chemical basis of these cements, and Johnson established the importance of sintering the

CLASSIFICATION

Based on source of cement

1. Natural cement
2. Artificial cement

1. Natural cement

Natural cement is obtained by burning and crushing of 20-40% clay, carbonate of lime and small amount of magnesium carbonate. It is brown in colour and best variety known as Roman cement. The natural cement resembles very costly element hydraulic lime and sets very quickly and strongly as compare to artificial cement. It finds very limited application

2. Artificial cement

Artificial cement is obtained by burning of calcareous mixture at very high temperature. Mixture of ingredients should be intimate and they should be in correct proportion. Calcined product is known as Clinker. A small quantity of gypsum added to clinker and pulverized to fine powder is known as cement or ordinary cement or normal setting cement. After setting, this cement closely a variety of sandstone which is found in abundance in Portland in UK. Therefore, it is also known as Portland cement.

Based on broad sense cement

1. Natural cement
2. Puzzolana cement
3. Slag cement
4. Portland cement

1. Natural cement

It is prepared from naturally occurring lime stone by heating it to a high temperature and subsequently pulverizing it. During heating both siliceous and calcareous material are oxidized and combined to give calcium silicates and calcium aluminates.

2. Puzzolana cement

It is the material which when mixed with lime without heating gives hydraulic cement. They mainly contains silicates of aluminum, iron and calcium natural Puzzolana which is found in deposits of volcanic ash consist of glassy material and simple mixing and grinding gives the cement. Similarly slaked lime also gives Puzzolana cement but they are the cement of ancient time and at present hardly used.

3. **Slag cement**

It is made by mixing blast furnace slag and hydrated lime. Furnace slag largely contains silicates of calcium and aluminum which is granulated by pouring it into cold water. Later it is dried and mixed with hydrated lime and the mixture is finally powdered to increase the rate of setting. Accelerator like clay, salt or caustic soda may be added.

4. **Portland cement**

It is refine powder of calcined product of clay and lime stone. It has controlled composition and therefore setting property. It is named after the paste of cement with water which resembled in colour and hardness to the Portland stone.

Based on the application, appearance and constituent of cement

1. Acid resistance cement
2. Blast furnace cement
3. Coloured cement
4. White cement
5. Rapid hardening cement
6. High alumina cement
7. Puzzolana cement
8. Hydrophobic cement
9. Expanding cement
10. Low heat cement
11. Quick setting cement
12. Sulfate resisting cement

1. **Acid resistance cement**

It is composed of

- Acid resistant aggregates like quartz
- Additives such as Na_2SiF_6
- Aqueous solution of sodium silicate or sodium glass

Sodium fluorosilicate accelerates the hardening process of soluble glass and increase the resistance to acid.

Soluble glass (water solution of sodium or potassium silicate) is used as binding material.

The cement has poor water resistance and fails when attacked by water or weak acids. By adding 0.5% linseed oil or 2% ceresit, its resistance to water is increased and cement is known as acid and water resistance cement.

It is used in acid resistant and heat resistant coatings or insulations in chemical industry.

2. Blast furnace cement

The cement is prepared from slag obtained from blast furnace. Slag is the waste product in manufacturing of pig iron and contains the basic elements of cement like alumina, lime and silica. Clinkers of cement are ground with 60-65% slag. The properties are same as ordinary cement except less strength in early days. It requires longer curing periods.

3. Coloured cement

It can be obtained by intimately mixing mineral pigments of desired colour with ordinary cement. The amount of colouring material may vary from 5 to 10 %. If it exceeds 10 %, the strength of cement is affected. Chromium oxide gives green colour, while cobalt imparts blue colour. Iron oxide in different proportions gives brown, red or yellow colour. Manganese dioxide is used to produce black or brown coloured cement.

Coloured cements are widely used for finishing of floors external surfaces, artificial marble, window sill slabs, textured panel faces, stair treads etc.

