Admixtures And Special Concretes

Prof. Manu Santhanam

Indian Institute of Technology Madras

Department of Civil Engineering

Lecture 04

Overview of Cement Chemistry: Hydration of Cement

Cement Hydration:

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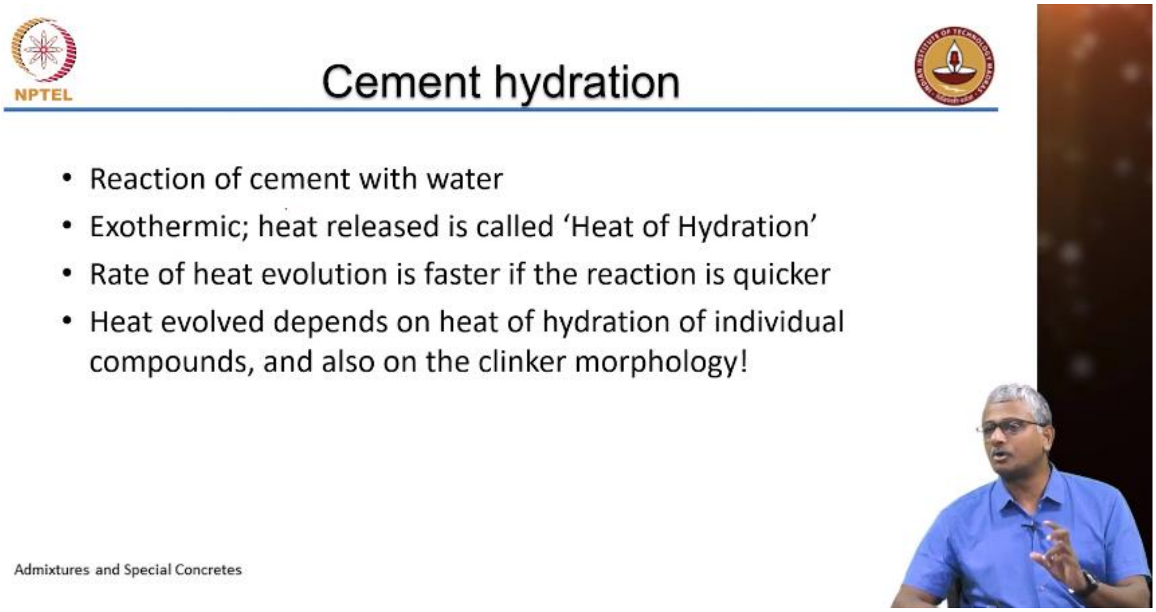

Cement hydration

- Reaction of cement with water
- Exothermic; heat released is called 'Heat of Hydration'
- Rate of heat evolution is faster if the reaction is quicker
- Heat evolved depends on heat of hydration of individual compounds, and also on the clinker morphology!

Admixtures and Special Concretes

Cement reacts with water and this process is called hydration, this process is exothermic, it releases heat and the heat of hydration depends on each individual compound that is present and also the morphology.

Why morphology? Because sometimes the degree of irregularity may be different depending upon the type of processing that happens inside the kiln. We learn a lot more detail in cement chemistry but for now we will not really look at that in more detail.

