Cement

Lecture - 3

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Content

- Compound in Portland Cement
- Function of compound of cement
- Hydration of cement
- Rate of Hydration
- Water requirement for hydration

Compound Present in Cement

Compound of cement

Tri-calcium Silicate (Alite)

Designated as C_3S, C for calcium and S for silicate; also written as $3CaO.SiO_2$

Di-calcium Silicate (Belite)

Designated as C_2S, also written as $2CaO.SiO_2$

Tri-calcium Aluminate (Celite)

C_3AL:Al for aluminum; also written as $3CaO.\ Al_2O_3$

Tetra-Calcium-Alumino-Ferrite (Felite)

C_4ALFe: C for calcium, Al for Aluminum and Fe for the Iron

Function of Tri-calcium Silicate

- Presented in all types of Portland Cement. Its proportion ranges from 25 to 50 percent. This compound imparts following properties to the cement on setting.
- Hydrates rapidly generating high heat and develops an ***early hardness*** and ***strength***.
- The hydrolysis of C_3S is mainly responsible for 7 day ***strength*** and ***hardness***.
- The rate of hydrolysis of C_3S and the character of ***gel*** developed are the main cause of hardness and early strength of cement paste. Heat of hydration is 500 J/g.

Function of Di-calcium Silicate

- Second Major Compound – 25 to 40%

- It is the next main compound after tri-calcium silicate and forms

25-40 %. Its main character is its ***slow rate of hydration reaction***. This lead to slow hardening of the cement on setting. Whereas, all the tri-calcium silicate may set within first 28 days, this compound may begin hardening only after that time.

Function of Di-calcium Silicate

- It may continue hardening for many weeks and months after the cement is laid.
- 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.

Function of Di-calcium Silicate

- The heat of hydration is 260 J/g.

- It is therefore, a desirable compound in slow hardening cement required for hydraulic structures. ***But in case of rapid hardening cement is required its content is kept to the lower side by adjusting the ratio of ingredients.***

Function of Tri-calcium Aluminate

- Third major compound found in cements (5 – 11%)
- Average is 10.5 % in the ordinary cement. This is because evolution of too much heat during the reaction is an undesirable property in most type of construction.
- It is fast reacting with a lot of heat evolution during the reaction. Therefore, it is an important compound of all types of rapid hardening cements.

Function of Tri-calcium Aluminate

- The rapidity of action is regulated by the addition of 2-3% of gypsum at the time of grinding cement. Tricalcium aluminate is responsible for the initial set, 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. The heat of hydration of 865 J/g.

