INDUSTRIAL CHEMISTRY
UNIT-V
CEMENT

CEMENT

It is defined as an extremely finely ground product.

It is obtained by heating a mixture of argillaceous (clay containing) and calcareous (lime containing) raw materials to about 1500 c. It is then mixed with gypsum to increase the quick setting and hardening property.

MANUFACTURE OF PORTLAND CEMENT

Raw materials :

(i) Calcareous materials , CaO Ex: Limestone, chalk.
(ii) Argillaceous materials, Al_2O_3 and SiO_2 Ex: clay, slate etc
(iii) Powdered coal (or) fuel oil.
(iv) Gypsum ($CaSO_4.2H_2O$)

Manufacture of Portland cement involves the following steps:

(i) Mixing of raw materials
(ii) Burning
(iii) Grinding
(iv) Storage and Packing

(i) Mixing of raw materials:

(a) Dry Process (b) Wet Process

(a) Dry Process: In dry process, the raw materials like limestone and clay(3:1) are dried, and mixed in definite proportions

(b) Wet process : In wet process, the raw materials in definite proportions are finely ground with water and the slurry (past like) is fed at the top of the rotary kiln.

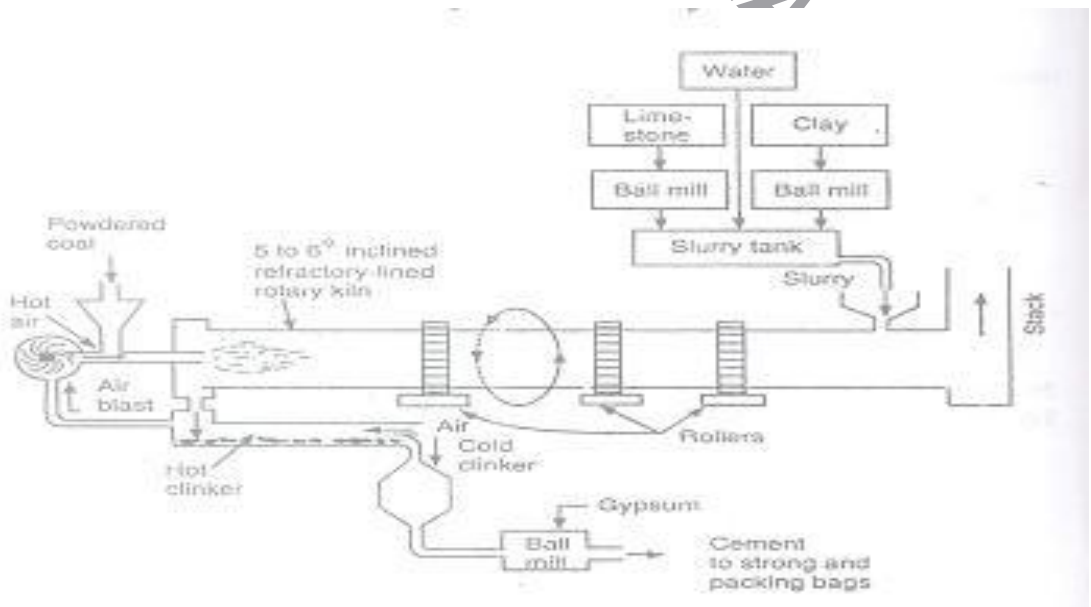


Fig. 9.1 Rotary cement kiln

(ii) Burning

The burning process is usually done in rotary kiln which is a long horizontal steel cylinder coated with refractory bricks and capable of rotating at 1 rpm 9 Revolution per minute) . The rotary kiln is set at a slight inclination of about 5-6^0 in order to allow the raw materials fed at one end to travel slowly to the firing and discharge exit end.

The slurry of raw materials is allowed to enter from the top end of the rotary kiln. Simultaneously the burning fuel (like powdered coal or oil) and air are introduced from the lower end of kiln . The slurry gradually comes down in the kiln into the different zones (Drying Zone at 400^o :Calcination zone at 700 -1000 ^{o} C and clinkering zone at 1250-1500 ^{o} C of increasing temperatures.

(a) Drying Zone: The upper part of the rotary kiln is known as drying zone ,where the temperature is about 400 ^{o} C . Due to the presence of hot gases in this zone, water is evaporated from the slurry.

