

Cement : Manufacture, Chemical Composition, Heat of Hydration

Lecture No. 2

Cement

- ▶ In the most general sense of the word, a **cement** is a binder, a substance that sets and hardens independently, and can bind other materials together.
- ▶ Cement used in construction is characterized as hydraulic or non-hydraulic. Hydraulic cements (e.g., Portland cement) 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.



History of the origin of cement

- ▶ John Smeaton made an important contribution to the development of cements when he was planning the construction of the third Eddystone Lighthouse (1755–9) in the English Channel. He needed a hydraulic mortar that would set and develop some strength in the twelve hour period between successive high tides.
- ▶ In 1824, Joseph Aspdin patented a similar material, which he called Portland cement, because the render made from it was in colour similar to the prestigious Portland stone.



History of the origin of cement

- ▶ The investigations of L.J.Vicat led him to prepare an artificial hydraulic lime by calcining an intimate mixture of limestone and clay.
- ▶ Later in 1845 Isaac Charles Johnson burnt a mixture of clay and chalk till the clinkering stage to make better cement and established factories in 1851.
- ▶ The German standard specification for Portland cement was drawn in 1877.



History of the origin of cement

- ▶ The British standard specification was first drawn up in 1904. The first ASTM specification was issued in 1904.
- ▶ In India, Portland cement was first manufactured in 1904 near Madras, by the South India Industrial Ltd. But this venture failed.
- ▶ Between 1912 and 1913, the Indian Cement Co. Ltd., was established at Porbander (Gujarat) and by 1914 this Company was able to deliver about 1000 tons of Portland cement.