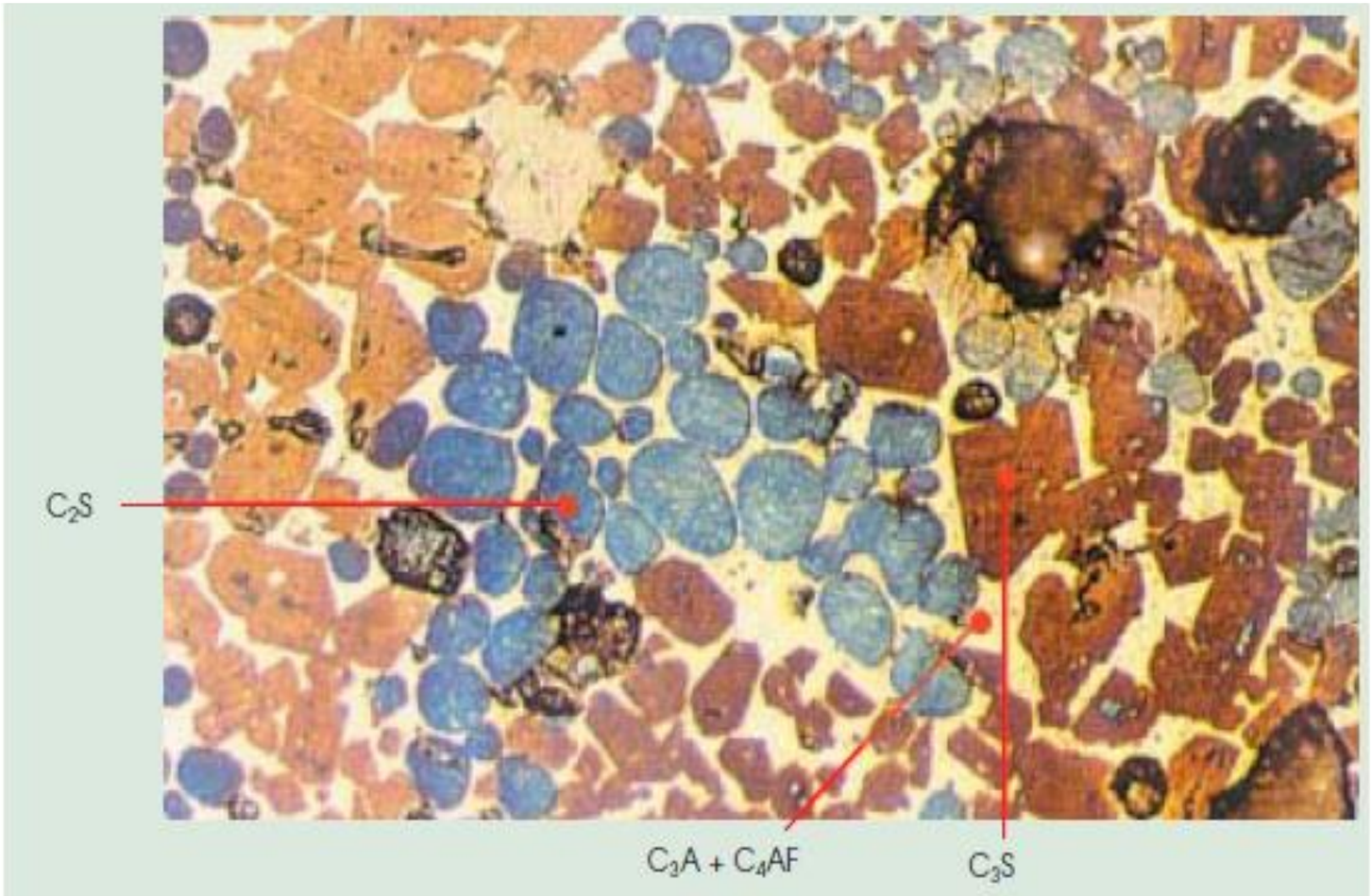
Function of Tetra-calcium-Alumino-Ferrite

- Fourth compound formed due to mutual reactions of ingredients during heating of the raw material in the kilns (8 to 14%).
- Average of 9 % is available in OPC
- It is least important of the compounds of portland cements as it has poor cementing value and a slow rate of reaction during setting.

Function of Tetra-calcium-Alumino-Ferrite

- It is responsible for flash set but generates less heat. It has poorest cementing value. Raising the C4AF content reduces the strength slightly. The heat of hydration is 420 J/g.

Schematic Presentation of various Compounds in Clinker



Schematic presentation of various compounds in clinker

Courtesy : All the photographs on manufacture of cement are by Grasim Industries Cement Division

Mehta, Pk, Concrete Microstructure, Properties and Material

Brief about the Function of Compound Present in Cement

S. No	Compound	Abbreviation	Range (%)	Typical characters
1	Tricalcium Silicate (Alite)	C_3S	25-55	Medium reacting; Medium heat evolution; early strength
2	Dicalcium Silicate (Belite)	C_2S	25-40	Slow reacting; Slow hardening; give strength after 28 days
3	Tricalcium Aluminate (Celite)	C_3Al	5-11	Fast reacting; High heat evolution; Early hardening
4	Tetra-Calcium Alumino-ferrite (Felite)	C_4AlFe	8-14	Poor binding properties

Heat of Hydration of Pure Compound

Compound	Heat of Hydration	
	j/g	Cal/g
C_3S	502	120
C_2S	260	62
C_3A	867	207
C_4AF	419	100

Note

Reduction in the proportions of C_3A and C_3S, the heat of hydration (and its rate) of cement can be reduced. Fineness of cement affects the heat development but not the total amount of heat liberated, which can be controlled in concrete by the quantity of cement in the mix.

