Cement and Glass
Unit - 05
Applied Chemistry-II

mercury discharge tube etc.

Cement : Cement is an important building material. First of all Joseph Aspdin in (1788–1853), an English person discovered portland cement on 21 st October 1824. It may be defined as "The material having the property of adhesion and cohesion and joining of bricks, stones and other materials with each other the material is called cement." Particularly it is the mixture of alumino silicate and calcium silicate. When water is mixed with cement it starts setting and hardnening due to the chemical reactions. It is called

"hydraulic cement". The material which is formed as a result of hardening of cement is similar to a stone. The colour of this material is just like stone found in England which is called portland. Hence, the cement is called **'portland cement'**.In India, the cement industry was started in the year 1914. Now, India is producing about 130 million tonnes of cement per year.

Types of cement :- The cement may be of the following types :

Composition of cement : Mainly cement is the mixture of silicates of calcium and aluminium. It consists of some amount of tetra calcium alumino ferrite. Its average percentage composition is :

Quick lime (CaO)	:	60–70 %
Silica (SiO_2)	:	17–25%
Alumina (Al_2O_3)	:	3–10%
Iron oxide (Fe_2O_3)	:	2–4%
Magnesium oxide (MgO)	:	2–5%
Sulphur trioxide (SO_3)	:	1–3%
Alkali oxide	:	0.3–1.5%
Gypsum ($CaSO_4 \cdot 2H_2O$)	:	2–3%

The ratio of silica and alumina in the cement is about 2.5 to 4.0%. The cement does not consist of iron oxide is called 'white cement'. For a good quality of cement the ratio of calcium oxide (CaO) and the mixture of ($SiO_2 + Al_2O_3 + Fe_2O_3$) is about 1.9 to 2.1%.

The percentage composition of various compounds in partland cement is:

	Name of Compounds	Chemical Formula	Percentage Composition
1.	Tricalcium silicate	$3CaO \cdot SiO_2$	45 %
2.	Diclacium silicate	$2CaO \cdot SiO_2$	25 %
3.	Tricalcium aluminate	$3CaO \cdot Al_2O_3$	1 %
4.	Tetracalcium alumino ferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	9 %
5.	Calcium sulphate	$CaSO_4$	5 %
6.	Calcium oxide	CaO	2 %
7.	Magnesium oxide	MgO	4 %

Functions of the Ingradients of Cement

(1) Quicklime (CaO) : The quantity of CaO in cement should be proper. The strength of cement is affected by decreasing or increasing the quantity of calcium oxide.

(2) Silica (SiO_2) : It imparts the strength to the cement.

(3) Alumina (Al_2O_3) : It helps in the quick setting of the cement.

(4) Iron oxide (Fe_2O_3) : It imparts colour to the cement. It also gives red colour to the cement.

Raw Materials Used in the Manufacture of Cement

The following raw materials used in the manufacturing of cement :

(1) Calcareous material : These materials may be substituted in place of lime in the manufacture of cement. Specially lime stone ($CaCO_3$) and shales are used for this purpose.

(2) Argillaceous materials : These materials are used as a fraction of silica, alumina and iron oxide in the manufacture of cement. *e.g.*, china clay ($H_4Al_2Si_2O_9$), shale, slag of blast furnace or flyash etc.

(3) Coal powder.

(4) Gypsum ($CaSO_4 \cdot 2H_2O$) : It is mixed in the cement from 2 to 3%.

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Manufacture of cement : The manufacture of cement may be done in the following way.

(1) Powdering of raw materials by finely grinding : The raw materials used in the manufacture of cement are finely grinding in the grinding machines.

(2) Mixing of powdered raw material : The powder of raw material is mixed in the proper ratio. Two methods are used for the manufacture of cement :

(a) Dry process : When the raw material is very hard the fuel is very costly, this method is used. In this method the raw materials are mixed in the dry state and finely powdered in the ball mill.

(b) Wet process : When the raw material is not hard, atmosphere consists of humidity and the fuel is not so expensive, this method is used. In India, wet process is used for the manufacture of cement, wet process is always preferred over dry process because it affords an easier control of the composition of the cement. This process is performed by the following operations :

(i) Preparation of slurry
(ii) Calcination
(iii) Cooling of clinker
(iv) Grinding and storing

(i) Preparation of slurry : Clay and lime stone are crushed,finely powdered and

mixed in the ratio of 1 : 3 by weight. This mixture is then pulverised in a stream of water. The paste so formed is called as **slurry.** It contains about 30 to 40% of water. This slurry is contained in storage tanks.