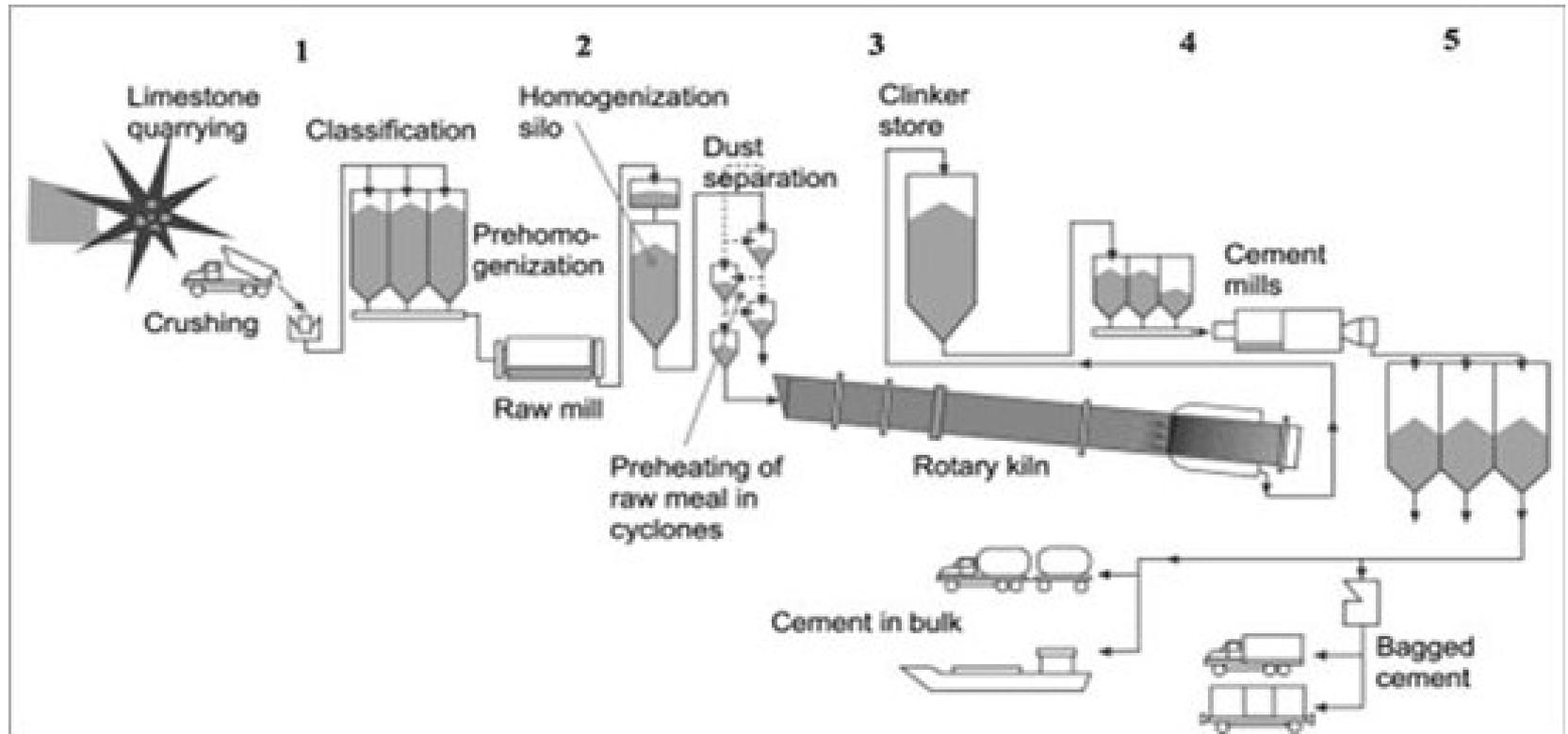


Manufacture of Portland Cement

- ▶ Cement is made by heating limestone (calcium carbonate) with small quantities of other materials (such as clay) to 1450 °C in a kiln, in a process known as calcination, whereby a molecule of carbon dioxide is liberated from the calcium carbonate to form calcium oxide, or quicklime, which is then blended with the other materials that have been included in the mix.
- ▶ The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder to make 'Ordinary Portland Cement', the most commonly used type of cement (often referred to as OPC).



Manufacture of Portland Cement



Manufacture of Portland Cement

- ▶ Step 1 – Quarrying Limestone and a 'cement rock' such as clay or shale are quarried and brought to the cement works. These rocks contain lime (CaCO_3), silica (SiO_2), alumina (Al_2O_3) and ferrous oxide (Fe_2O_3) - the raw materials of cement manufacture.
 - ▶ Step 2 - Raw material preparation To form a consistent product, it is essential that the same mixture of minerals is used every time. For this reason the exact composition of the limestone and clay is determined at this point, and other ingredients added if necessary. The rock is also ground into fine particles to increase the efficiency of the reaction.
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Manufacture of Portland Cement

▶ The dry process :

The quarried clay and limestone are crushed separately until nothing bigger than a tennis ball remains. Samples of both rocks are then sent off to the laboratory for mineral analysis. If necessary, minerals are then added to either the clay or the limestone to ensure that the correct amounts of aluminium, iron etc. are present. The clay and limestone are then fed together into a mill where the rock is ground until more than 85% of the material is less than $90\mu\text{m}$ in diameter.



Manufacture of Portland Cement

▶ The wet process :

The clay is mixed to a paste in a washmill - a tank in which the clay is pulverised in the presence of water. Crushed lime is then added and the whole mixture further ground. Any material which is too coarse is extracted and reground. The slurry is then tested to ensure that it contains the correct balance of minerals, and any extra ingredients blended in as necessary.



Manufacture of Portland Cement

- ▶ Step 3 – Clinkering The raw materials are then dried, heated and fed into a rotating kiln. Here the raw materials react at very high temperatures to form $3\text{CaO} \cdot \text{SiO}_2$ (tricalcium silicate), $2\text{CaO} \cdot \text{SiO}_2$ (dicalcium silicate), $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (tricalcium aluminate) and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (tetracalcium alumino-ferrate).



Manufacture of Portland Cement

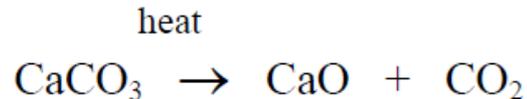
- ▶ The kiln :The kiln shell is steel, 60m long and inclined at an angle of 1 in 30. The shell is supported on 3 roller trunions and weighs in at over 1100 T. The kiln is heated by injecting pulverised coal dust into the discharge end where it spontaneously ignites due to the very high temperatures. Coal is injected with air into the kiln at a rate of 9 - 12 T/hr.



Manufacture of Portland Cement

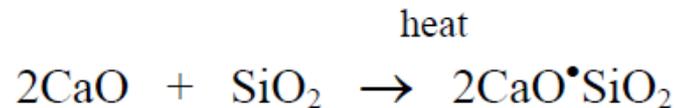
Zone 1: 0 - 35 min, 800 - 1100°C

Decarbonation. Formation of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ above 900°C. Melting of fluxing compounds Al_2O_3 and Fe_2O_3 .