Neville AM and Brooks JJ Concrete Technology

Hydration of Cement

Cement + Water → hydration products start depositing on the outer periphery of the nucleus of hydrated cement.

Active Compound

C_4AF, C_3A, C_3S and C_2S

This reaction proceeds slowly for 2-5 hours and is called induction or dormant period.

Hydration of Cement

As the hydration proceeds, the deposit of hydration products on the original cement grain makes the diffusion of water to unhydrated nucleus more and more difficult, consequently reducing the rate of hydration with time.

At any stage of hydration, the cement paste consists of gel (a fine-grained product of hydration having large surface area collectively), the unreacted cement, calcium hydroxide, water and some minor compounds.

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Hydration of Cement

- The reactions of the compounds and their products are as follows:

C_3S + H_2O → C-S-H * + $Ca(OH)_2$

Tri-calcium Silicate + Water → (Calcium Silicate Hydrate + Calcium Hydro oxide)

C_2S + H_2O → C-S-H + $Ca(OH)_2$

Di-calcium Silicate + Water → (Calcium Silicate Hydrate + Calcium Hydro oxide)

C_3A + H_2O → C_3AH_6

Tri-calcium Aluminate + Water → (Cement Hydrates - Thermodynamically stable cement structure derived from calcium aluminate cement hydrate compounds – Pure form is called Katotite cement)

C_3A + H_2O + CaSO4 → C A C $S^{\#}$ H_{12} (Calcium sulpho-aluminate)

C_4AF + H_2O → C3AH6 + CFH

Tetra-Calcium-Alumino-Ferrite

Hydration Product

H * is H2O

$S^{\#}$ is SO_3

Hydration of Cement

C-S-H — *Also known as* → ***Tobermorite Gel***

Tobermorite Gel → Crystals – fibrous, platey or tubular in shape varying from less than 2mm to 10mm

Tobermorite Gel → ***Occupies 50-60% volume of solids in a completely hydrated cement***

