

**Hydration, Porosity and Strength of Cementitious Materials**  
**Prof. Sudhir Mishra and Prof. K. V. Harish**  
**Department of Civil Engineering**  
**Indian Institute of Technology, Kanpur**

**Lecture – 13**  
**Portland Cement Based Paste Systems**

Hi good morning to one and all, I am K V Harish assistant professor department of civil engineering IIT Kanpur you are watching MOOC lecture course on hydration, porosity and strength of cementitious material. Today we will see lecture 30 Portland cement based paste systems.

(Refer Slide Time: 00:31)



 **Department of Civil Engineering**  
**Indian Institute of Technology Kanpur**

---

**LECTURE 13**  
**PORTLAND CEMENT BASED PASTE SYSTEMS**

*Textbooks or Reference Materials*

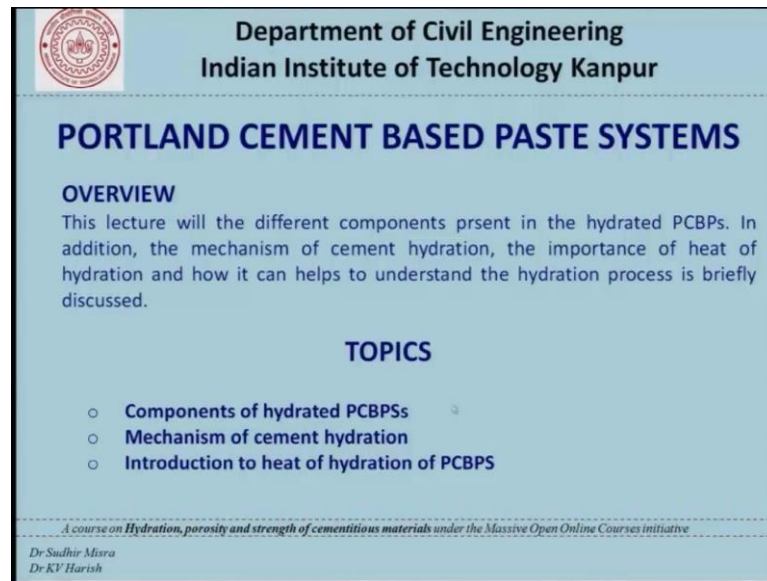
- [1] Sidney, M., Young, J.F., and Darwin, D. Concrete, 2<sup>nd</sup> Edition, Prentice-Hall, Pearson Education, Inc., New Jersey, 2003.
- [2] Mehta, P.K., and Monteiro P.J.M., Concrete – Microstructure, Properties and Materials, Third Edition, McGraw Hill Education (India) Private Limited, New Delhi, Prentice-Hall, Inc., 1993 or 2006.
- [3] Neville, A.M., Properties of concrete, 5<sup>th</sup> Edition, Pitman Publishers, 1996.
- [4] Taylor, H.F.W., Cement Chemistry (2<sup>nd</sup> Edition), Thomas Telford Services, New York, USA
- [5] Indian Standard Specifications (IS 383, IS 456, IS 2386 and others)
- [6] Other websites and web based sources

---

*A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative*

Dr Sudhir Mishra  
Dr KV Harish

(Refer Slide Time: 00:38)



The slide features a light blue background with a black border. At the top left is the IIT Kanpur logo. The header text reads 'Department of Civil Engineering' and 'Indian Institute of Technology Kanpur'. The main title is 'PORTLAND CEMENT BASED PASTE SYSTEMS'. Below it, the 'OVERVIEW' section states that the lecture will cover components of hydrated PCBPs, the mechanism of cement hydration, and the importance of heat of hydration. The 'TOPICS' section lists three items: 'Components of hydrated PCBPs', 'Mechanism of cement hydration', and 'Introduction to heat of hydration of PCBPS'. At the bottom, it mentions the course title and the lecturers, Dr. Sudhir Misra and Dr. KV Harish.

**Department of Civil Engineering**  
**Indian Institute of Technology Kanpur**

**PORTLAND CEMENT BASED PASTE SYSTEMS**

**OVERVIEW**  
This lecture will the different components present in the hydrated PCBPs. In addition, the mechanism of cement hydration, the importance of heat of hydration and how it can help to understand the hydration process is briefly discussed.

**TOPICS**

- **Components of hydrated PCBPs**
- **Mechanism of cement hydration**
- **Introduction to heat of hydration of PCBPS**

*A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative*  
Dr. Sudhir Misra  
Dr. KV Harish

The textbook and reference materials are shown here. So, today's topics will be components of hydrated Portland cement based paste systems, mechanism of cement hydration, introduction to heat of hydration of PCBPs. This lecture will provide different compounds present in the hydrated cement paste in addition the mechanism of cement hydration, the importance of heat of hydration and how it can help to understand the hydration process is also discussed.

(Refer Slide Time: 01:27)

Department of Civil Engineering  
Indian Institute of Technology Kanpur

### Components of hydrated PCBPSs

- C-S-H gel
- CH
- Ettringite (Aft)
- Monosulfoaluminates (Afm)
- Minor compounds
- Unhydrated cement
- Pores (capillary, gel, entrained air, entrapped air)
- Water filled in pores (pore solution)

*A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative*

Dr Sudhir Misra  
Dr KV Harish

Now, the first one is components of hydrated cement paste. So, typically the hydrated system contains several compounds are components, first one is calcium silicate hydrate gel many times referred as tobermorite gel calcium hydroxide, remember that calcium silicate hydrate gel and calcium hydroxide primarily comes from the hydration of calcium silicates, that is tricalcium silicate and dicalcium silicate.

The third one is Ettringite, and fourth one is monosulphoaluminates A f m and remember that ettringite and monosulphoaluminates or hydrated products from tricalcium aluminate, and in addition to these four compounds which are generally referred as major hydrated compounds, you also have some minor compounds, you also have unhydrated cement which means of the entire comment that you have initially put in water may not fully hydrate. So, you may have in our PCBPS system that some cement grains are still not fully hydrated. You also have pores where you have capillary pores, gel force entrained air entrapped air and you may also have water filled in pores some pores may be completely empty some pores may contain water. So, you may have water filled pores which are many times called as pore solution. In this lecture we will concentrate only on the first four components the other four components will be covered at a later stage.

(Refer Slide Time: 03:06)

**Department of Civil Engineering  
Indian Institute of Technology Kanpur**

**Components of hydrated PCBPSs**

Compound	Specific Gravity	Crystallinity	Morphology in Pastes	Typical Crystal Dimensions in Pastes	Resolved by <sup>a</sup>
C-S-H	2.3-2.6 <sup>b</sup>	Very poor	Spines; Unresolved morphology	1 × 0.1 μm (Less than 0.01 μm thick)	SEM, TEM
CH	2.24	Very good	Nonporous striated material	0.01-0.1 mm	OM, SEM
Etringite	-1.75	Good	Long slender prismatic needles	10 × 0.5 μm	OM, SEM
Monosulfoaluminate	1.95	Fair-good	Thin hexagonal plates; irregular "rosettes"	1 × 1 × 0.1 μm	SEM

<sup>a</sup>OM, optical microscopy; SEM, scanning electron microscopy; TEM, transmission electron microscopy.  
<sup>b</sup>Depends on water content.