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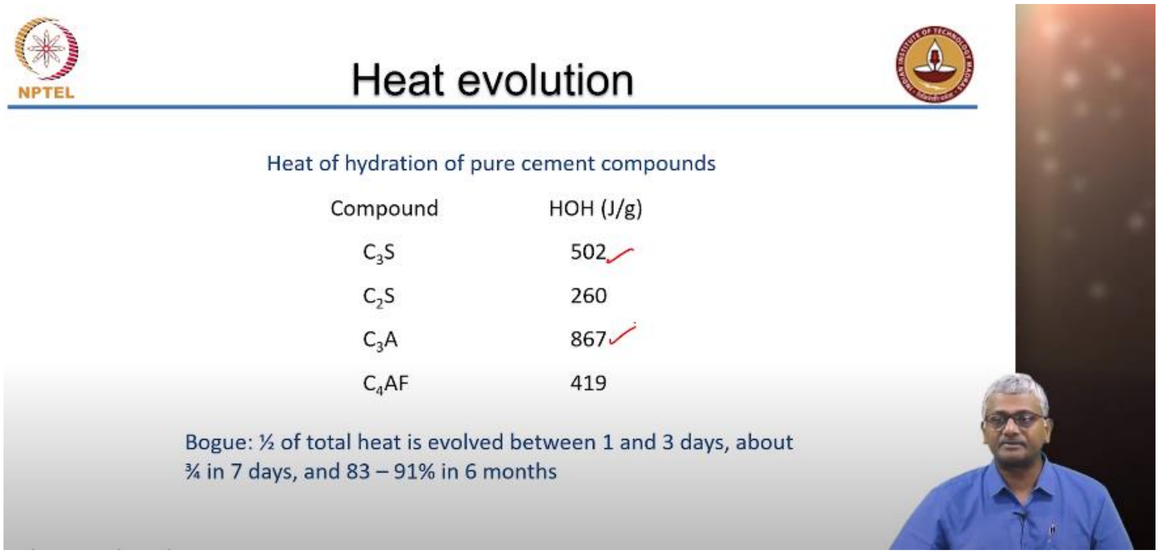

Heat evolution

Heat of hydration of pure cement compounds

Compound	HOH (J/g)
C_3S	502 ✓
C_2S	260
C_3A	867 ✓
C_4AF	419

Bogue: ½ of total heat is evolved between 1 and 3 days, about ¾ in 7 days, and 83 – 91% in 6 months

Now each compound has a different rate of heat evolution as you can clearly see C_3S and C_3A evolve maximum heat. So this heat is represented in J/g but this is the heat evolution or total heat evolution from reacting 1 gram of this material. This also has to be looked at from a different perspective.

Heat evolution pattern:

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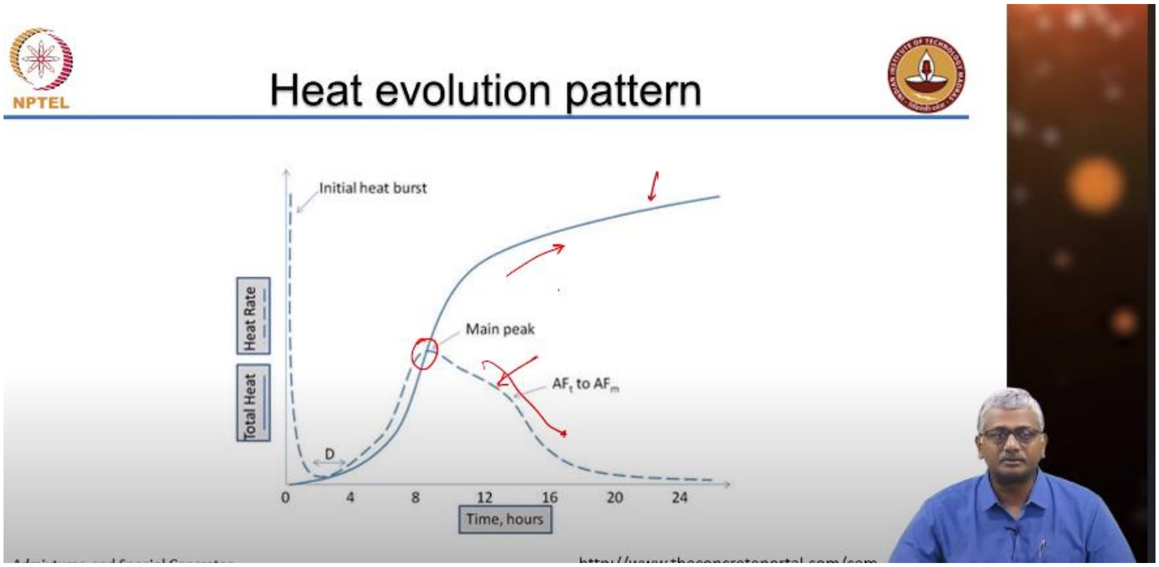

What is the rate of this heat evolution? One gram can release 500 joules but at what rate? And that is where it is even more important to understand that C_3A and C_3S can liberate a significant rate of heat in the early stages and for that we need to understand the heat evolution pattern not just from the total heat, this is the total heat but also from the rate of heat evolution. So this peak rate is of great significance. Because in early stages if your cement is evolving a lot of heat your concrete temperature is continuously rising. Even beyond when the rate of heat evolution is low it is still evolving heat so the overall heat is still building up. Now of course evolution of heat is directly related to the amount of reaction that is happening, more reaction more heat. But this has practical significance for understanding how concrete and large structural elements are behaving.

