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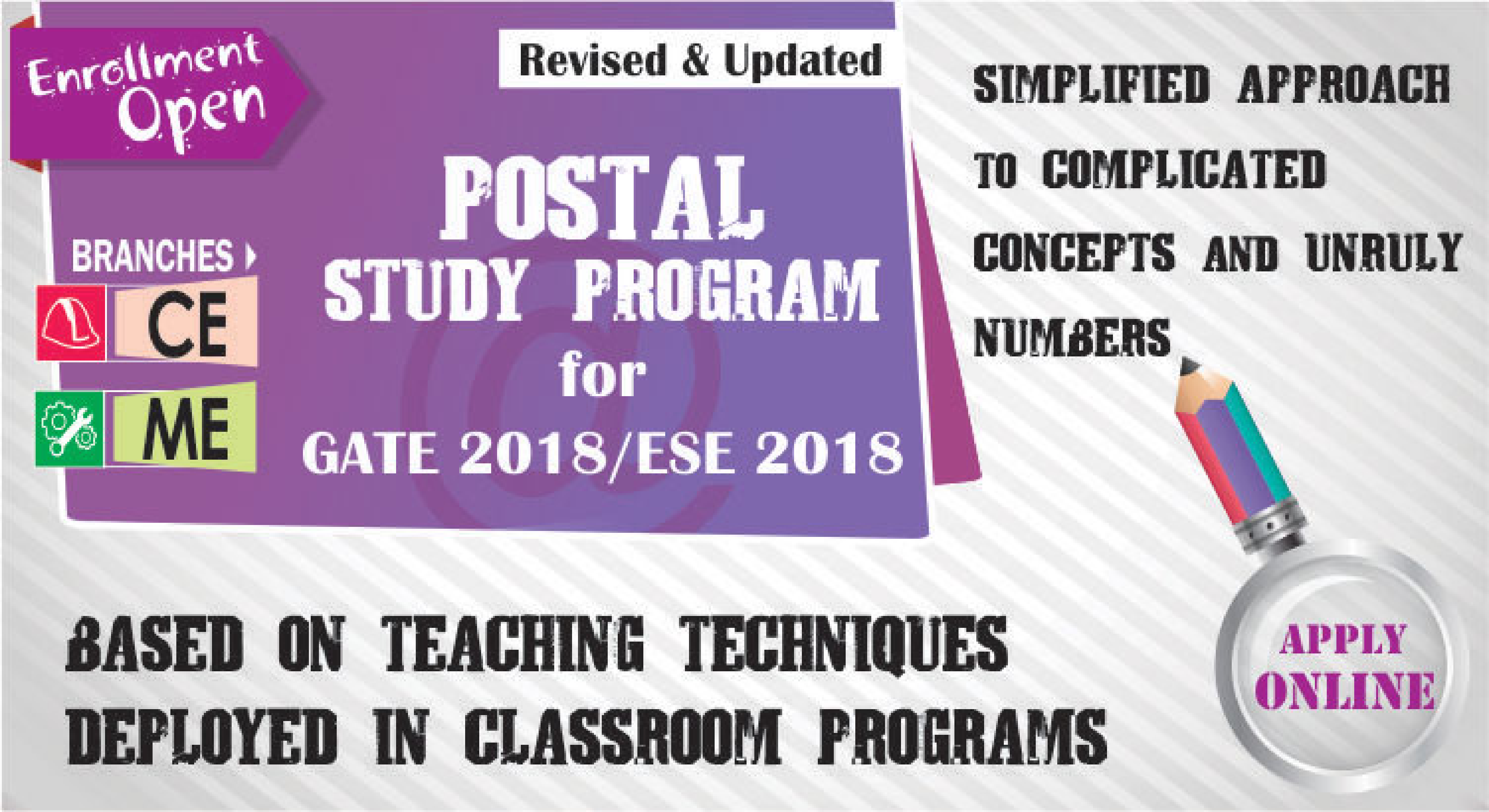
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CHAPTER

1

Cement

INTRODUCTION

- Cement is a material which has cohesive and adhesive properties in the presence of water.
- Standard density of cement is 1440 kg/m^3 and 1 bag of cement is of 50 kg; thus volume would be : 50 kg ÷ 1440 kg/m^3 = 0.0347 m^3.