*A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative*

Dr Sudhir Misra  
Dr KV Harish

Courtesy: Schem, M. Young, I.F., and Darwin

Now, the four major compounds are listed and what this table shows briefly is some of the important morphological properties or micro structural properties. So, usually you see specific gravity ranges from 2.3 to 2.6 for calcium silicate hydrate, calcium hydroxide somewhere about 2.24, ettringite 1.75, and monosulphoaluminates 1.95. If you carefully see ettringite and mono sulphur laminates have lower specific gravity primarily because the water content if you see the formula for ettringite and monosulphoaluminates, you have more amounts of water in the case ettringite it is h 32; in the case of monosulphoaluminates it is h 12 to h 16. So, the specific gravity of since the specific gravity of water is one you gently find that ettringite and monosulphoaluminates have lower specific gravity compared to the C-S-H and calcium hydroxide.

Now, from the point of crystallinity what we see is that calcium silicate hydrate is explained to have very poor crystallinity, calcium hydroxide very good, ettringite good, and monosulphoaluminates fairly good. In a case of morphology that is if you see at the micro level because all these compounds are at the micro level, basically at the macro level we cannot see or understand the morphology. So, we need scanning electron microscope or TEM or optical microscope to understand how it actually looks at the micro level. So, in a case of calcium silicate hydrate morphology is explained as spines

or unresolved morphology, in the case of calcium hydroxide non porous striated material, in a case of ettringite long slender prismatic needles, in the case of monosulfo aluminates thin hexagonal plate or irregular rosettes.

We will see some of the scanning electron microscope images in the coming slides, and also approximate crystal dimensions are shown. As I already mentioned these are the micro level and hence you see that these are approximately in the range of say 0.1 micron metre to about 10 micron metres. So, if you take calcium silicate hydrate gel one cross 0.1 micron metre calcium hydroxide is 0.01 to 0.1 mm, ettringite is 10 cross 0.5 micron metre and monosulphoaluminate is one cross one crores 0.1 micron metre.

(Refer Slide Time: 06:08)



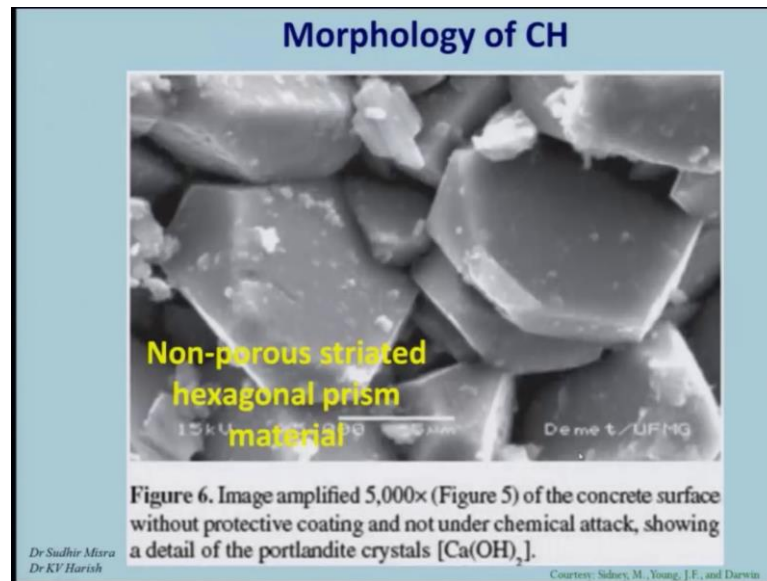
Now, if you see the scanning electron microscope images, calcium silicate hydrate gel typically looks like this and remember that in the table it is explained as spine or unresolved morphology; which means the morphology changes depending upon the situation that exist in the system, if you have more water it may slightly change if you have more temperature it may change to other and something like that.

(Refer Slide Time: 06:39)



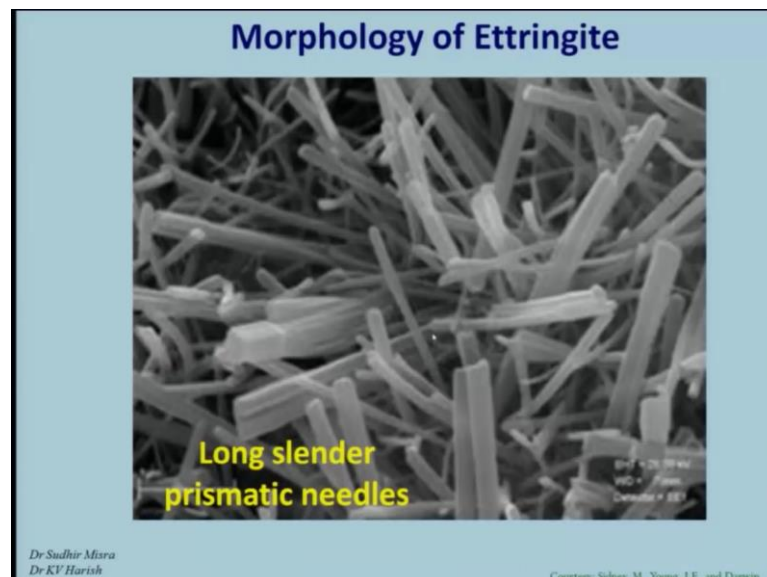
So, the next SCM figure shows at different stages morphology of calcium silicate hydrate gel. So, when you add water to cement and when the system is very fresh which is explained as wet, you see that the calcium silicate hydrate gel looks like this. After say about 16 hours of drying from the time water is added to cement, if you take a scanning electron microscope this looks like this and say after two weeks typically 14 days pc that calcium silicate hydrate looks like spines. So, you can see that the morphology slowly changes; in addition to that even this morphology is not completely fixed in the sense that if temperature inside concrete changes substantially then the water comes out of the system and this again slightly changes.

(Refer Slide Time: 07:35)



The second one is morphology of calcium hydroxide and it is explained as non porous striated, and you also have hexagonal prism.

(Refer Slide Time: 07:51)



So, these appear like hexagonal prisms and it has non porous and striated, and the third one ettringite where you see that you have prismatic needle like structure and which is



long and slender.

(Refer Slide Time: 08:03)



And in the fourth one you have monosulphoaluminates where you have the morphology looking pretty much like thin hexagonal plates, and what you see here is something like petals of rose flower. So, it is explained many times as irregular rosettes.