4. White cement

It is a variety of ordinary cement having white colour. It is prepared from colourless oxides of iron, manganese or chromium. For burning of this cement, oil fuel is used instead of coal. It should not set earlier than 30 minutes. It should be carefully transported and stored in closed containers only. It is more costly than

- Increased the frequency of use of formwork of concrete, due to possible earlier removal
- Structural members constructed with this cement may be loaded earlier.
- Requires short period of cutting
- It obtains strength in a short period. Compressive strength at the end of one day is about 115 kg/cm^2 and after 3 days is about 210 kg/cm^2. Similarly tensile strength at the end of one day is about 20 kg/cm^2 and that after 3 days is about 30 kg/cm^2
- It is light in weight
- Allows higher permissible stresses in the design. It therefore results in economic design.

6. High alumina cement

It is produced by grinding clinkers formed by calcining bauxite (ore of Aluminium) and lime. It is specified that total alumina content should not less than 32% and the ratio by weight of alumina to lime should be between 0.85 and 1.30.

Advantage

- Can withstand high temperatures
- Initial setting time is more than 3 hours. Final setting time is about 5 hours. Therefore, it allows more time for mixing and placing operations
- Evolves great heat during setting, hence, not affected by frost
- Resists the action of acids in a better way
- Sets quickly and it attains compressive strength of about 400 kg/cm^2 after 1 day and that after 3 days is about 500 kg/cm^2
- Its setting action mainly depends on the chemical reactions and hence, it is not necessary to grind it to fine powder

Disadvantage

- Extreme care is to be taken to see that it does not come in contact with even traces of lime or ordinary cement.
- It cannot be used in mass construction as it evolves great heat.
- It is costly.

7. Puzzolana cement

Puzzolana is a volcanic powder. It is found in Italy near Vesuvius. It resembles surkhi which is prepared by burning bricks made from ordinary soils. It can also be processed from shales and certain types of clays. Puzzolana material should be used in between10 to 30%.

Advantage

- Evolves less heat during setting
- Possesses higher tensile strength
- Imparts higher degree of water tightness
- Attains comprehensive strength with age
- Can resist action of sulfates
- Imparts plasticity and workability to mortar and concrete prepared from it.
- Offers great resistance to expansion
- It is cheap

Disadvantages

- Compressive strength in early days is less
- Possesses less resistance to erosion and weathering action

This cement is used to prepare mass concrete of lean mix and for marine structures. It is also used in sewage works and for laying concrete under water.

8. Hydrophobic cement

It contains hydrophobic admixtures such as acidol, naphthelene soap, oxidized petroleum etc., which decrease the wetting ability of cement grains and uniformly distributed and thus the frost resistance and the water resistance of such concrete are considerably increased.

9. Expanding cement

It is produced by adding an expanding medium like sulfoaluminate and establishing agent to ordinary cement. Hence this cement expands whereas other cements shrink.

It is used for the construction of water retaining structures and for repairing the damaged concrete surfaces.

10. Low heat cement

Considerable heat is produced during the setting action of cement. It contains lower percentage of tricalcium aluminate (C_3A) and higher percentage of dicalcium silicate (C_2S) which reduce the amount of heat produced.

This type of cement possesses less compressive strength. Initial setting time is about one hour and usual setting time is about 10 hours. It is mainly used for mass concrete work.

11. Quick setting cement

It is produced by adding a small percentage of aluminium sulfates and by finely grinding the cement. Percentage of gypsum or retarder for setting action is also greatly reduced. Addition of aluminium sulfate and fineness of grinding accelerate the setting of cement. The setting action of cement starts within five minutes addition of water and it becomes hard like stone in less than 30 minutes. Mixing and placing of concrete should be completed within very short period. This cement is used lay concrete under static water or running water.

12. Sulfate resisting cement

In this cement percentage of tricalcium aluminate is kept below 5 to 6% which increase in resisting power against sulphates.

This cement is used for structures which are likely to be damaged by severe alkaline conditions such as canal linings, culverts, syphons etc.