  Hence volume of 1 bag of cement can be approximated as 0.035 m^3 or 35 litres.
- Cement is a product obtained by pulverizing clinker formed by calcinating raw-materials primarily consisting of Lime (CaO) , Silicate (SiO_2), Alumina (Al_2O_3) and Iron oxide (Fe_2O_3).
- It was invented by Joseph Aspdin of UK in 1824. He named it portland cement because the hardened concrete made out of the cement aggregate and water in definate proportion resembled the natural stone occurring at portland in England.

Note: **Pulverize** : Make into a powder by breaking up or cause to become dust

Clinker : A hard brick used as a paving stone.

Calcination : The process of heating a substance to a high temperature in the absence or limited supply of oxygen but below the melting or fusing point, causing loss of moisture, reduction on oxidation, and dissociation into simpler substances.

- When cement is mixed with water it forms a paste which hardens and binds aggregates (fine and coarse) together to form a hard durable mass called concrete.
- Cements used in construction industry can be classified as hydraulic and non hydraulic.
- Hydraulic cement set and harden extremely fast in presence of water (Due to the chemical action between cement and water known as hydration) and results in water-resistant product which is stable. This allows setting in wet condition or underwater and further protects the hardened material from chemical attack. eg. Portland cement.
- Non-hydraulic cements are derived from calcination of gypsum or limestone because their products of hydration are not resistant to water; however, the addition of pozzolanic materials can render gypsum and lime cement hydraulic. Thus, it will not set in wet conditions or underwater, rather, it sets as it dries and reacts with carbon-dioxide in the air. It can be attacked by some aggressive chemicals after setting. Ex-Plaster of Paris.
- Cement can be manufactured either from natural cement stones or artificially by using calcareous and argillaceous materials. Examples of natural cements are Roman cement, Pozzolona cement and Medina cement and of artificial cement are Portland cement and special cements.


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Note:

Argillaceous	Calcareous
• Shale and clay • Blast furnace slag • Slate	• Cement rock • Limestone • Chalk • Marine shells • Marl

- Certain clays formed during volcanic eruption, known as volcanic ash or pozzolana found near Itlay have properties similar to that of portland cement.
- Various varieties of artificial cement (exceeding 30 in number) are available in the market at present.

CHEMICAL COMPOSITION OF RAW MATERIALS

- The three basic constituents of hydraulic cements are lime, silica and alumina.
- The relative proportions of these oxide compositions are responsible for influencing the various properties of cement.
- An increase in lime content beyond a certain value makes it difficult to combine completely with other compounds.
- Consequently, free lime will exist in the clinker and will result in an unsound cement. An increase in silica content at the expense of alumina and ferric oxide makes the cement difficult to fuse and form clinker.
- The approximate limits of chemical composition in cement are given in table.

Constituents of Portland Cement (Raw Material)

Oxide	Function	Composition (%)	Average
Lime, CaO	Controls strength and soundness. Its deficiency reduces strength and setting time. Excess of it cause unsoundness.	60-65	63
Silica, SiO_2	Gives strength. Excess of it causes slow setting.	17-25	20
Alumina, Al_2O_3	Responsible for quick setting, if in excess, it lowers the strength.	3-8	6
Iron oxide, Fe_2O_3	Gives colour and helps in fusion of different ingredients. i.e., it acts as a flux	0.5-6	3
Magnesia, MgO	Imparts colour and hardness. If in excess, it causes cracks in mortar and concrete and unsoundness.	0.5-4	2
Soda and/or potash, $Na_2O + K_2O$	These are residues, and if in excess cause efflorescence and cracking.	0.5-1	1
Sulphur trioxide, SO_3	Excess of it makes cement unsound.	1-2	1.5

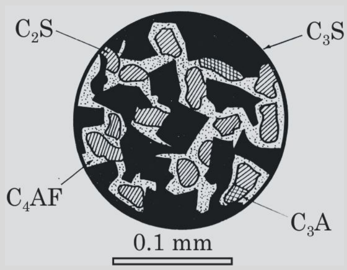
Note:
1. Rate of setting of cement paste is controlled by regulating the ratio $SiO_2/(Al_2O_3 + Fe_2O_3)$.
2. When development of heat of hydration is undesirable, the silica content is increased to about 21 per cent, and the alumina and iron oxide contents are limited to 6 per cent each.