(Refer Slide Time: 08:29)

**Department of Civil Engineering  
Indian Institute of Technology Kanpur**

**Mechanism of cement hydration**

- Portland cement contains clinker compounds and gypsum
- Two proposed mechanism for explaining cement hydration
  - [1] Through solution hydration mechanism
  - [2] Topochemical or solid state hydration mechanism

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative


Dr Sudhír Misra  
Dr KV Harish

The slide is from the Department of Civil Engineering at the Indian Institute of Technology Kanpur. It is titled 'Mechanism of cement hydration'. It contains two main bullet points: 'Portland cement contains clinker compounds and gypsum' and 'Two proposed mechanism for explaining cement hydration'. The second bullet point is further detailed with two sub-points: '[1] Through solution hydration mechanism' and '[2] Topochemical or solid state hydration mechanism'. At the bottom, there is a small text line: 'A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative'. The slide is attributed to Dr Sudhír Misra and Dr KV Harish.



Now, the second topic is mechanism of cement hydration; in mechanism of cement hydration we have two proposed mechanisms, one is through solution hydration mechanism the other one is topochemical or solid state hydration mechanism we will see each of the mechanism in detail.

(Refer Slide Time: 08:50)

 Department of Civil Engineering  
Indian Institute of Technology Kanpur

**Through solution hydration mechanism**

- Through-solution mechanism is perceived to be dominant the moment water is added to cement until some period between its initial and final setting time
- Re-organization of constituents of the original compounds happens during this mechanism
  - Dissolution of anhydrous compounds into their ionic constituents
  - Formation of hydrates in the solution
  - Eventual precipitation of hydrates from the supersaturated solution due to the low solubility of hydrates

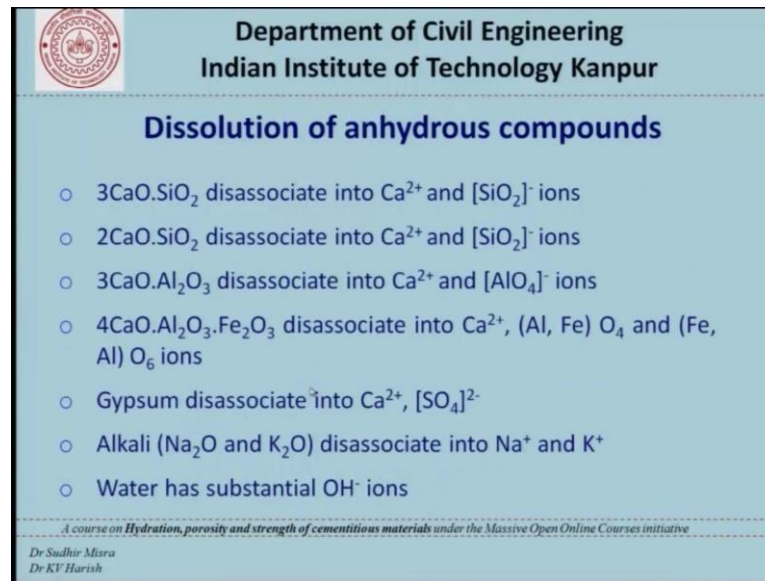
A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

Through solution hydration mechanism is perceived to be dominant the movement water is added to cement, until some period between its initial and final setting time.

So, which means through solution dominates that the mixture is relatively plastic when the mixture is relatively wet, and what happens in through solution is that reorganisation of constituents of the original compounds happen dissolution of anhydrous compounds in to its ionic constituents, formation of hydrates into the solution, eventual precipitation of hydrates from the supersaturated solution due to the low solubility of hydrates.

(Refer Slide Time: 09:40)



**Department of Civil Engineering**  
**Indian Institute of Technology Kanpur**

**Dissolution of anhydrous compounds**

- $3\text{CaO}\cdot\text{SiO}_2$  disassociate into  $\text{Ca}^{2+}$  and  $[\text{SiO}_2]^-$  ions
- $2\text{CaO}\cdot\text{SiO}_2$  disassociate into  $\text{Ca}^{2+}$  and  $[\text{SiO}_2]^-$  ions
- $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  disassociate into  $\text{Ca}^{2+}$  and  $[\text{AlO}_4]^-$  ions
- $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  disassociate into  $\text{Ca}^{2+}$ ,  $(\text{Al}, \text{Fe})\text{O}_4$  and  $(\text{Fe}, \text{Al})\text{O}_6$  ions
- Gypsum disassociate into  $\text{Ca}^{2+}$ ,  $[\text{SO}_4]^{2-}$
- Alkali ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) disassociate into  $\text{Na}^+$  and  $\text{K}^+$
- Water has substantial  $\text{OH}^-$  ions

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

So, three things happen and in order to understand the dissolution process what you have to know is that, the tricalcium silicate disassociate into calcium two plus ions. So, remember that in the morphology of the compounds we have already seen that they exist as calcium ions and silicate ions. So, tricalcium and dicalcium disassociate into calcium two plus ions and  $\text{SiO}_2$  minus ions. In the case of aluminates dissociate into calcium ions and  $\text{AlO}_4$  minus ions remember you have 6 numbers.

In the fourth one you have tetracalcium alumino ferrite getting dissociated into calcium two plus ions and aluminium ion  $\text{O}_4$  ions or iron aluminium  $\text{O}_6$  ions, and you also have fifth compound gypsum dissociating into calcium ions and sulphate ions  $\text{SO}_4^{2-}$  minus, and in addition to that you also have minor compounds like alkalis namely  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  which dissociate into  $\text{Na}^+$  and  $\text{K}^+$  ions, and remember that since water is present since we are adding water to the system water is also substantially present as  $\text{H}^+$  plus and  $\text{OH}^-$  minus ions, and in this case  $\text{OH}^-$  minus largely dominates. Now formation of hydrates in to solution.

(Refer Slide Time: 11:15)

Department of Civil Engineering  
Indian Institute of Technology Kanpur

**Formation of hydrates in solution**

- $[\text{AlO}_4]^-$ ,  $[\text{SO}_4]^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  ions are faster in reacting
- $[\text{SiO}_2]^-$ ,  $(\text{Al}, \text{Fe}) \text{O}_4$  and  $(\text{Fe}, \text{Al}) \text{O}_6$  ions are relatively slower in reacting
- First reaction: Formation of  $A_{ft}$ , which depends upon the sulfate to aluminate ratio

$$[\text{AlO}_4]^- + 3[\text{SO}_4]^{2-} + 6[\text{Ca}]^{2+} + \text{aq.} \rightarrow \text{C}_6\text{A}_3\text{H}_{32}$$

*(Ettringite or  $A_p$ )*

$$[\text{AlO}_4]^- + [\text{SO}_4]^{2-} + 4[\text{Ca}]^{2+} + \text{aq.} \rightarrow \text{C}_4\text{A}_1\text{H}_{12}$$