Hydration of Cement

$Ca(OH)_2$

Liberated during the silicate paste crystallizes in the available space

Occupies 20-25% volume of solids in a completely hydrated cement

strength contributing potential is limited

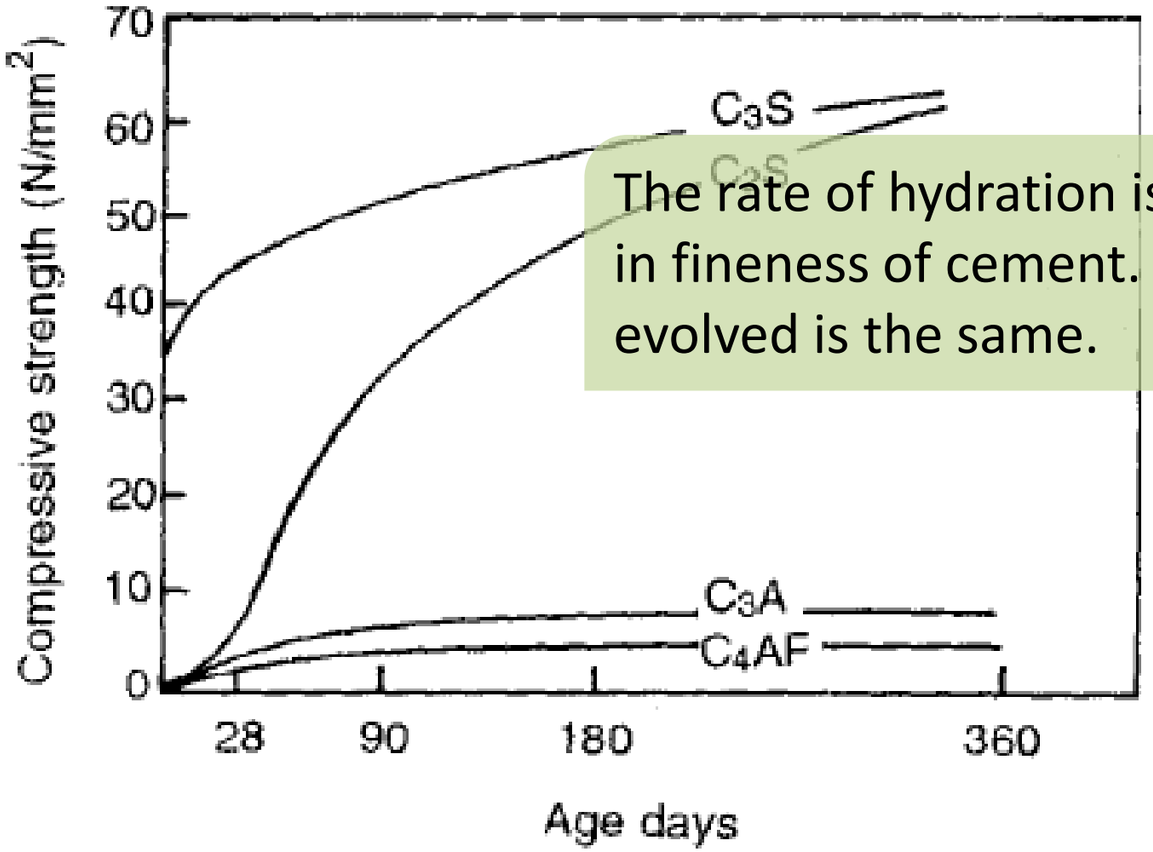
As hydration proceeds, the CSH & $Ca(OH)_2$ crystal types become more heavily interlocked increasing the strength, though the main cementing action is provided by the gel which occupies two-thirds of the total mass of hydrate.

Hydration of Cement

It has been found that hydration of C_3S produces lesser calcium sillicate hydrate and more $Ca(OH)_2$ as compared to the hydration of C_2S. Since $Ca(OH)_2$ is soluble in water and leaches out making the concrete porous, particularly in hydraulic structures, a cement with percentage of C_3S and more C_2S is recommended for use in hydraulic structures.