When do you release the formwork? Especially in mass concrete this can be quite a challenging thing to do to decide when to release the formwork, meaning remove the redundant formwork of course the load bearing formwork you will not remove but redundant formwork when you remove it you are exposing the concrete to the external environment. But at that stage if this rate of heat evolution is still very high your concrete inside is continuing to evolve with respect to heat and the concrete in the surface is dissipating heat to the environment if you open up the formwork. So what will happen as a result of this? You will have cracking because there is a temperature differential from the core to the surface. And you will see today in many of the construction projects this is the principal problem. All our job site specifications are written up in terms of construction that we did in the past, where we opened up the formwork at 24 hours and started curing. But for many of the mass concrete structures this cannot be applied directly. At 24 hours could be the time where the core of the concrete is at its peak temperature. And to understand that well you need to actually do measurements of temperature whenever you design concrete with large cross sections. Again this is a very important part of our chapters and we will discuss this in mass concrete.

Heat Peaks:

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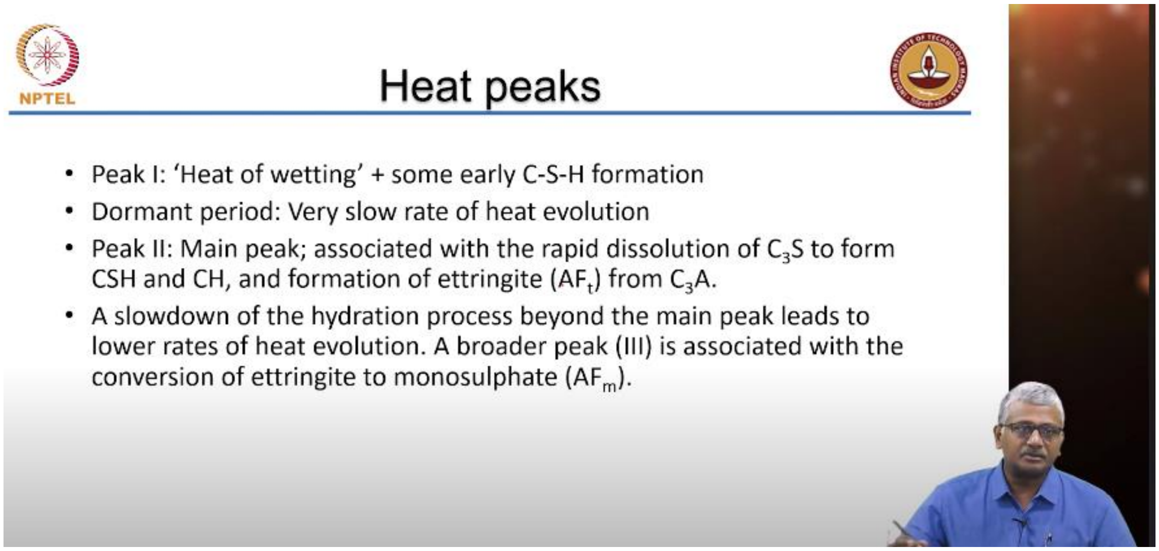

NPTEL

Heat peaks

- Peak I: 'Heat of wetting' + some early C-S-H formation
- Dormant period: Very slow rate of heat evolution
- Peak II: Main peak; associated with the rapid dissolution of C_3S to form CSH and CH, and formation of ettringite (AF_t) from C_3A.
- A slowdown of the hydration process beyond the main peak leads to lower rates of heat evolution. A broader peak (III) is associated with the conversion of ettringite to monosulphate (AF_m).

So just some descriptions about what these peaks in the rate of heat evolution curve are.