*(Monosulphoaluminate or  $A_{ps}$ )*

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

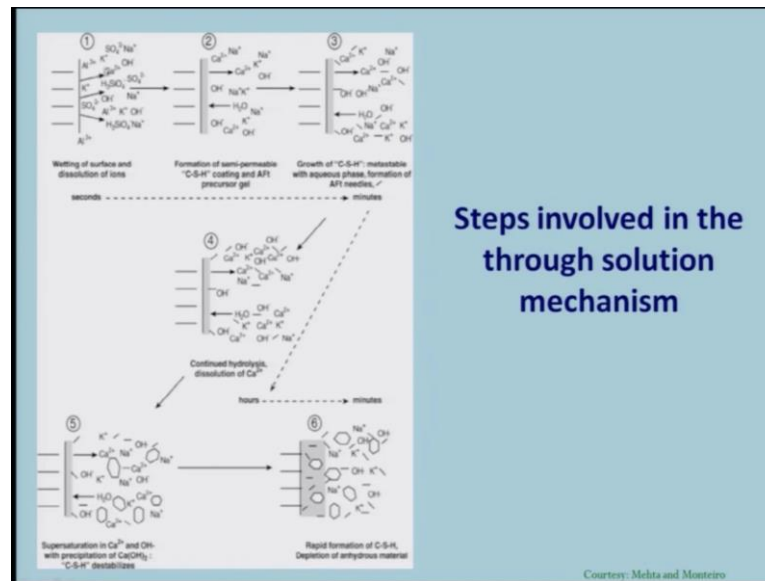
Dr Sudhir Misra  
Dr KV Harish

So, basically what you have to know is that in the previous slide we have seen that the compounds basically dissociate in to respective ions, and we also have to know which ions or reactive which ions or less faster in reaction. So,  $\text{AlO}_4$  minus ions  $\text{SO}_4$  2 minus ion, sodium ions, potassium ions, calcium ions these are very fast and reacting and especially the aluminate and the sulphate ions are extremely fast.

The ions which are relatively less faster or silicone ions  $\text{SiO}_2$  minus  $\text{AlFeO}_4$ ,  $\text{FeAlO}_6$  ions now. So, the first reaction that actually happens is the formation of  $A_{ft}$  which is ettringite, and this depends primarily on sulphate to aluminate ratio done in the previous lecture. So,  $\text{AlO}_4$  minus ion plus  $3\text{SO}_4$ , 2 minus ions plus 6 calcium ions in the presence of water remember that here aqueous a q refers to aqueous which means you have substantial  $\text{OH}$  minus ions and  $\text{H}$  plus ions that gives ettringite and remember that this reaction we have already seen it in the previous lecture, and likewise the aluminate ions and sulphate ions in the presence of calcium can also give monosulphoaluminates.

Now, what those figure shows is to understand step by step what happens with time. So, there are totally six different cases that are provided.

(Refer Slide Time: 13:07)

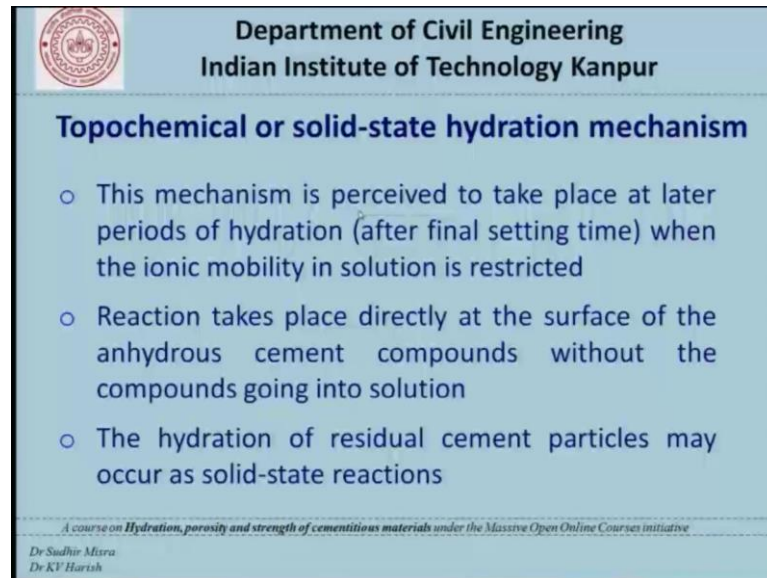



In the first case where wetting of surface and dissolution of ions happen you can see here that you have  $\text{Al}^{3+}$ ,  $\text{K}^+$  plus sulphate ions  $\text{OH}^-$  minus ions calcium. So, all the ions from the compounds just come out into solution and in the second one what you see is that there is a formation of semi permeable calcium silicate hydrate coating, and you also have ettringite AFt that is formed. So, you see that in this layer you have this gel and AFt getting formed and the remainder goes into solution and in the third phase what you find is that slowly the calcium silicate hydrate gel grows and it is explained as metastable with aqueous phase and formation of AFt needles, AFt is nothing but ettringite. So, we have seen that it has long slender needles, and remember that this entire stage one two three together happens within two seconds to about few minutes.

And with time continued hydrolysis takes which is step four, and you see that the calcium ions go in to solution and it goes to the fifth stage where it is explained as supersaturation in calcium ions and  $\text{OH}^-$  minus ions and precipitation of calcium silicate hydrate gel calcium hydroxide and others. And in the sixth stage there is rapid formation of calcium silicate hydrate gel and there is depletion of anhydrous material. So, what you find is that there are different stages right from 1 to 6, and what is happening within few seconds to within few minutes to within few hours; we will now head on to the topochemical hydration process this mechanism is perceived to take place at later periods

of hydration that is after final setting time.

(Refer Slide Time: 15:23)



 Department of Civil Engineering  
Indian Institute of Technology Kanpur

**Topochemical or solid-state hydration mechanism**

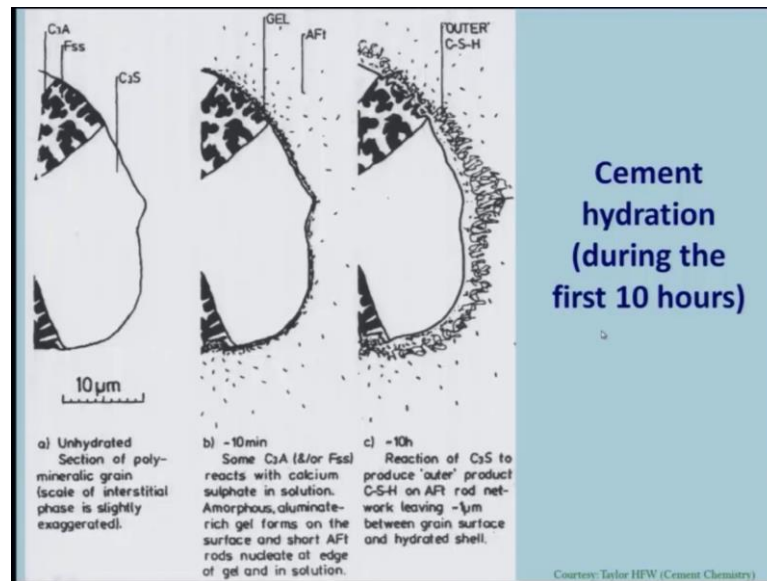
- This mechanism is perceived to take place at later periods of hydration (after final setting time) when the ionic mobility in solution is restricted
- Reaction takes place directly at the surface of the anhydrous cement compounds without the compounds going into solution
- The hydration of residual cement particles may occur as solid-state reactions

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

Remember that in the case of topochemical, it is explained to take place from the time water is added to cement to its initial setting time or final setting time. So, in this case it is what is happening after final setting time reaction takes place directly at the surface of anhydrous cement compounds without the compounds going into solution. This is very very important because the system will remain in the wet state only for some time and hence the through solution mode can dominate only up to a certain point of time, after that once some compounds are formed then it is a topochemical mode which actually dominates.