MANUFACTURE OF PORTLAND CEMENT

Coal = 250-400kg
Water = 3000kg
Electricity = 80kWH

The most commonly used composition on % basis by mass for the Portland cement manufacturing is given below

Component	% range by mass
Lime (CaO)	60-69
Silica (SiO_2)	17-25
Alumina (Al_2O_3)	3-8
Iron oxide (Fe_2O_3)	2-4
Magnesium oxide (MgO)	1-5
Sulfur trioxide (SO_3)	1-3
Alkali Oxide (Na_2O + K_2O)	0.3-1.5

<u>Significance of constituents</u>

Lime

Lime is also defined as non-hydraulic cement mainly consisting of calcium oxide and small amount of magnesium oxide. It is prepared by calcining the lime

Sulfur trioxide

If present in small amount it imparts soundness to cement but excess of it is undesirable

Alkalis

Most of the alkalis present in raw materials are carried away by the flue gases during heating and cement contains only a small amount of alkalis. If present in excess causes the efflorescent to cement.

CEMENT MANUFACTURE

MANUFACTURE

It involves the following steps

1. Mixing of raw material
2. Burning
3. Grinding
4. Storage and packaging

1. **Mixing of raw material**

   Mixing can be done by any one of the following two processes

   (a) Dry process
   (b) Wet process

a) Dry Process

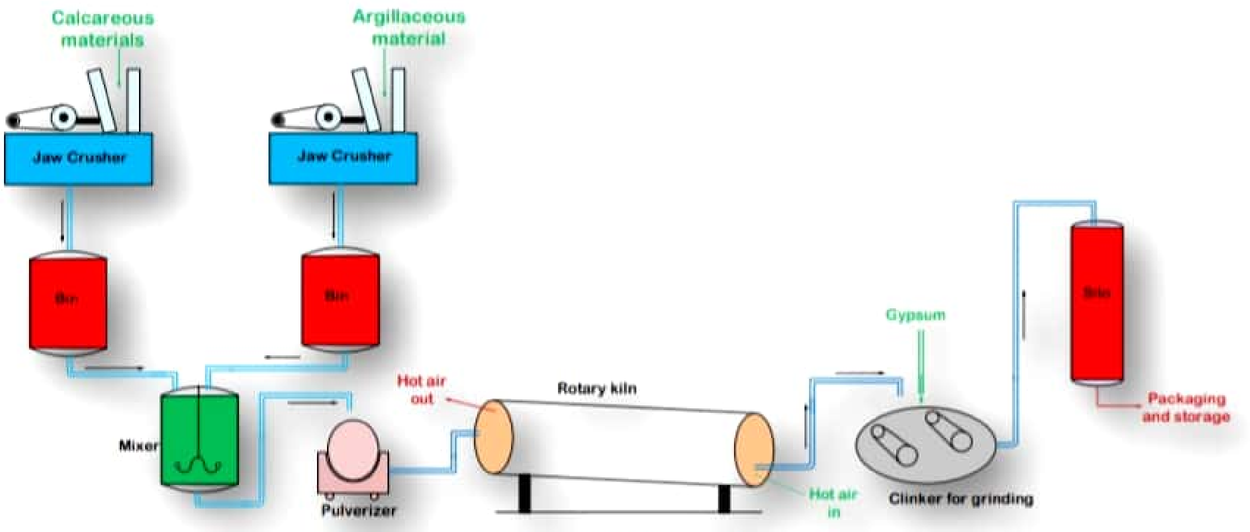

Figure: Manufacturing of Cement by Dry Process

Block diagram of manufacturing process

Diagram with process equipment

[Animation](#)

Lime stone or chalk and clay are crushed into gyratory crusher to get 2-5 cm size pieces. Crushed material is ground to get fine particle into ball mill or tube mill. Each material after screening stored in a separate hopper. The powder is mixed in require proportions to get dry raw mix which is stored in silos (storage tank) and kept ready to be fed into the rotary kiln. Raw materials are mixed in required proportions so that average composition of the final product is maintained properly.