(ii) **Calcination :** The above slurry is then fed into a rotary kiln (Fig. 5.3). This Kiln consists of a cylinderical furnace made up of steel sheets. It is about 100 to 125 meter in length and about 3 to 4 meter In diameter. It is mounted on rotating gears at an angle of 15–20° to the horizontal axis. The internal lining of this kiln is made up of fire resistant bricks. It rotates at a speed of one to two revolutions per minute. The fuel is burnt in the lower end and hot gases are passed from one end to the other with the help of a burner.

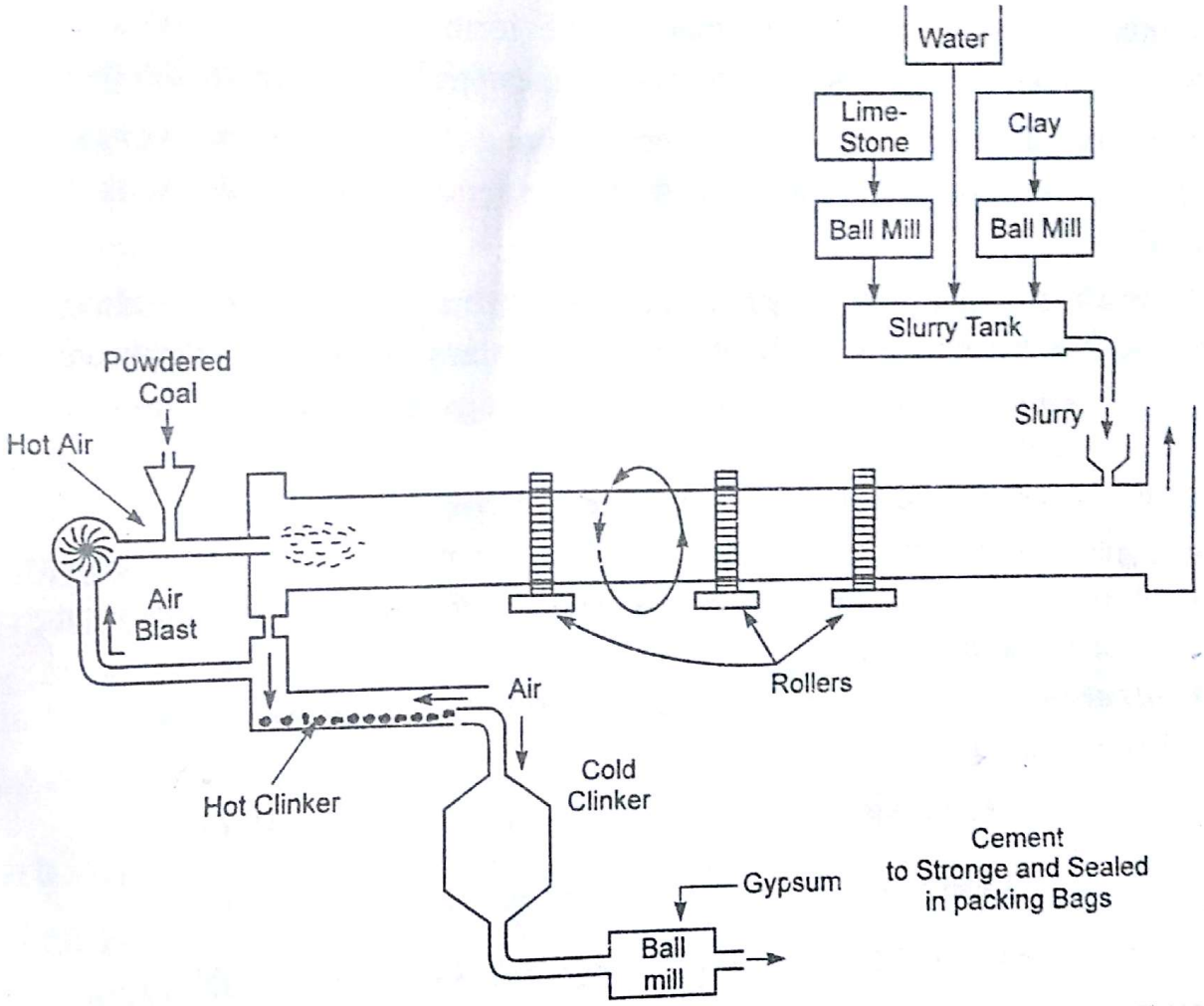

Fig. 5.3 Rotary Cement Kiln

The temperature of the furnace is about 1400–1450°C. The CO_2 gas is evolved in this furnace and calcium silicates and aluminates are formed.