(Refer Slide Time: 16:26)



The hydration of residual cement particles may occur as solid state reactions. So, how do we have to understand? Two figures are shown here, one is what is happening during the first ten hours the other one is what is happening just before 24 hours and until 14 days. So, let us first go to the first figure. So, in this figure again you have three different cases one is the unhydrated case or less hydrated case, the second one is approximately 10 minutes after adding water, and the third one is approximately 10 hours; this will actually explain each of the case during the first 10 hours.

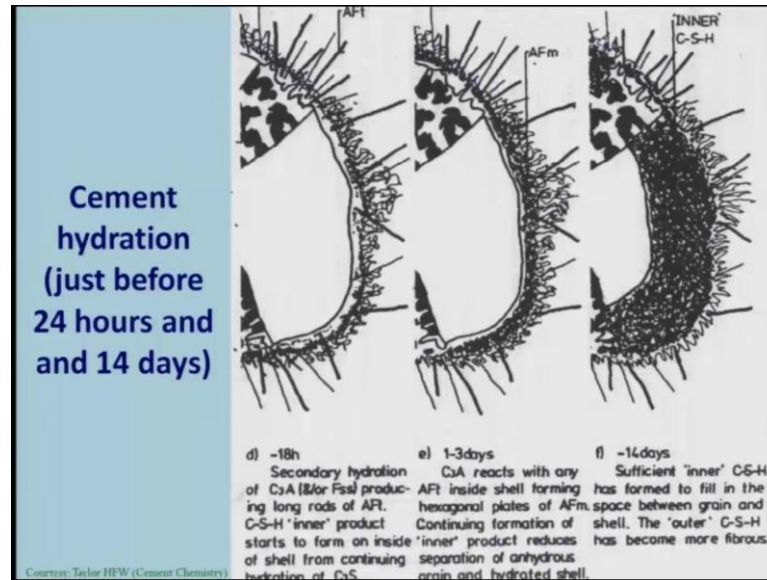
So, what you find in the first figure is that during the first few seconds or minutes C<sub>3</sub>A reacts faster where as C<sub>4</sub>AF does not react. So, and C<sub>3</sub>S also does not react. So, C<sub>3</sub>A basically reacts and forms ettringite which is actually shown in the second figure F s s which actually indicates C<sub>4</sub>AF that also doesnt react and C<sub>3</sub>S reacts. Next stage you find that the ettringite is already formed which is needle shaped, and slowly the calcium silicate hydrate gel is formed which means C<sub>3</sub>S starts hydrating and it basically forms a coat on the cement grain.

So, what is shown in this diagram is just one cement grain particle and the formation of this coat basically stops the water that is present in the outside of the cement grain to actually enter inside of the cement grain; and with time what happens is this gel slightly



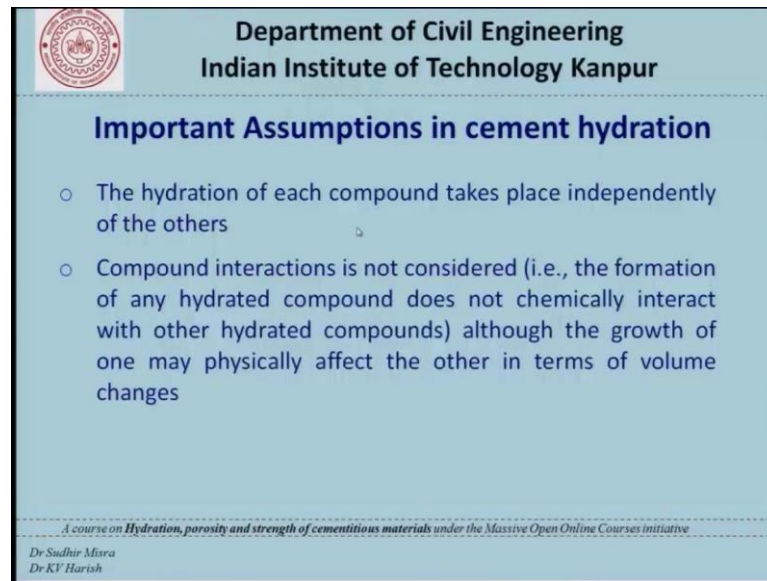
grows thicker and it completely restricts the free movement of water from outside to inside. So, this happens during the first ten hours.


(Refer Slide Time: 18:30)



Now, in the seconds what you find is that approximately at 18 hours, you find the AFt is shown as needles, you also have calcium silicate hydrate gel, you will also find that  $C_4AF$  slowly starts reacting and say between one to three days you will typically find all compounds reacting together at the same time, and at 14 days you see that the hydrated compounds become larger. So, what we can understand in the 14 day figure is that you have some portion of the cement grain that is unhydrated and some portion this black colour region showing that the hydrated compounds are formed and all these things happen as a solid state reaction and water cannot completely get into the cement grain and it can do only through process called.

(Refer Slide Time: 19:34)



 Department of Civil Engineering  
Indian Institute of Technology Kanpur

**Important Assumptions in cement hydration**


- The hydration of each compound takes place independently of the others
- Compound interactions is not considered (i.e., the formation of any hydrated compound does not chemically interact with other hydrated compounds) although the growth of one may physically affect the other in terms of volume changes

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

So, some of the important assumptions in cement hydration are as follows. The hydration of each compound takes place independently of the others, compound interactions is not considered that is the formation of any hydration compound does not chemically react with other hydrated compounds, although the growth of one may physically affect the other in terms of volume changes. So, what does it mean is that when you have different compounds that are getting formed here, one compound will not chemically affect the other, but you can physically effect in terms of their presence.