Zone 2: 35 - 40 min, 1100 - 1300°C

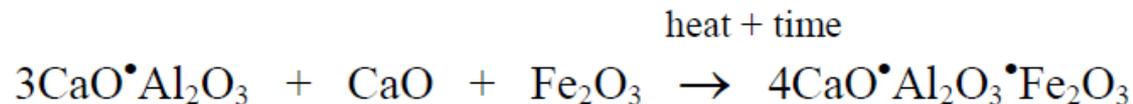
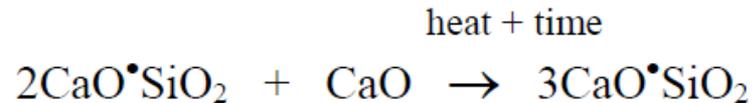
Exothermic reactions and the formation of secondary silicate phases as follows:



Manufacture of Portland Cement

Zone 3: 40 - 50 min, 1300 - 1450 - 1300°C

Sintering and reaction within the melt to form ternary silicates and tetracalcium aluminoferrates:



Zone 4: 50 - 60 min, 1300 - 1000°C

Cooling and crystallisation of the various mineral phases formed in the kiln.



Manufacture of Portland Cement

- ▶ Step 4 - Cement milling The 'clinker' that has now been produced will behave just like cement, but it is in particles up to 3 cm in diameter. These are ground down to a fine powder to turn the clinker into useful cement.



Chemical Composition of Portland Cement

- ▶ The raw materials used for the manufacture of cement consist mainly of lime, silica, alumina and iron oxide. These oxides interact with one another in the kiln at high temperature to form more complex compounds. The relative proportions of these oxide compositions are responsible for influencing the various properties of cement; in addition to rate of cooling and fineness of grinding.



Chemical Composition of Portland Cement

Table 1.4. Approximate Oxide Composition Limits of Ordinary Portland Cement

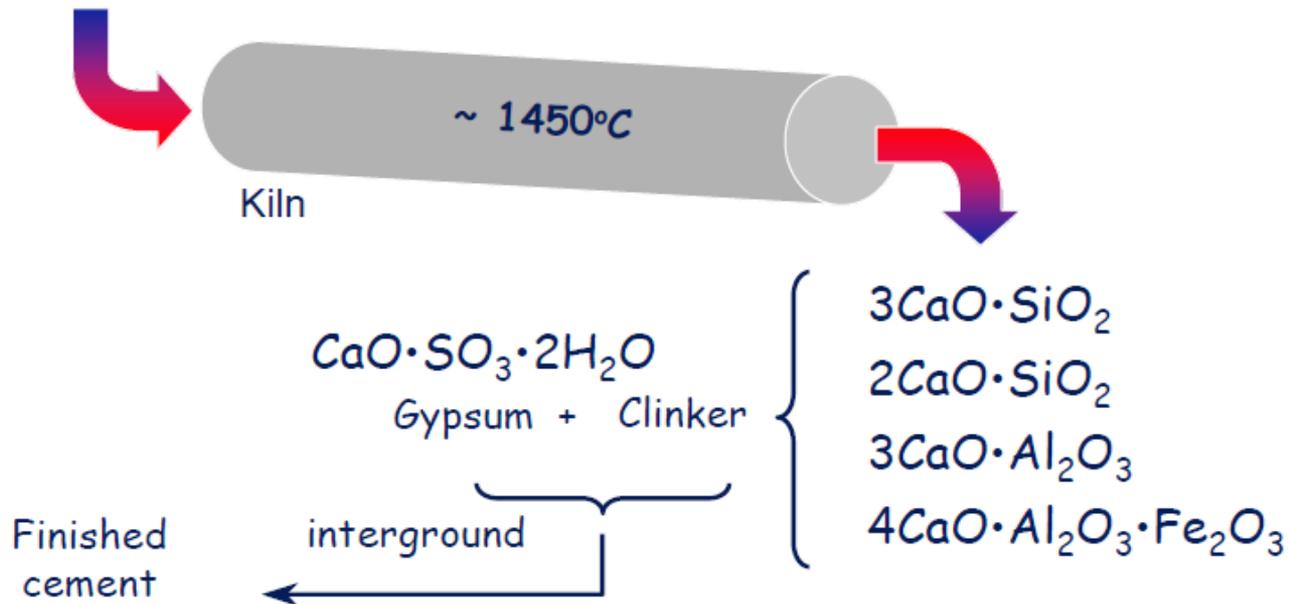
<i>Oxide</i>	<i>Per cent content</i>
CaO	60–67
SiO ₂	17–25
Al ₂ O ₃	3.0–8.0
Fe ₂ O ₃	0.5–6.0
MgO	0.1–4.0
Alkalies (K ₂ O, Na ₂ O)	0.4–1.3
SO ₃	1.3–3.0