(b) Calcinations zone: The middle part of the rotary kiln is known as calcining zone where the temperature ranges from 700 -1000 ^{o} C. In this zone lime stone is decomposed into CaO and CO_2

$$CaCO_3 \xrightarrow{700\text{ -}1000\ ^oC} CaO + CO_2$$

Lime Stone Quick lime

(c) Clinkering Zone: The lowest part of the zone is called as clinkering zone, where the temperature is maintained about 1250-1500 ^{o} C. In this zone lime reacts with clay (Containing Al_2O_3, Fe_2O3 and SiO_2) and forms aluminates and silicates

$$2CaO + SiO_2 \text{ --------> } 2CaO.SiO_2$$

Dicalcium Silicate(C2S)

$$3CaO + SiO_2 \text{ --------> } 3CaO.SiO_2$$

Tri calcium Silicate (C3S)

The mixture is then finely powdered and fed into the top of the rotary kiln.

$$3CaO + Al_2O_3 \text{--------> } 3CaO.Al_2O_3$$

Tri calcium Aluminate(C3A)

$$4CaO + Al_2O_3 + Fe_2O_3 \text{--------> } 4CaO.Al_2O_3.Fe_2O_3$$

Tetra calcium alumino Ferrate

Cooling : the hot clinker is cooled with atmospheric air and the hot air thus produced is used for drying the coal before grinding.

(iii) Grinding : The cooled clinker is then finely pulverized with 2-6% gypsum acts as a retarding agent for quick setting of cement.

(iv) Storage and Packing: The cement coming out from the grinding mills is stored in a concrete storage silos.

Then the cement is packed in jute bags by automatic machines. Each bag contains 50kgs of cement.

PROPERTIES

Setting and Hardening of cement:

When the cement is mixed with water, hydration and hydrolysis of cement begin, resulting in the formation of gel and crystalline products.

Setting: It is defined as the stiffening of the original plastic mass, due to initial gel formation. Hardening: It is defined as the development of strength, due to crystallization.

Chemical reactions involved in setting and hardening of cement:

When water is mixed with cement, hydration of tricalcium aluminate occurs rapidly and the paste becomes quite hard within a short time. This process is known as initial setting of cement.

$3CaO.Al_2O_3$ (C3A) $+6H_2O$-------> $3CaO.Al_2O_3.6H_2O$

Role of gypsum in cement:

(i) In initial setting process gypsum is added during grinding of cement clinkers to retard.

Gypsum reacts with C3A to form insoluble calcium sulphoaluminate complex. C3A + $3CaSO_4.2H_2O$--------> $C_3A.3CaSO_4.2H_2O$

(ii) After the hydration of C3A,C3S begins to hydrate to give tobermonite gel and crystalline $Ca(OH)_2$. The hydration of C3S takes place within 7days.

$2(3CaO.SiO_2)$ + $6H_2O$---------> $3CaO.2SiO_2.3H_2O$ + $3Ca(OH)_2$ + 500kj/kg

(iii) Dicalcium silicate reacts with water slowly and gets finished 7-28days.

$2(2CaO.SiO_2)$ + 4 H_2O --------> $3CaO.2SiO_2.3H_2O$ +$Ca(OH)_2$ + 250kj/kg

(iv) Hydration of tetra calcium alumina ferrite takes place initially, the hardening takes place finally through crystallization along with C2S.

$4CaO.Al_2O_3.Fe_2O_3$ + $7H_2O$----------> $3CaO.Al_2O_3.6H_2O$ + $CaO.Fe_2O_3.H_2O$ + 420KJ

Crystalline gel

Thus the final setting and hardening of cement is due to the formation of tobermonite gel plus crystallization of $Ca(OH)_2$ and hydrated tricalcium aluminate.

SPECIAL CEMENT

Water Proof Cement :

It is obtained by adding water proofing agents like calcium stearate and gypsum with tannic acid to ordinary Portland cement during grinding.

Functions of water- Proof cement:

Functions of water- proof cement

(i) To make concrete impervious to water under pressure.
(ii) To resist the adsorption of water.