b) Wet process

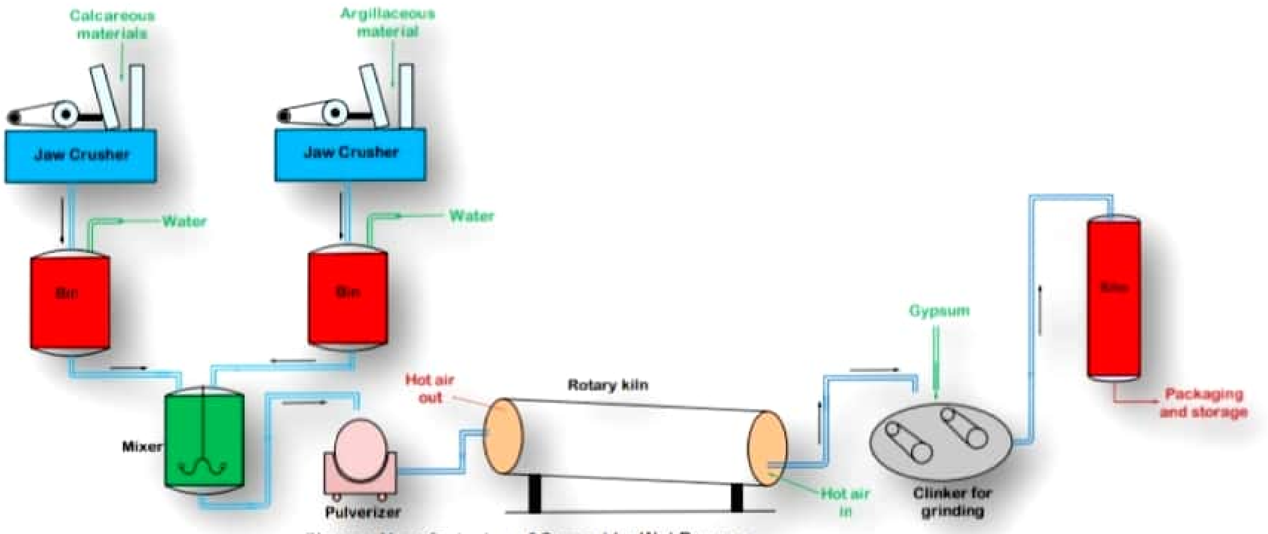

Figure: Manufacturing of Cement by Wet Process

[Block diagram of manufacturing process](#)

[Diagram with process equipment](#)

[Animation](#)

Raw materials are crushed, powdered and stored in silos. The clay is washed with water in wash mills to remove adhering organic matter. The washed clay is

Comparison of dry process and wet process

Criteria	Dry process	Wet process
Hardness of raw material	Quite hard	Any type of raw material
Fuel consumption	Low	High
Time of process	Lesser	Higher
Quality	Inferior quality	Superior quality
Cost of production	High	Low
Overall cost	Costly	Cheaper
Physical state	Raw mix (solid)	Slurry (liquid)

The remaining two operations burning and grinding are same for both the process.

2. Burning

Burning is carried out in rotary kiln which rotating at 1-2 rpm at its longitudinal axis. Rotary kiln is steel tubes having diameter in between 2.5-3.0meter and length varies from 90-120meter. The inner side of kiln is lined with refractory bricks. The kiln is rested on roller bearing and supported columns of masonry or concrete in slightly inclined position at gradient of 1 in 25 to 1 in 30. The raw mix or corrected slurry is injected into the kiln from its upper end. Burning fuel like powdered coal or oil or hot gases are forced through the lower end of the kiln so long hot flame is produced.

Due to inclined position and slow rotation of the kiln, the material charged from upper end is moving towards lower end (hottest zone) at a speed of 15meter/hour. As gradually descends the temperature is rises. In the upper part, water or moisture in the material is evaporated at 400^0C temperature, so it is known as drying zone.