3. Resistance to the action of sulphate waters is increased by raising further the silica content to 24 per cent and reducing the alumina and iron contents in 4 per cent each.
4. The variation in composition depends largely on the ratio of CaO to SiO_2 in the raw materials.
5. Alkalis accelerate the setting of cement paste.
6. Small percentage of iron oxide renders the highly siliceous raw materials easier to burn. However, if these are in excess, a hard clinker, difficult to ground, is produced.

COMPOSITION OF CEMENT CLINKER AND THEIR SETTING ACTION

- When these raw materials are put in kiln then it fuses and following four major compounds are formed and they are known as Bogue compounds.

The principal mineral compounds in Portland cement	Formula	Name	Symbol
1. Tricalcium silicate	$3CaO.SiO_2$	Alite	C_3S
2. Dicalcium silicate	$2CaO.SiO_2$	Belite	C_2S
3. Tricalcium aluminate	$3CaO.Al_2O_3$	Celite	C_3A
4. Tetracalcium alumino ferrite	$4CaO.Al_2.Fe_2O_3$	Felite	C_4AF



Schematic representation of the composition of portland cement

- Besides major compounds 2 minor compounds are also formed K_2O and Na_2O (Alkalies) which play an important role in the Alkali-aggregate reaction.
- The mixing of cement and water results in formation of various complicated chemical compounds, are not simultaneous.
- But setting action of cement continues for a long time. The mixing of cement and water results in a sticky cement paste and it goes on gradually thickening till it achieves a rock like state.
- It is found that ordinary cement achieves about 70% of its final strength in 28 days and about 90% in 1 year.
- Properties of portland cement varies significantly with the proportions of the above four compounds, as substantial difference is observed in their individual behaviour.

1. Tricalcium Silicate C_3S– (25 – 50%)– Normally 40%

- It is considered as best cementing material and is well burnt cement.
- It enables clinker easy to grind , increases resistance to freezing and thawing.
- It hydrates rapidly generating high heat and develops an early hardness and strength.
- Raising of C_3S content beyond the specified limits increases heat of hydration and solubility of cement in water.
- Hydrolysis of C_3S is mainly responsible for 7 days strength and hardness.
- Rate of hydrolysis of C_3S and the character of gel developed are the main cause of the hardness and early strength of cement paste.
- Heat of hydration is 500 J/gm.

2. Dicalcium Silicate (C_2S) (25 – 40%) (Normally 32%)

- It hydrates and hardens slowly and takes long time to add to the strength (after a year or more) i.e. it is responsible for ultimate strength.
- It imparts resistance to chemical attack.
- Raising of C_2S content renders clinker harder to grind, reduces early strength, decreases resistance to freezing and thawing at early ages and decreases heat of hydration.
- At early ages, less than a month, C_2S has little influence on strength and hardness. While after one year, its contribution to the strength and hardness is proportionately almost equal to C_3S.
- Heat of hydration is 260 J/g

3. Tricalcium Aluminate (C_3A) (5 – 11%) (Normally 10.5%).

- It rapidly reacts with water and is responsible for flash set of finely grounded clinker.
- Rapidity of action is regulated by the addition of 2-3% of gypsum at the time of grinding the cement.
- It is most responsible for the initial setting, high heat of hydration and has greater tendency to volume changes causing cracking.
- Raising the C_3A content reduces the setting time, weakens resistance to sulphate attack and lowers the ultimate strength, heat of hydration and contraction during air hardening.
- Heat of hydration of 865 J/g.