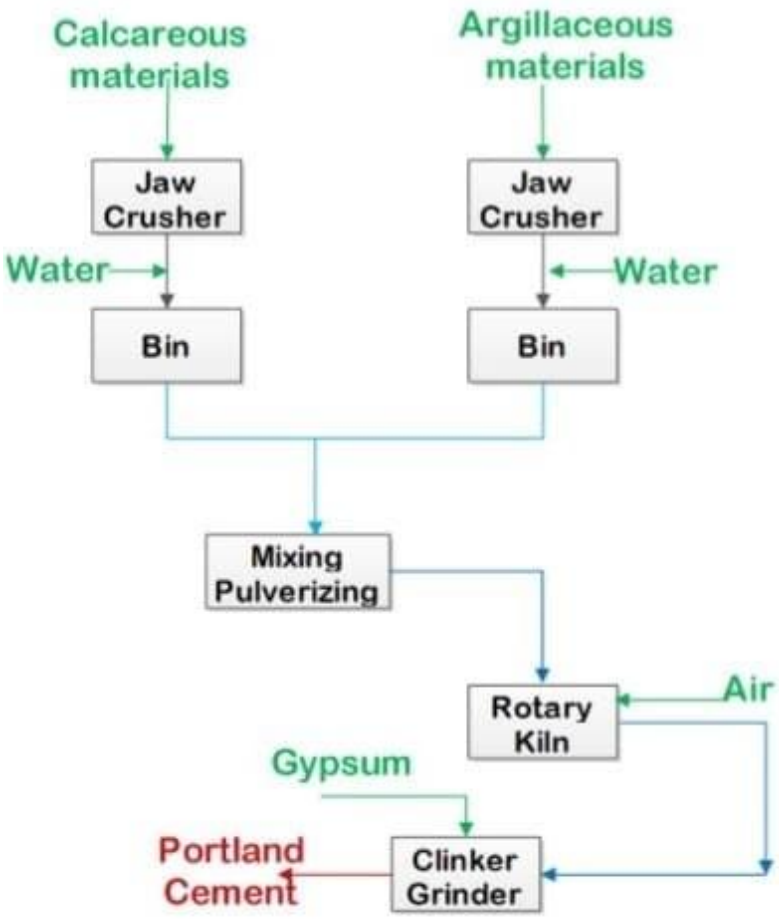
White cement or White Portland cement

It is obtained by heating the raw materials free from iron oxides. It is white in color due to the absence of ferric oxide.

It issued for making tiles, mosaic works with some coloring agents like yellow ochre, Venetian red etc.

It is used for repairing and joining marble pillars and blocks.

FLOW CHART FOR CEMENT MANUFACTURING



Reinforced concrete:

Reinforced concrete (RC) (also called **reinforced cement concrete** or **RCC**) is a composite material in which concrete's relatively low tensile strength and ductility are counteracted by the inclusion of reinforcement having higher tensile strength or ductility.

GLASS

Glass is an amorphous, hard brittle, transparent, super cooled liquid of infinite viscosity. Glass may be represented as $xR_2O.yMO.6SiO_2$

General Properties of Glass:

1. It is amorphous.
2. It is very brittle.
3. It softens on heating.
4. It has no definite melting point.
5. It is affected by alkalis.
6. It is a good electrical insulator.
7. It can absorb, reflect or transmit light.
8. It is not affected by air water, acids and chemical agents.

Manufacture of Glass

1. Melting :

The raw materials in proper proportions are mixed and finely powdered.

This homogeneous mixture is known as BATCH is fused with some broken glass called CULLET in the pot of the furnace.

The furnace is heated by burning producer gas and air mixture over the charge. The cullet melts at a low temp and assists in melting the rest of the charge.

$$CaCO_3 + SiO_2 \text{------>} CaSiO_3 + CO_2$$

$$Na_2CO_3 + SiO_2 \text{ -----> } Na_2SiO_3 + CO_2$$

Forming and Shaping

The molten glass is then worked into articles of desired shapes by either blowing or moulding or pressing between rollers.

Annealing:

Glass articles are then allowed to cool gradually to room temperature. Sudden cooling must be avoided, because cracking occurs. Longer the annealing period, the better is the quality of the glass.