In the central part (calcination zone), temperature is around 1000^0C, where decomposition of lime stone takes place. After escapes of CO_2, the remaining material in the forms small lumps called nodules.

$$CaCO_3 \longrightarrow CaO + CO_2$$

The lower part (clinkering zone) have temperature in between $1500\text{-}1700^0C$ where lime and clay are reacts to yielding calcium aluminates and calcium silicates. This aluminates and silicates of calcium fuse to gather to form small and hard stones are known as clinkers. The size of the clinker is varies from 5-10mm.

$$2CaO + SiO_2 \longrightarrow Ca_2SiO_4 \text{ (dicalcium silicate } (C_2S))$$
$$3CaO + SiO_2 \longrightarrow Ca_3SiO_5 \text{ (tricalcium silicate } (C_3S))$$

$3CaO + Al_2O_3 \longrightarrow Ca_3Al_2O_6$ (dicalcium aluminate (C_2A))
$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10}$ (tetracalcium aluminoferrite(C_4AF))

As clinkers are coming from burning zone, they are very hot. The clinkers are cooled down by air admitting counter current direction at the base of rotary kiln. Resulting hot air is used for burning powdered coal or oil and cooled clinkers are collected in small trolleys or in small rotary kiln.

3. Grinding

Cooled clinkers are ground to fine powder in ball mill or tube mill. 2-3% powdered gypsum is added as retarding agent during final grinding. So that, resulting cement does not settle quickly, when comes in contact with water. After initial set, cement - water paste becomes stiff, but gypsum retards the dissolution of tri-calcium aluminates by forming tricalcium sulfoaluminate which is insoluble and prevents too early further reactions of setting and hardening.

$$3CaO.Al_2O_3 + xCaSO_4.7H_2O \longrightarrow 3CaO.Al_2O_3.xCaSO_4.7H_2O$$

4. Storage and packaging

The ground cement is stored in silos, from which it is marketed either in container load or 50kg bags.

Pretreatments to raw material

- **Wet process**

Cement manufacture by wet process used either chalk or lime stone as one of the raw material. Following treatment should be given to them before its use. The remaining procedure after the treatment is same for both.

Chock should be finely broken up and dispersed in water in a wash mill. The clay is also broken up and mixed with water in wash mill. The two mixtures are now pumped so as to mix in predetermined proportions and pass through a series of screens. The resulting cement slurry flows into storage tanks.

Limestone should be blasted, then crushed, usually in two progressively smaller crushers (initial and secondary crushers), and then fed into a ball mill with the clay dispersed in water. The resultant slurry is pumped into storage tanks.

Impurity profile of raw materials

The amount of different components in Portland cement as oxides is tabulated in table: 1which shows that CaO and SiO_2 by far constitute the major part of the final product.

About one-third of the raw meal mass can be attributed to Loss on Ignition (LOI), which is almost exclusively due to the calcination of the $CaCO_3$ used as a precursor for forming CaO. This corresponds to the fact that the raw meal contains about 75 wt% of $CaCO_3$.

The mass loss in the calcination process corresponds to a raw meal to cement clinker ratio of about 1.5, if the raw meal is dry when fed into the kiln system. The raw meal composition stated in table: 1 is usually obtained by blending limestone and clay (clay being rich in Si, Fe and Al oxides). If needed, correctives like sand and iron ore can be added to the raw meal in order to achieve the correct composition.

In order to ensure the proper quality of the final product, the amount of certain minor components is limited. Column 4 in table: 1 shows some general upper limits for certain elements, but the exact amount that can be allowed depends on a wide range of factors such as what the cement will be used for, the amount of other impurities, production facilities and so on, which is why the acceptable amount must be determined from case to case. The limits stated in table: 1 cannot be exceeded significantly, and in many cases it is actually desirable to be well below these limits.