4. Tetracalcium Alumino Ferrite (C_4AF 8 –14%) (Normally 9%)

- It is responsible for flash set but generates less heat.
- It has poorest cementing value
- Raising the C_4AF content reduces the strength slightly.
- Heat of hydration 420 J/g

HYDRATION OF CEMENT

- When water is added to cement, a chemical reaction between water and cement takes place which is known as hydration of cement.
- Heat liberated (exothermic) during this chemical reactions is known as Heat of hydration.
- It has been observed that the significant product of hydration is $\left(CaO\ SiO_2\ H_2O\right)$ which is called as Tobermorite Gel because of its structural similarity to a naturally occurring mineral Tobermorite and commonly it is reffered C-S-H Gel.
- When portland cement combines with water during setting and hardening, Lime is librated from some of the compounds. The amount of lime librated appears to be about 15 to 20 percent of the cement weight.

Hydration of Silicate given by equations are:

- $$\underset{[100]}{2C_3S} + \underset{[24]}{6H} \longrightarrow \underset{[75]}{C_3S_2H_3} + \underset{[49]}{3Ca(OH)_2}$$
- $$\underset{[100]}{2C_2S} + \underset{[21]}{4H} \longrightarrow \underset{[99]}{C_3S_2H_3} + \underset{[22]}{Ca(OH)_2}$$

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The number in the bracket indicates the mass of the respective compound taking part in the reaction.

- From these two above equations it can be seen that hydration of C_3S produce lesser calcium silicate hydrates (C–S–H) and more $Ca(OH)_2$ as compared to the hydration of C_2S.
- Since $Ca(OH)_2$ is not a desirable product in the concrete mass because it is soluble in water and gets leached out making the concrete porous, particularly in hydraulic structure, that's why cement with small percentage of C_3S and more C_2S is recommmended for use in hydraulic structure.
- Alternative way to overcome this difficulty is to grind some pozzolanic material with cement (fly ash combined with lime). a pozzolana is a siliceous material which reacts with lime in presence of moisture to give a relatively stable strength producing calcium silicates.
- $Ca(OH)_2$ reacts with sulphate present in soil or water to form $CaSO_4$ which further reacts with C_3A and forms calcium sulphoaluminate (ettringite) which causes volume expansion such that expanded volume is approximately 227% of the volume of original aluminates, thus resulting in crack and subsequent disruption.
- Solid sulphate do not attack on cement compound. It is the sulphates in solution which permeate the concrete and attack $Ca(OH)_2$, hydrated calcium aluminate and even hydrated silicates. This is known as sulphate attack.
- The only advantage of $Ca(OH)_2$ is that being alkaline in nature maintain $PH \simeq 13$ in concrete which resist the corrosion of reinforcement.
- **Hydration of Cement depends on following factor:**
  (i) **Temperature at which hydration takes place:** Higher the temperature rapid is the hydration. It is for this reason that in cold weather, sometimes the aggregates are heated before they are used for making concrete.
  (ii) **Fineness of Cement:** Finner the cement rapid is the hydration because finer cements have larger surface areas. However, a very fine ground cement is susceptible to air-set and deteriorates earlier.
  (iii) **The ingredients of cement:** The reaction can be made rapid or slow by changing the proportions of the ingredients of the cement.
- C_3S readily reacts with water, producing more heat of hydration and is responsible for early strength of Concrete.
- C_3S is the best cementing material and by increasing its percentage, the quality of cement can be improved.
- C_2S hydrates more slowly, produces less heat of hydration and is responsible for later strength of Concrete. The calcium silicate hydrate formed is dense. The hydration products of C_2S are considered better than those of C_3S.
- For most of cements, the sum of percentage of C_3S and C_2S is nearly (usually 70 to 72%).
- The reaction of pure C_3A with water is very fast and may lead to flash set. Gypsum is added at time of grinding to prevent this flash set (addition of gypsum increases the soundness of cement). The hydrated aluminates, do not contribute anything to the strength of the paste. On the other hand, their presence is harmful to the durability of Concrete, in situations where the concrete is likely to be attacked by sulphates.
- The hydrated product due to C_4AF, also, does not contribute anything to the strength, through they are more resistant to sulphate attack.

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