(Refer Slide Time: 20:26)



**Department of Civil Engineering  
Indian Institute of Technology Kanpur**

**General**

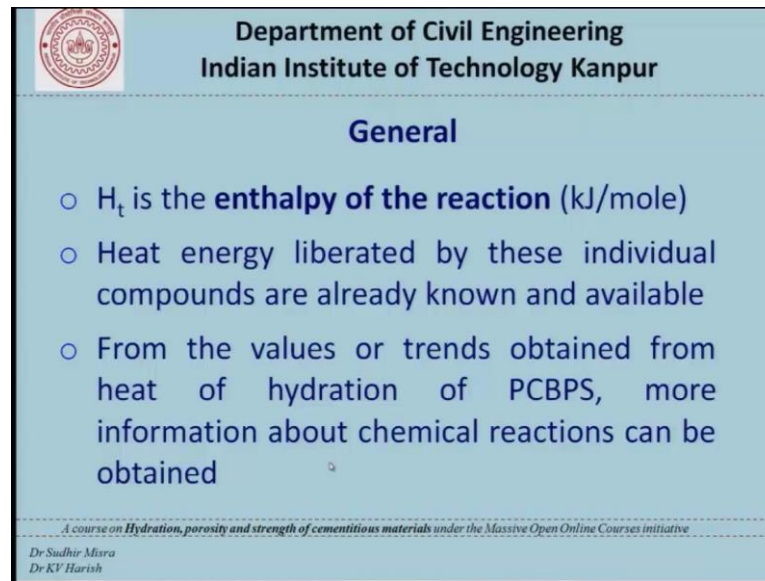
- The hydration of each compound takes place independently of the others
- All cement hydration reactions are accompanied by the release of heat ( $C_3A$ ,  $C_4AF$ ,  $C_3S$  and  $C_2S$ )
- Heat of hydration at any time ( $H_t$ ) is the measure of the **amount of heat evolved (or heat energy) for each unit mass of anhydrous compound that has reacted (J/g)**

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

So, now we are going to the third topic which is introduction to heat of hydration of Portland cement based systems, the hydration of each compound takes place independently of the other all hydration reactions are accompanied by the release of heat, heat of hydration at anytime  $H_t$  is a measure of the amount of heat evolved or heat energy for unit mass of anhydrous compound that has reacted, and it is many times expressed in joules per gram or joules per mole of cement.

(Refer Slide Time: 20:57)



Department of Civil Engineering  
Indian Institute of Technology Kanpur

**General**

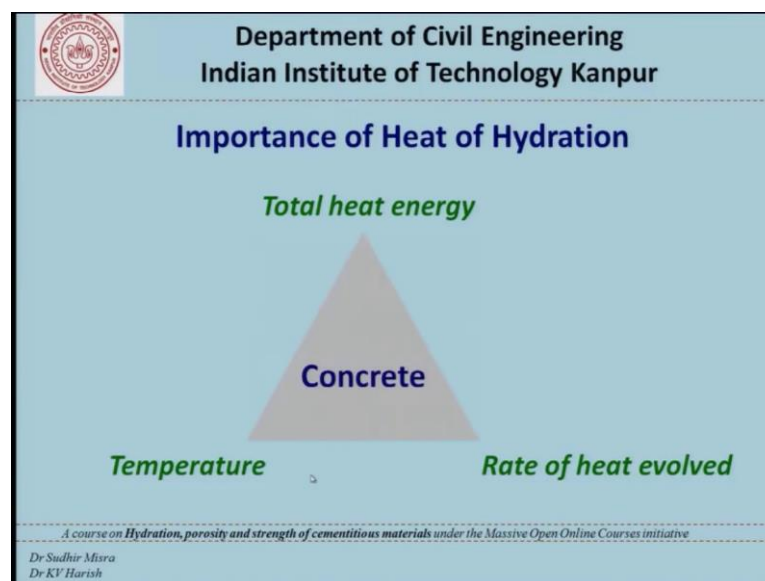
- $H_t$  is the **enthalpy of the reaction** (kJ/mole)
- Heat energy liberated by these individual compounds are already known and available
- From the values or trends obtained from heat of hydration of PCBPS, more information about chemical reactions can be obtained

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

$H_t$  is also referred many times as enthalpy of the reaction expressed in kilojoules per mole. Heat energy liberated by these individual compounds are already known and available, from the values are trends obtained from heat of hydration of the system more information about chemical reactions can be obtained.

(Refer Slide Time: 21:24)



Department of Civil Engineering  
Indian Institute of Technology Kanpur

**Importance of Heat of Hydration**

*Total heat energy*

**Concrete**

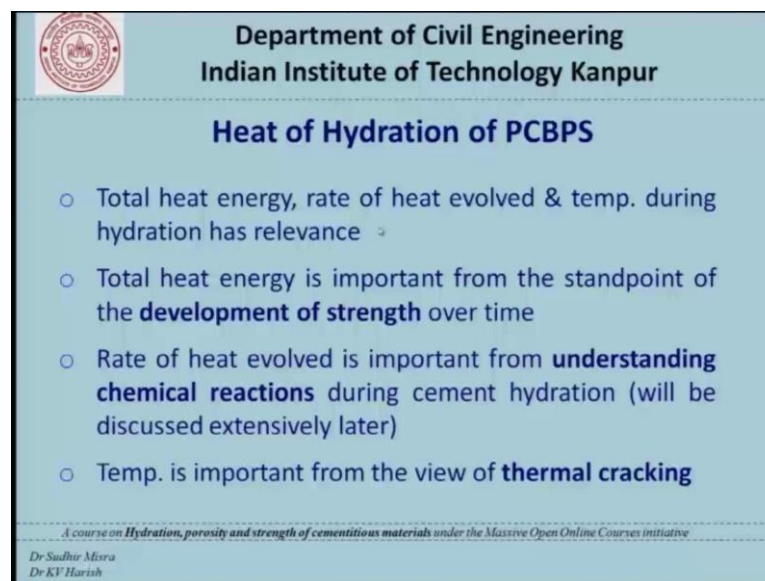
*Temperature*      *Rate of heat evolved*


A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

Now, what is the importance of heat of hydration? Heat of hydration is important from three different angles: number one total heat energy, number two temperature, number three rate of heat evolved. Total heat energy is important from the standpoint of knowing the development of properties with time, temperature is important from the standpoint of thermal cracking, and rate of heat evolved is important from the standpoint of understanding chemical reactions that happen in Portland cement.