Components	**Content in clinker**	**Content in raw meal**	**Impurity limits**
	Wt. %	Wt. %	Wt. %
CaO	63.8-70.1	~43	
SiO_2	19.7-24.3	~14	
Al_2O_3	3.8-6.8	~4	
Fe_2O_3	1.3-1.6	~5	

Engineering aspects

Cyclone preheater

The raw materials are preheated or calcined in preheater or series of cyclones before entering to the rotary kiln. A preheater, also called as suspension preheater is a heat exchanger in which the moving crushed powder is dispersed in a stream of hot gas coming from the rotary kiln. Common arrangement of series of cyclones is shown in figure.

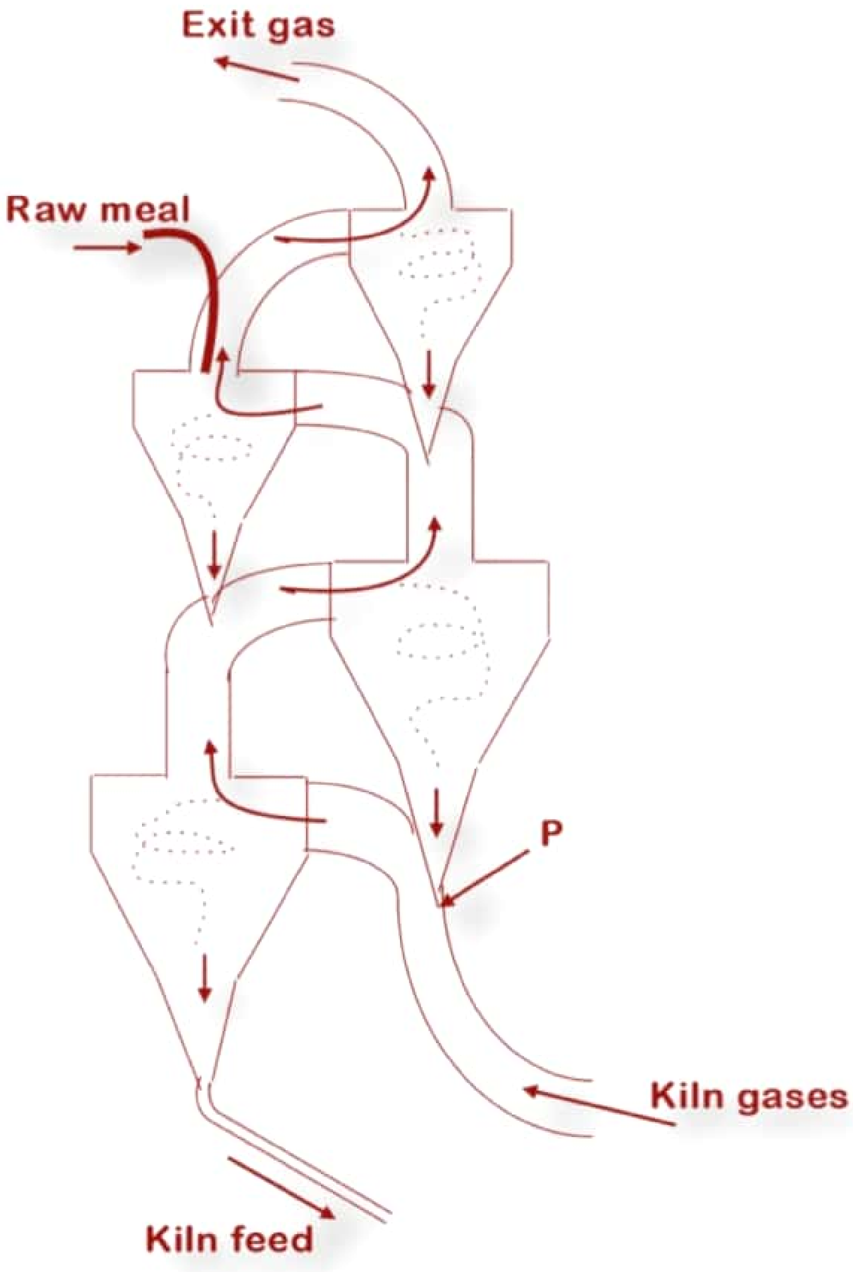

Figure: Cyclone preheaters

The heat transfer of hot kiln gases to raw meal is takes place in co-current. The raw materials are heated upto 800°C within a less than a minutes. About 40% of the calcite is decarbonated during the heat transfer.