Chemical Composition of Portland Cement

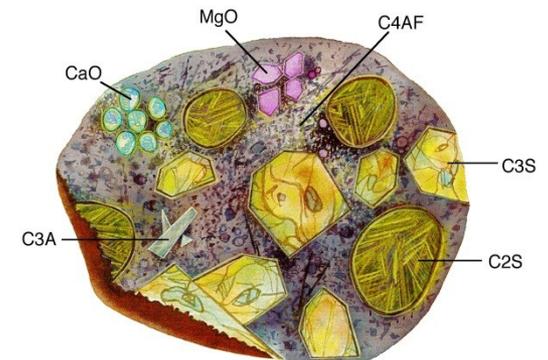
Cement Composition

CaCO_3 (limestone)
 $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ (clay, shale)
 Fe_2O_3 (iron oxide)
 SiO_2 (silica sand)



Chemical Composition of Portland Cement

Mineral	Chemical formula	Oxide composition	Abbreviation
Tricalcium silicate (alite)	Ca_3SiO_5	$3\text{CaO}.\text{SiO}_2$	C3S
Dicalcium silicate (belite)	Ca_2SiO_4	$2\text{CaO}.\text{SiO}_2$	C2S
Tricalcium aluminate	$\text{Ca}_3\text{Al}_2\text{O}_4$	$3\text{CaO}.\text{Al}_2\text{O}_3$	C3A
Tetracalcium aluminoferrite	$\text{Ca}_4\text{Al}_n\text{Fe}_{2-n}\text{O}_7$	$4\text{CaO}.\text{Al}_n\text{Fe}_{2-n}\text{O}_3$	C4AF



Hydration of cement

- ▶ When Portland cement is mixed with water its chemical compound constituents undergo a series of chemical reactions that cause it to harden. This chemical reaction with water is called "hydration".
- ▶ Each one of these reactions occurs at a different time and rate. Together, the results of these reactions determine how Portland cement hardens and gains strength.



Hydration of cement

- ▶ Hydration starts as soon as the cement and water are mixed.
- ▶ The rate of hydration and the heat liberated by the reaction of each compound is different.
- ▶ Each compound produces different products when it hydrates.
- ▶ Tricalcium silicate (C3S). Hydrates and hardens rapidly and is largely responsible for initial set and early strength. Portland cements with higher percentages of C3S will exhibit higher early strength.



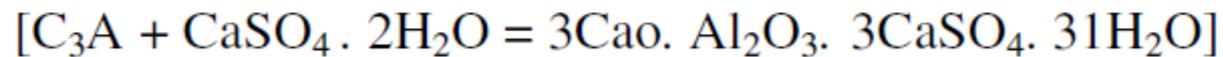
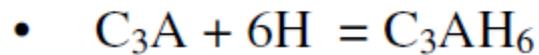
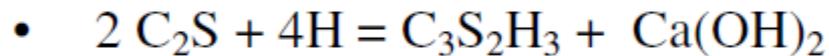
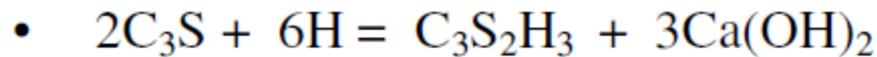
Hydration of cement

- ▶ Tricalcium aluminate (C3A). Hydrates and hardens the quickest. Liberates a large amount of heat almost immediately and contributes somewhat to early strength. Gypsum is added to Portland cement to retard C3A hydration. Without gypsum, C3A hydration would cause Portland cement to set almost immediately after adding water.
- ▶ Dicalcium silicate (C2S). Hydrates and hardens slowly and is largely responsible for strength increases beyond one week.
- ▶ Tetracalcium aluminoferrite (C4AF). Hydrates rapidly but contributes very little to strength. Its use allows lower kiln temperatures in Portland cement manufacturing. Most Portland cement color effects are due to C4AF.