- As soon as you mix cement and water there is some **initial CSH formation** and this heat of wetting. Any powder if you wet any powder there is initial heat evolution even when you mix water into atta. Of course we cannot measure that heat evolution. You cannot feel it in your hand also but still there is heat evolution. Why because any particle will have surface atoms which are at a high energy level. When water touches the surface the interface that is created between water and the surface atoms has now a lower energy level so excess energy is released as heat. Any surface will have that issue. For instance I pour water on top of this table. Also a new interface is getting created and some minuscule amount of heat is going to come out. So that is the first peak and it is usually a very high peak because it happens in a fraction of a second. We are talking about a rate. So the rate is going to be extremely high. Even a very small amount of heat is evolved in a fraction of a second that is why the initial rate is high.
- Then there is a **dormant period**, a period where relatively lesser rate of heat is evolved. Heat is continuously evolving but rate of heat evolution is low in this dormant period. What is the significance of the dormant period from the point of view of working with the cement? Workability: We need concrete workability at that time. If the cement starts setting and hardening obviously we cannot get workability from the concrete. So this dormant period dictates the time that we have with the concrete or we sometimes call it the open time, workable time with the concrete.
- Towards the end of the dormant period the sudden increase in the rate of heat evolution happens and you reach what is called the **main peak** where C3S leads to the formation of CSH and C_3A in combination with the gypsum leads to the formation of a compound called ettringite. And then the reaction slows down but still heat is continuously evolving. Reaction is still happening and continuously evolving heat the rate of heat evolution only is reducing. So heat is continuing to build up with time. So this happens because of continuing reactions in the longer term. You may or may not have additional peaks but yes there are other reactions that are continuing to happen at the longer term.

Hydration reactions:

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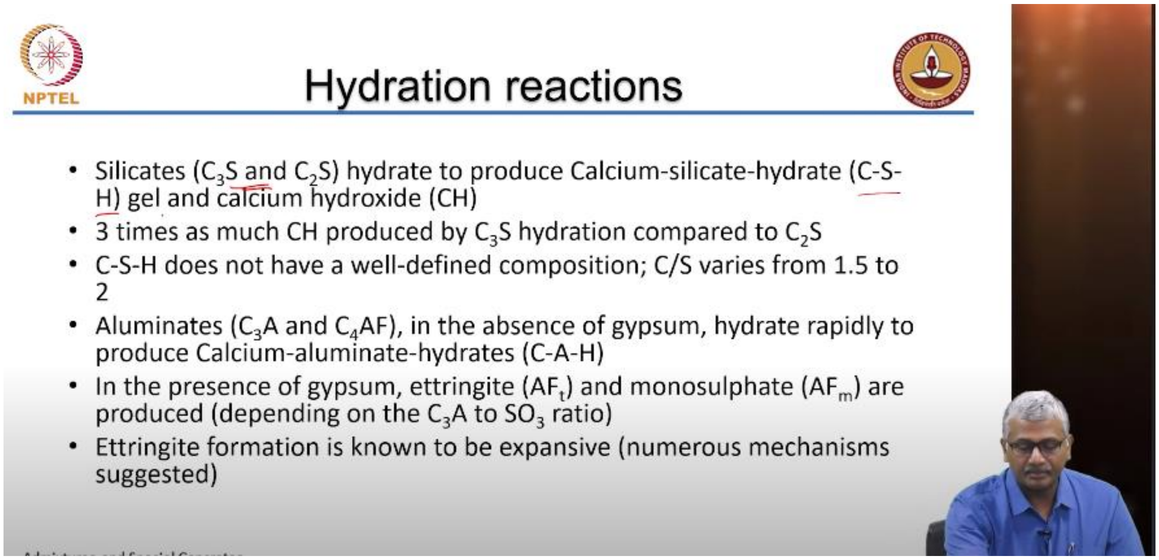

Hydration reactions

- Silicates (C_3S and C_2S) hydrate to produce Calcium-silicate-hydrate (C-S-H) gel and calcium hydroxide (CH)
- 3 times as much CH produced by C_3S hydration compared to C_2S
- C-S-H does not have a well-defined composition; C/S varies from 1.5 to 2
- Aluminates (C_3A and C_4AF), in the absence of gypsum, hydrate rapidly to produce Calcium-aluminate-hydrates (C-A-H)
- In the presence of gypsum, ettringite (AF_t) and monosulphate (AF_m) are produced (depending on the C_3A to SO_3 ratio)
- Ettringite formation is known to be expansive (numerous mechanisms suggested)

Again more specifics of hydration reactions are given. The silicates C_3S and C_2S react with water to produce CSH and calcium hydroxide. We term CSH as gel because it does not have a very well defined crystalline structure nor is it completely amorphous. It is in between phases that is why we call it gel.