Finishing:

All glass articles after annealing, are subjected to finishing processes such as
(a) Cleaning (b) grinding (c) polishing (d) cutting (e) sand blasting

TYPES OF GLASSES

1.Soda-lime or soda glass
2. Potash lime or Hard glass
3. Lead glass or Flint glass

4. Borosilicate glass or Pyrex glass or Jena glass
5. Alumina silicate glass
6. Optical or Crookes glass
7. Glass wool

1.Soda-lime or soda glass or soft glass

(i) Raw materials: Silica , calcium carbonate and soda ash
(ii) Composition: $Na_2O.\ CaO.\ 6SiO_2$

Properties:

(a) They are low in cost.
(b) They are resistant to water
(c) They are attacked by common reagents like acids.
(d) They melt easily"

Uses: They are used as window glasses, electric bulbs, bottles, plate-glasses, jars, cheaper table wares, where high temperature resistance and chemical stability are not required.

2. Potash lime or Hard glass

(i) Raw materials : Silica, $CaCO_3$, K_2CO_3
(ii) Composition: $K_2O.\ CaO.6SiO_2$

(iii) Properties:
(a) They have high melting point.
(b) They do not fuse easily.
(c) They are less acted upon acids alkalis, solvents.

Uses: Used for manufacturing combustion tubes, chemical apparatus

3. Lead glass or Flint glass

(i) Raw materials: Lead oxide, silicva, K_2O
(ii) Composition: $K_2O.PbO.6SiO2$

(iii) Properties:
(a) It is bright and lustrous
(b) It has high specific gravity. (3 to 3.3)
(c) It is more expensive to manufacture.
(d) It has a lower softening temperature than soda glass.
(e) It has higher refractive index.

Uses: (a) These are used for high quality tablewares.
(b) They are used in neon sign tubings, optical lenses, electrical insulators, cathode ray tube.

4. Borosilicate glass or Pyrex glass or Jena glass

(i)Raw materials: Silica, borax with small amount of alumina and some oxides.

(ii) Composition : SiO_2 (80.5%); B_2O_3 (13%); Al_2O_3(3%); K_2O (3%) Na_2O (0.5%)

(iii) Properties

(i) It possess low thermal coefficient of expansion and high chemical resistance.

(2)It possesses very high softening points and excellent resistivity.

Uses: It is used in industry for pipe lines for corrosive liquids, gauge glasses,

5. Alumino silicate glass

Raw materials: It has 5% or more alumina

(i)Composition: SiO_2 . Al_2O_3, B_2O_3, MgO, CaO, Na_2O K_2O

Properties:

They possess high softening temperature.

Uses: (a)Used in high pressure mercury discharge tubes

(b)Chemical combustion tubes.

6. Optical or Crookes glass

Raw materials: It contains phosphorus, lead silicate with small amount of cerium oxide.

Properties:

(a) Cerium oxide present in the glass absorbs uv light,

(b) They have low melting point.

Uses: optical glasses are used for making lenses.

7. Glass wool

Glass wool is fibrous wool like material It is composed of intermingled fine threads or filaments of glass.

Properties: It is a very good heat and fire proof materials

Its electrical conductivity is low.

Uses; It is used for heat insulation purposes

8. Lead glass (or) flint glass

Raw materials: lead oxide (instead of calcium oxide) and silica are fused.

For dense optical glasses, as much as 80% of PbO is incorporated. In addition, K_2O is used, instead of sodium oxide.

Composition: The approximate composition is $K_2O.PbO.6SiO_2$.

Properties:

1. It is bright, lustrous and possesses high specific gravity (3 to 3.3).
2. It has a lower softening temperature than soda glass.
3. It has higher refractive-index and excellent electrical properties.

Uses:

1. Lead glasses are used for high-quality table wares, neon sign tbings, optical purposes (like lenses etc), and electrical insulators.
2. High lead content glasses are used for extra-dense optical glasses for windows and shields to protect personnel from X-rays and gamma rays in medical and atomic energy fields respectively.

9. Quartz glasses

Raw material: Crystalline silica. It is fused at 1900^0C under vaccum.

Properties: Quartz glasses possess outstanding resistance to thermal shock and chemicals.

Uses: They are used in the manufacture of special lab ware, crucibles, reaction tubes etc.