Hydration of cement

- **Reactions of Hydration**



Calcium Sulfoaluminate

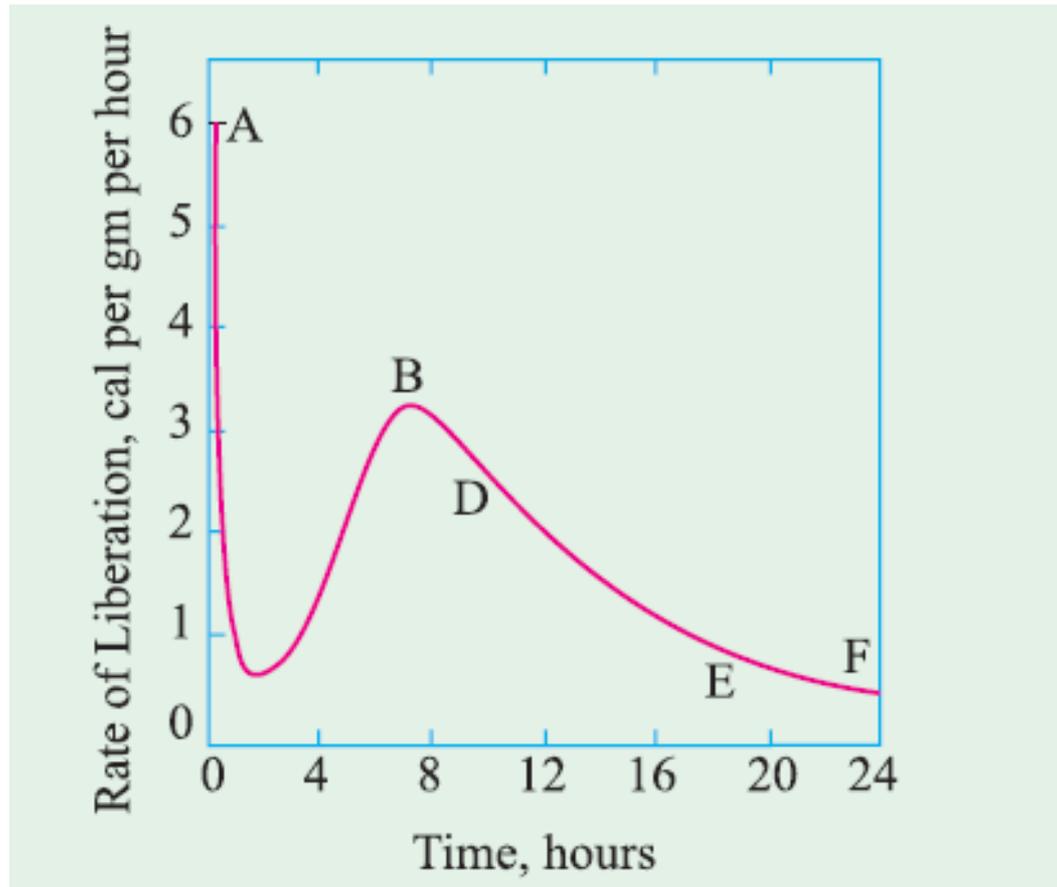


Heat of Hydration

- ▶ The reaction of cement with water is exothermic. The reaction liberates a considerable quantity of heat. This liberation of heat is called heat of hydration. This is clearly seen if freshly mixed cement is put in a vacuum flask and the temperature of the mass is read at intervals.
- ▶ The study and control of the heat of hydration becomes important in the construction of concrete dams and other mass concrete constructions. It has been observed that the temperature in the interior of large mass concrete is 50°C above the original temperature of the concrete mass at the time of placing and this high temperature is found to persist for a prolonged period.



Heat of Hydration



Heat of Hydration

- ▶ The heat of hydration is the heat generated when water and Portland cement react. Heat of hydration is most influenced by the proportion of C3S and C3A in the cement, but is also influenced by water-cement ratio, fineness and curing temperature. As each one of these factors is increased, heat of hydration increases.
- ▶ For usual range of Portland cements, about one-half of the total heat is liberated between 1 and 3 days, about three-quarters in 7 days, and nearly 90 percent in 6 months.
- ▶ The heat of hydration depends on the chemical composition of cement.



Properties of Hydrated Cement Compounds

C_3S	Tricalcium silicate (alite)	Hydrates & hardens rapidly Responsible for initial set and early strength
C_2S	Dicalcium silicate (belite)	Hydrates & hardens slowly Contributes to later age strength (beyond 7 days)
C_3A	Tricalcium aluminate	Liberates a large amount of heat during first few days Contributes slightly to early strength development Cements with low % ages are more resistant to sulphates
C_4AF	Tetracalcium aluminoferrite (ferrite)	Reduces clinkering temperature Hydrates rapidly but contributes little to strength Colour of hydrated cement (gray) due to ferrite hydrates