Gel is basically a representation of a colloidal system but more or less this is what the CSH structure is like. The more C_3S that you have the more calcium hydroxide you produce. So 3 times as much calcium hydroxide is produced by C3S hydration compared to C_2S. We talked earlier that a pozzolan has reactive silica and this silica combines with calcium hydroxide to produce CSH. In a high C3S system where more CSH is available your possibility of pozzolanic reaction is going to be more. More C3S, more calcium hydroxide, more available lime for pozzolanic reaction. CSH again just like other cement chemistry terms it is also written very loosely as C-S-H. It does not have a very clear cut formulation but within the structure of CSH the calcium to silica ratio varies from 1.5 to 2. That is the typical nature of CSH.

The aluminates in the absence of gypsum you form rapid hydration of aluminates happens to form calcium aluminate hydrate. What is this phenomenon called in the absence of gypsum? Flash setting. When the aluminates immediately react with water and do not really have a controlled rate of hydration. In the presence of gypsum the aluminates will react with the sulfate to form ettringite and monosulphate depending on the overall composition that you have in your system. Ettringite formation causes expansion.

In the early stages of hydration when concrete is still pliable and malleable this expansion does not have any problem. But imagine if this reaction happens in the long term. If your concrete is sitting in a soil that is rich in sulfate and that sulfate enters concrete and reacts with the aluminates to form ettringite what will happen? Expansion and then cracking. Expansion will lead to cracking. So if sulphate rich soils and waters are present then you need to avoid this ettringite formation in the long term. That is why sulphate resistant cement has low C_3A. So lower aluminate implies lesser possibility of ettringite formation.

Hydration reactions:

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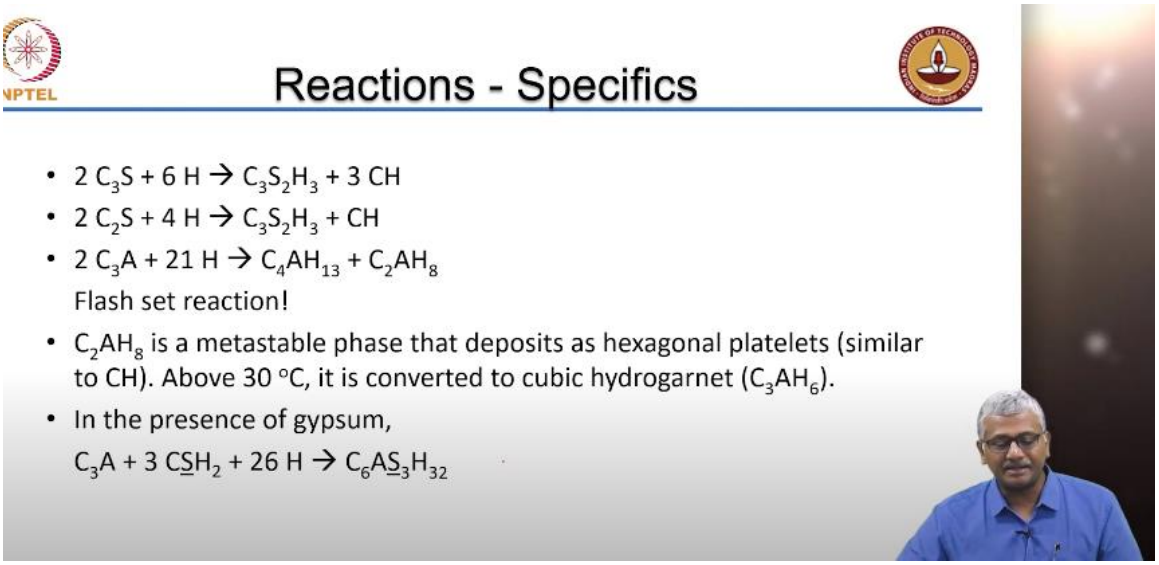