(Refer Slide Time: 22:06)



 Department of Civil Engineering  
Indian Institute of Technology Kanpur

### Heat of Hydration of PCBPS

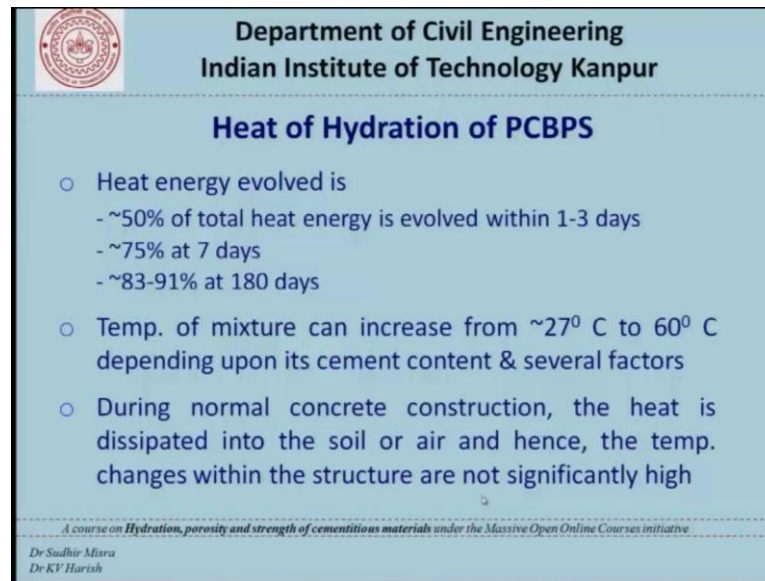
- Total heat energy, rate of heat evolved & temp. during hydration has relevance
- Total heat energy is important from the standpoint of the **development of strength** over time
- Rate of heat evolved is important from **understanding chemical reactions** during cement hydration (will be discussed extensively later)
- Temp. is important from the view of **thermal cracking**

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

Total heat energy rate of heat evolved and temperature during hydration has relevance, total heat energy from development of strength, rate of heat evolved from chemical reactions temperature from thermal cracking.

(Refer Slide Time: 22:20)



**Department of Civil Engineering  
Indian Institute of Technology Kanpur**

**Heat of Hydration of PCBPS**

- Heat energy evolved is
  - ~50% of total heat energy is evolved within 1-3 days
  - ~75% at 7 days
  - ~83-91% at 180 days
- Temp. of mixture can increase from  $\sim 27^{\circ}\text{C}$  to  $60^{\circ}\text{C}$  depending upon its cement content & several factors
- During normal concrete construction, the heat is dissipated into the soil or air and hence, the temp. changes within the structure are not significantly high

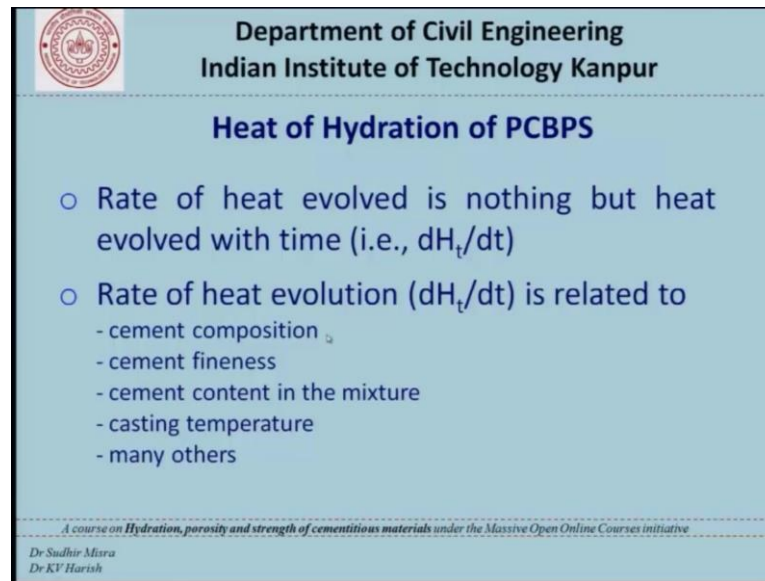
A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

Total heat energy evolved is approximately 50 percentage of the total heat energy evolve within 1 to 3 days, and it is also approximately 75 percentage at 7 days and the same value is approximately 83 to 91 percentage at 180 days. Temperature of mixture can increase from 27 degree Celsius to as highest 60 degree Celsius depending upon the amount of cement content present and several other factors. During normal concrete operation the heat is dissipated into the soil or air, and hence the temperature changes within the structure or not significantly high.



(Refer Slide Time: 23:06)



Department of Civil Engineering  
Indian Institute of Technology Kanpur

### Heat of Hydration of PCBPS

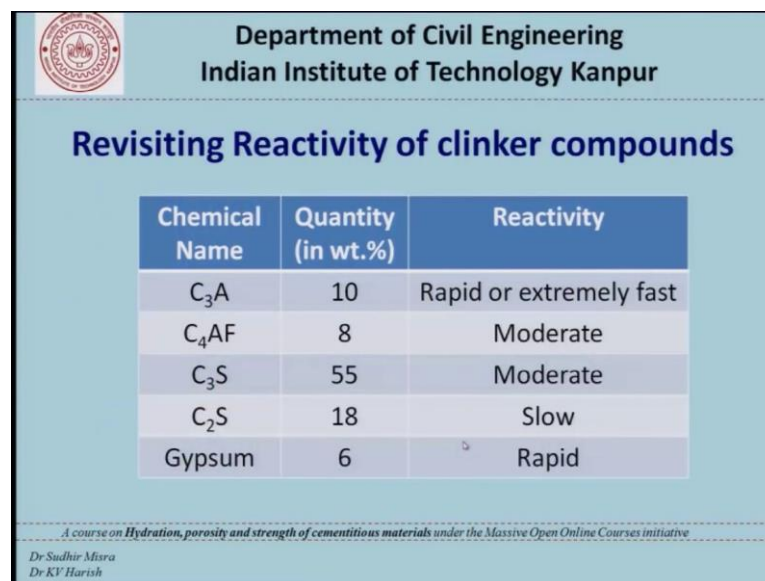
- Rate of heat evolved is nothing but heat evolved with time (i.e.,  $dH_t/dt$ )
- Rate of heat evolution ( $dH_t/dt$ ) is related to
  - cement composition
  - cement fineness
  - cement content in the mixture
  - casting temperature
  - many others

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

Rate of heat evolved is nothing, but heat evolved with time that is rate of heat evolution  $dH_t/dt$  divided by  $dt$  is related to many parameters including a cement composition fineness cement content casting temperature and many others.

(Refer Slide Time: 23:26)



Department of Civil Engineering  
Indian Institute of Technology Kanpur

### Revisiting Reactivity of clinker compounds

Chemical Name	Quantity (in wt.%)	Reactivity
C <sub>3</sub> A	10	Rapid or extremely fast
C <sub>4</sub> AF	8	Moderate
C <sub>3</sub> S	55	Moderate
C <sub>2</sub> S	18	Slow
Gypsum	6	Rapid

A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative

Dr Sudhir Misra  
Dr KV Harish

Just revisiting the slide that we saw in the previous lecture regarding reactivity of clinker

compounds, these four compounds have different reactivity.