The following chemical reactions occur in this process :

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

$$Al_2SiO_5 \longrightarrow Al_2O_3 + SiO_2$$

$$3CaO + SiO_2 \longrightarrow Ca_3SiO_5 (C_3S)$$
(Tricalcium silicate)

$$3CaO + Al_2O_3 \longrightarrow Ca_3 \cdot Al_2O_6 (C_3A)$$
(Tricalcium aluminate)

$$2CaO + SiO_2 \longrightarrow 2CaO \cdot SiO_2 \quad \text{or} \quad Ca_2SiO_4$$
(Dicalcium silicate)

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 \ (C_4AF) \text{ or } Ca_4Al_2Fe_2O_{10}$$
(Tetracalcium alumino ferrite)

The sintered mass which is obtained in the form of small globules of grey-black pebbles are called **cement clinkers.** The size of these pebbles is about 0.5 to 1 cm.

(iii) Cooling of cement : The clinkers obtained from the kiln are very hot. They are to hot to grind. Now, they are cooled at room temperature in a cooler with the help of a blast of cold air.

(iv) Grindling and storing : The clinkers are then subjected to grinding in grinding machines. During this process 2-3% of gypsum by mass is added in the above clinkers. It is finely powdered and packed in jute or polythane bags. The gypsum slows down the rate of setting of cement.

The cement so obtained is called **'portland cement'.**

Setting and hardening of cement : When we mix water in the cement, it starts hardening after absorbing water. It is called **'setting of cement'**. The following chemical reactions occur in the process :

(1) Hydration : Tricalcium silicate and di-calcium silicates are hydrated and convert into colloidal gel :

$$2\,CaO \cdot SiO_2 + x\,H_2O \longrightarrow 2\,CaO \cdot SiO_2 \cdot x\,H_2O$$

$$3\,CaO \cdot SiO_2 + x\,H_2O \longrightarrow 3CaO \cdot SiO_2 \cdot x\,H_2O$$

$$3\,CaO \cdot Al_2O_3 + 6H_2O \longrightarrow 3\,CaO \cdot Al_2SiO_2 \cdot 6H_2O$$

(2) Hydrolysis : When tricalcium silicate and tricalcium aluminate are hydrolysed hydroxides of calcium and aluminium are formed :

$$3\,CaO \cdot Al_2O_3 + 6H_2O \longrightarrow 3\,CaO(OH)_2 + 2Al(OH)_3$$

$$3\,CaO \cdot SiO_2 + H_2O \longrightarrow Ca(OH)_2 + Ca_2SiO_4$$

$Ca(OH)_2$ helps in binding the particles of calcium silicate and $Al(OH)_3$ fills the gap of cement particles. So the material becomes hard after hydrolysis.

(3) Reaction with gypsum : Tricalcium aluminate is quick setting material.

Gypsum **retards the rate of setting** of **cement**. The following chemical reaction occurs with gypsum :

$$3\,CaO\cdot Al_2O_3 + 3CaSO_4 + 2H_2O \longrightarrow \underset{\text{(Calcium sulphide-aluminate)}}{3\,CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 2H_2O}$$

In the setting of cement-tricalcium aluminate immediately sets into hard mass and is responsible for the internal strength of the cement. Tetracalcium alumino-ferrite also sets but not as quick.

Tricalcium silicate (also sets quickly and develops considerable strength with in a few days. But dicalcium silicate (C_2S) sets slowly and develops more strength after one month.

Main Definitions Related to Cement

(1) Mortar : When a paste is prepared by mixing a mixture of lime ($Ca(OH)_2$, sand (SiO_2) and water, it is called mortar. When it is placed in air, it absorbs CO_2 and forms $CaCO_3$ as a result it becomes hard.

(2) Concrete : When pebbles, stone or pieces of bricks are mixed with cement, sand and water, the mixture is called **concrete.** A solid structure is formed by its setting.

(3) Slurry : The dense mixture of finely powdered lime stone, clay and water is called slurry.

(4) Reinforced concrete : When the mixture of pebbles of stone, cement, sand and water is filled in wire net or in between the net of iron rods, the strong and hard structure is formed, the structure so formed is called reinforced concrete.

Uses of portland cement : Mainly cement is used in the construction of buildings, roads, bridges and dams etc. The mixture of cement, sand and water is used for the plastering of walls of buildings.

Cement Industries in India

(1) Uttar Pradesh (Churk, Pipari, Allahabad and Mirzapur)
(2) Uttarakhand (Dehradun, Bhagwanpur etc.)
(3) Rajasthan (Chittorgarh and Jaipur)
(4) Gujarat (Barodara)
(5) Maharashtra (Bhurawa)
(6) Orrisa (Rajjugpura)
(7) Himachal Pradesh
(8) Assam
(9) Karnataka
(10) Tamil Nadu etc.