Reactions - Specifics

- $2\ C_3S + 6\ H \rightarrow C_3S_2H_3 + 3\ CH$
- $2\ C_2S + 4\ H \rightarrow C_3S_2H_3 + CH$
- $2\ C_3A + 21\ H \rightarrow C_4AH_{13} + C_2AH_8$
  Flash set reaction!
- C_2AH_8 is a metastable phase that deposits as hexagonal platelets (similar to CH). Above 30 °C, it is converted to cubic hydrogarnet (C_3AH_6).
- In the presence of gypsum,
  $C_3A + 3\ C\underline{S}H_2 + 26\ H \rightarrow C_6A\underline{S}_3H_{32}$

Again I am not delving deeper into this set of reactions. You do not have to remember the chemical formulation and all that. This is just for your benefit to understand that you have various sets of reactions possible. Again these are approximate reactions. These are not exact. So this is just for the purpose of balancing the equation that very nice complete reactions are written. It is not always like this.

You can see here that it has got a large amount of water for hydration. H is H2O. H is not hydrogen, H is water. So H_{32} means 32 molecules of water are bound in the structure of the ettringite. Similarly CSH has water bound in its structure. So what will happen when you heat cement paste, when you heat concrete what will happen? What is going to happen to this water? It is going to get removed. When you take cement and mix it with water and hydrate it all these products are formed. The same cement paste if you heat it you will slowly evolve the water, release the water that is present. It just so happens that the water released from these products happens at different temperatures. So CSH the water loss is at less than 300°C. Ettringite around 100 to 120 °C, you will lose all the water. Calcium hydroxide you lose the water only between 450 and 500 °C. So this is a very important technique for us to understand the overall composition of cement or cement paste which is called thermal analysis. All you do is take your material and heat it to different ranges of temperatures.

So what happens to concrete in the case of fire? This is what will happen as the temperature increases the different phases will dehydrate. But why does spalling happen in fire? Why does spallng happen? I mean why should dehydration cause spalling? Moisture basically is trying to come out through the fine pores. It converts to steam so water expands when it converts to steam it is trying to come out rapidly through the pores and that causes the spalling. So overall concrete deterioration will occur over a large temperature range but spalling may start quite early.

Evolution of hydration:

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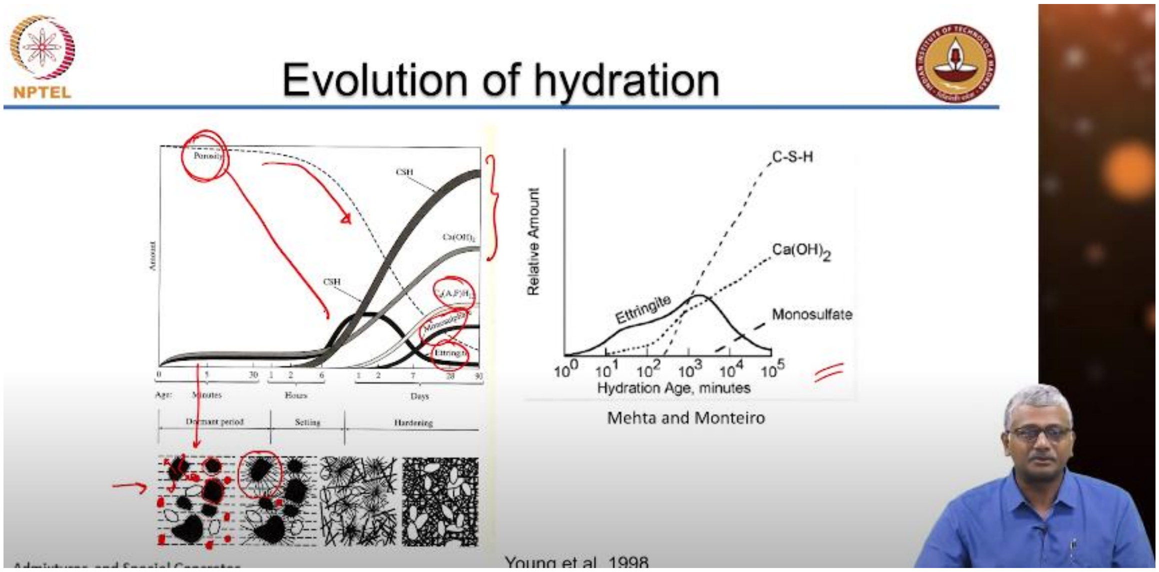