(Refer Slide Time: 23:39)

**Total heat of hydration of the cement compounds after 1 year (assumed to be fully hydrated)**

TABLE 4.3 Heats of Hydration of the Cement Compounds

Reaction	$\Delta H$ (J/g) for Complete Hydration <sup>a</sup>			
	Pure Compounds		Clinker <sup>b,d</sup>	Cement <sup>c,d</sup>
	Calculated	Measured	Measured	Measured
$C_3S \rightarrow C-S-H + CH$	~380	520	570	490
$C_2S \rightarrow C-S-H + CH$	~170	260	260	225
$C_3A \rightarrow C_4AH_{13} + C_3AH_8$	~1160	-	-	-
→ $C_3AH_8$	900	880	840	-
→ ettringite	1670	1670	-	-
→ monosulfoaluminate	1150	1140	-	1170
$C_4AF \rightarrow C_3(A,F)H_6$	420	420	335	-
→ monosulfoaluminate	-	-	-	380
→ ettringite	730	0-	-	-

<sup>a</sup>These values should be negative since they refer to exothermic reactions, but they are customarily written without the negative sign.  
<sup>b</sup>One-year-old pastes of ground clinker (no added gypsum).  
<sup>c</sup>One-year-old pastes assumed to be completely hydrated.  
<sup>d</sup>Individual contributions determined by multiple linear regression analysis.

Courtesy: Salicy, M., Young, J.F., and Davis

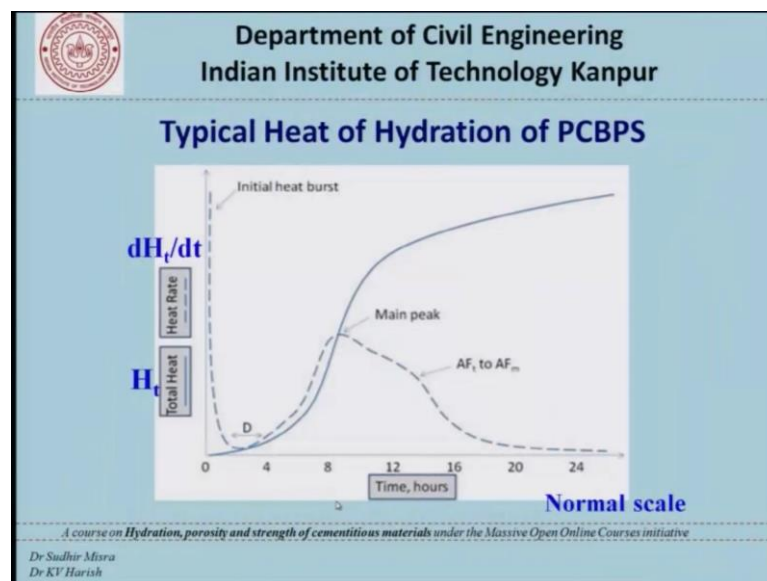
And in terms of heat of hydration of cement compounds, we see that each and every reaction produces its own heat energy and in this table you have the reactions given in this column, pure compounds given in this column impure compounds given in this column and cement as a whole is given in this column, and you find that impure compounds heat of energy can be measured in two different ways one is calculated the other one is measured; calculated refers to using some mathematical equations and measure is using calorimetry.

Now, for the first reaction which is reaction tricalcium silicate reactions, we find that this is approximately 380 joules per gram and remember that here we have assumed that complete hydration takes place. In real complete hydration does not take place, but we take a hypothetical situation that if 100 percentage of the cement grains are hydrated then approximately 380 joules per k g of heat is evolved from nearly this reaction hydration of tricalcium silicate. Likewise if you see for C2S it is 170, C3A is 1160 extremely high and again individually for hydra different hydrated compounds it is given and if you take C4AF it is 420. You may have to compare this figure with the reactivity that as shown in the previous slide for understanding which is higher and which is lower; and likewise we

also see that even in the measured case we have similar trends, but remember that the calculator and measure may not be necessarily same, but the trends that you get for example, if you take the values of heat values of the hydrated compounds of C3A say 900, 1670, and 1150 these values are generally much higher than others and that trend is also reflected in measured values.

Now, you may have to also compare what values you get for the pure cement compounds with that of what you get for the clinker compounds; and remember that pure compounds does not have impurities while clinker has impurities. So, you see that the measured values of the pure compounds is approximately similar to the measured values for clinker compounds. So, here it is 520, 570, 260 260 880 840 420 335 somewhere lesser and primarily some impurities can actually cause substantial changes to the heat of hydration, and likewise cement measured is also provided for comparison with the others.

(Refer Slide Time: 26:49)

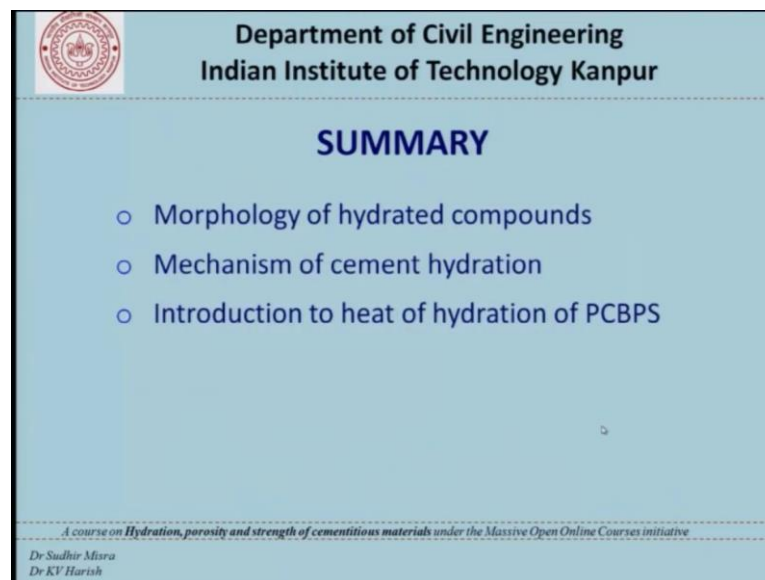


The next one is that; what is the typical heat of hydration trend that we get? So, if you take in the x axis ranging from 0 time 0 two say about 24 hours and in the y axis lets first take the total heat which is represented as  $H_t$  denoted by continuous line. So, what you find is that with increase in time the total heat slowly increases and then suddenly increases and then it flattens the other graph which is heat rate  $dH_t/dt$  is shown by the

dotted line.

So, what you find is that at the initial stage rate of heat is extremely high and it suddenly comes down within few seconds, and for few minutes it does not fully reacts stays for some time and then slowly the reaction picks up and then again it reduces and here that time is shown in 0 to 24 hours scale, and what you have to understand is that the chemical reactions have to be understood from the rate of hydration plot with respect to time which is actually done in the next lecture.

(Refer Slide Time: 28:15)



**Department of Civil Engineering**  
**Indian Institute of Technology Kanpur**

---

**SUMMARY**

- Morphology of hydrated compounds
- Mechanism of cement hydration
- Introduction to heat of hydration of PCBPS

---

*A course on Hydration, porosity and strength of cementitious materials under the Massive Open Online Courses initiative*

Dr Sudhir Misra  
Dr KV Harish

With this we come to the end for this lecture and what we have seen is morphology of hydrated compounds, mechanism of cement hydration, and introduction to heat of hydration of Portland cement based paste systems.

Thank you.