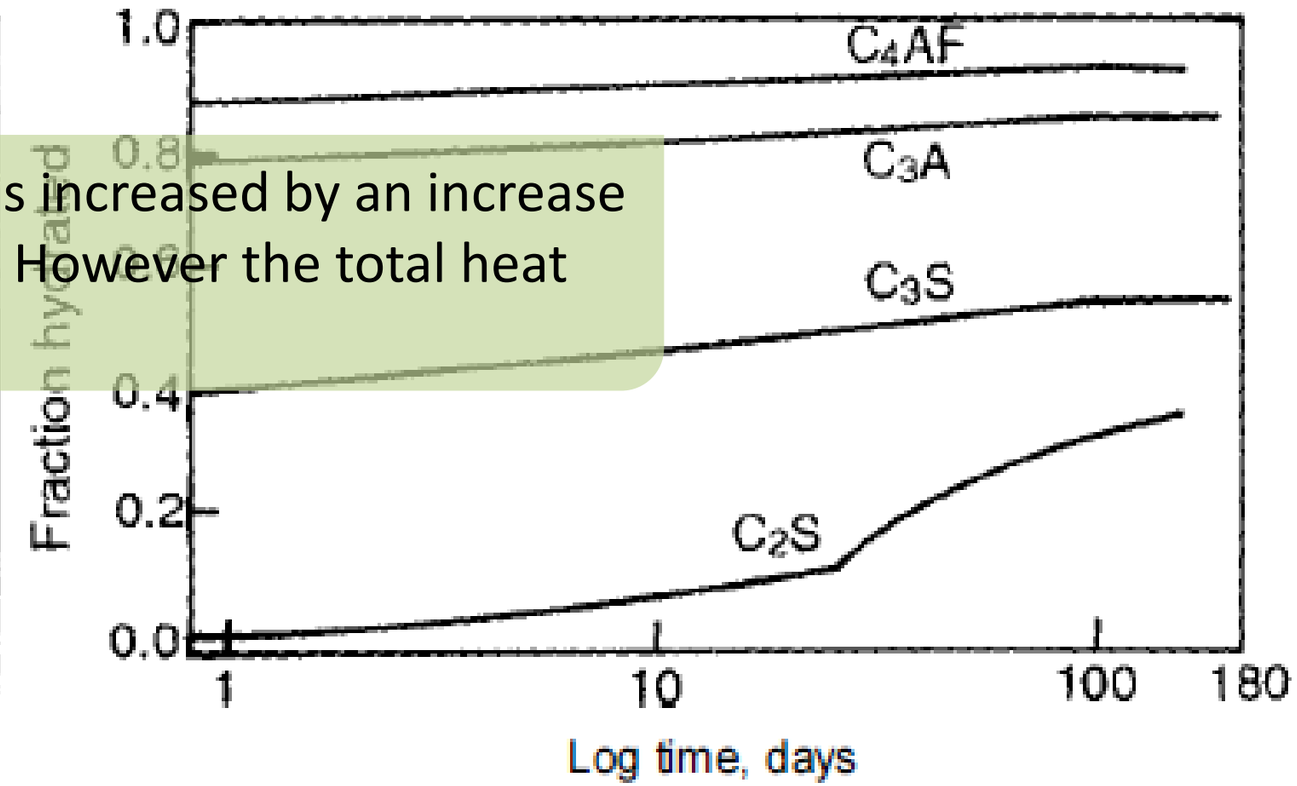
It is particularly important to note that setting (the change of cement paste from plastic to stiff solid state) and hardening (gain of strength with hydration is a chemical reaction, wherein water plays an important role) is not just a matter of drying out. Infect, setting and hardening stop as soon as the concrete become dry

Rate of Hydration



Contribution of cement compounds to the strength of cement

The rate of hydration is increased by an increase in fineness of cement. However the total heat evolved is the same.



Rate of hydration of pure cement compounds

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Rate of Hydration

- The reaction of compound C_3A with water is very fast and is responsible for flash setting of cement (stiffening without strength development) and thus it will prevent the hydration of C_3S and C_2S.
- Calcium sulphate ($CaSO_4$) present in the clinker dissolves immediately in water and forms insoluble calcium sulphoaluminate. It deposits on the surface of C_3A forming a colloidal membrane and consequently retards the hydration of C_3A.

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Rate of Hydration

- This membrane in the process breaks because of the pressure of the compounds formed during hydration and then again C_3A becomes active in the reaction.

- The hardening of C_3S can be said to be catalyzed by C_3A and C_3S becomes solely responsible for gain of strength up to 28 days by growth and interlocking of C-S-H gel. The increase in strength at later age is due to hydration of C_2S.

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Water Requirement for Hydration

Water Requirement for Hydration

28% water by wt. of cement

Complete hydration of Portland cement

Complete Hydration

+

This water combines chemically with the cement compounds and is known as <u>bound water</u>

15% water by wt. of cement

Required to Filling of cement gel pores (gel water)

Total Water Requirement

38% Water

Note

The general belief that a water/cement ratio less than 0.38 should not be used in concrete because for the process of hydration, the gel pores should saturated – is not valid. This is because as even if excess water is present, complete hydration of cement never takes place due to deposition of hydration products.

As a matter of fact water/cement ratio less than 0.38 is very common for high strength concretes. If excess water is present, it will lead to capillary cavities.

Adjustment in compound lead to varieties of cement

- ✓ *The % of compounds can be adjusted by varying the proportions of basic ingredients. Accordingly, the type of cement will differ in its qualities depending upon the final composition.*

Summary

- ✓ Compound available in cement
- ✓ Function of compound
- ✓ Rate of Hydration
- ✓ Water Requirement for hydration

Thank You