The quality and quantity of fuel used in the kiln can be reduced by introducing a proportion of the fuel into preheater. 50 – 65 % of the total amount of fuel is introduced into preheater or precalciner which is often carried out by hot air ducted from cooler.

The fuel in the precaliner is burnt at relatively low temperature, there so heat transfer to the raw meal is very efficient. The material has residence time in the hottest zone of a few seconds and its exit temperature is about 900°C, 90 – 95% of calcite is decomposed. Ash from the fuel burn in the precalciner is effectively incorporated into mix.

Advantages of precalination

- Decrease the size of kiln
- Decrease in capital cost
- Increase in rate of material passes to the kiln.
- Decrease in rate of heat provided which ultimately lengthens the life of refractory lining
- Less NOx is formed, since much of the fuel is burnt at a low temperature, and with some designs NOx formed in the kiln may be reduced to nitrogen.

Rotary Kiln

Rotary kiln is a tube, sloping at 3 – 4 % from the horizontal and rotating at 1 – 4 revolution/minute into which material enters at the upper end and then slides, rolls and flows counter to the hot gas produced by a flame at the lower or front end.

The kiln is lined with refractory bricks. The type and size of the bricks may vary depending up on the length of rotary kiln and the maximum temperature employed. Further, arranging the bricks in a ring requires perfect closing of the ring which is difficult, time consuming and expensive. Two types of the joints, the radial and axial joints are used for bricks. The redial joints are between the brick in each ring and axial joints are between the successive rings. The bricks are coated with thin layer of clinker for extending the life as well as insulation.

The rotary kiln used which precalciner is 50 – 100 meter long having length to diameter (L/D) ratio between 10 to 15. The kiln having very small L/D ratio ensures rapid clinker formation and quick reaction run without recrystallization phenomena. Due to this higher hydraulic activity of cement is achieved

Conveyors

The following types of conveyors are used during the cement manufacturing process.

- Belt conveyor
- Bucket conveyor
- Screw conveyor
- Roller conveyor

Animation

- **Belt conveyor**

Belt conveyor is used for transportation of raw material form storage to the initial crushing devises mostly jaw crusher. Belt conveyor consists of two or more pulleys, with a continuous loop of material or the conveyor belt which rotates about them. Either one or both of the pulleys are powered, moving the belt and the material on the belt forward. The powered pulley is called the drive pulley while the unpowered pulley is called the idler.

- **Bucket conveyor**

Bucket conveyor are used for transportation of crushed material and clay to mixing zone in cement industries. A bucket conveyor, also called a grain leg, is a mechanism for carrying the bulk materials vertically. It consists of buckets to contain the material, a belt to carry the buckets and transmit the pull, means to drive the belt and accessories for loading the buckets or picking up the material, for receiving the discharged material, for maintaining the belt tension and for enclosing and protecting the elevator.

- **Screw conveyor**

A screw conveyor or auger conveyor is a mechanism that uses a rotating helical screw blade, called a "flighting", usually within a tube, to move liquid or granular materials. Screw conveyors are often used horizontally or at a slight incline as an efficient way to move semi-solid materials. Screw conveyor are used for transportation of material for storage to homogeneous siloes.

- **Roller conveyor**

Roller conveyors are line restricted device and consist of rollers mounted between two side members. Bearings are usually incorporated in the idlers to cut down the mechanical losses. An unpowered gravity roller conveyor is set at an appropriate incline and goods move down it by gravity. In power unit normally an electric motor drive the rollers via chains or belt, providing controlled movement of goods. They are generally used for transportation of packed material.