Evolution of hydration

Mehta and Monteiro

Young et al. 1998

So this is the evolution of hydration products as hydration proceeds the maximum amount of the compounds available is for CSH and calcium hydroxide which is only expected because most of your cement is silicates. When silicates react they give you CSH and calcium hydroxide. The aluminates the ettringite that forms slowly converts to this phase called monosulphate and much of the ettringite has already converted by the time significant hydration actually takes place and you may also form other aluminate hydrates. So just to look at this, this is again another picture of what happens with the formation of these compounds over the long run. Now if you look at this picture here it just tells you that in the early stages the cement particles are dispersed in water. Only at the edges of the cement particles there is hydration happening only at the top surface of the cement particles. As hydration proceeds more and more of the particles start dissolving outwards and you get an increase in the amount of hydration products forming.

So as a result what is happening to the space in between? It is continuously reducing, the water filled space is continuously reducing. So in other words as hydration proceeds more and more the porosity will continuously reduce. Now in the beginning itself if I had more cement in the system, if I put more particles of cement in the system what will happen? Just look at it from this perspective, I said as continued hydration reduces porosity. In the beginning itself I have a lot of cement in the system that means I am choosing a low water to cement ratio.

When I choose a low water to cement ratio that means the space occupied by cement is now higher than in a high water cement ratio mix. So what happens then? Heat liberation is going to happen. More cement means more heat. There is lesser space available now for the hydration products to form. In other words my porosity reduction starts happening very early. My porosity reduction will start happening very early when I have more cement present. Now that also means that possibly in the long term I may not have sufficient space for hydration to happen at all. What does that mean again? Incomplete hydration. As I lower the water to cement ratio I get lesser and lesser hydration. Now this is counter intuitive no, we always think that when we want more strength we want to reduce the water to cement ratio. But now I am telling you that when you reduce the water to cement ratio the possibility of hydration also goes down. What is happening here? So what is strength dependent on? It is dependent on hydration but we just said that when you lower water to cement ratio you get lesser hydration.

So why does strength increase? Particle packing is going up but is that the only thing? Particle packing yes, but what is happening essentially is your porosity reduction is much more rapid in lower water cement ratio systems. Strength is dependent on porosity. The higher the porosity the lower the strength. So this explains two things for you. One is in low water cement ratio systems you have lesser porosity so higher strength. At the same time in low water cement ratio systems there is less hydration happening. That means you have a lot of cement that is sitting there as a filler.

Now why do you want to waste cement as a filler? So this is another case to understand the utilization of supplementary cementing materials or mineral admixtures.

Why do we want to waste cement as a filler? You could as well replace it with supplementary materials. So it is important to understand from the overall perspective. Now that does not mean that we do not cure concrete with low water cement ratio because hydration is only less. Why bother curing? It is not correct. There are other problems with it which we will talk about when we talk about high strength concrete.

Again this is just showing you the rate at which the properties of the cement or concrete develop. You have porosity reduction, you have permeability reduction. Why does permeability reduce? Porosity reduces. Why does permeability reduce? Why because the connection of the porosity also is reduced. With more hydration porosity reduces and the connectivity of the porosity also reduces. That is why permeability goes down. This is the reason why we do curing. We want to do curing to ensure that the porosity and permeability reduce in the system. And obviously when the porosity is coming down the strength is going to go up. Of course in the beginning when the concrete is not set yet there is no real meaning to strength. Only after the setting is completed the strength development is really taken into account.

Structure of hydration products:

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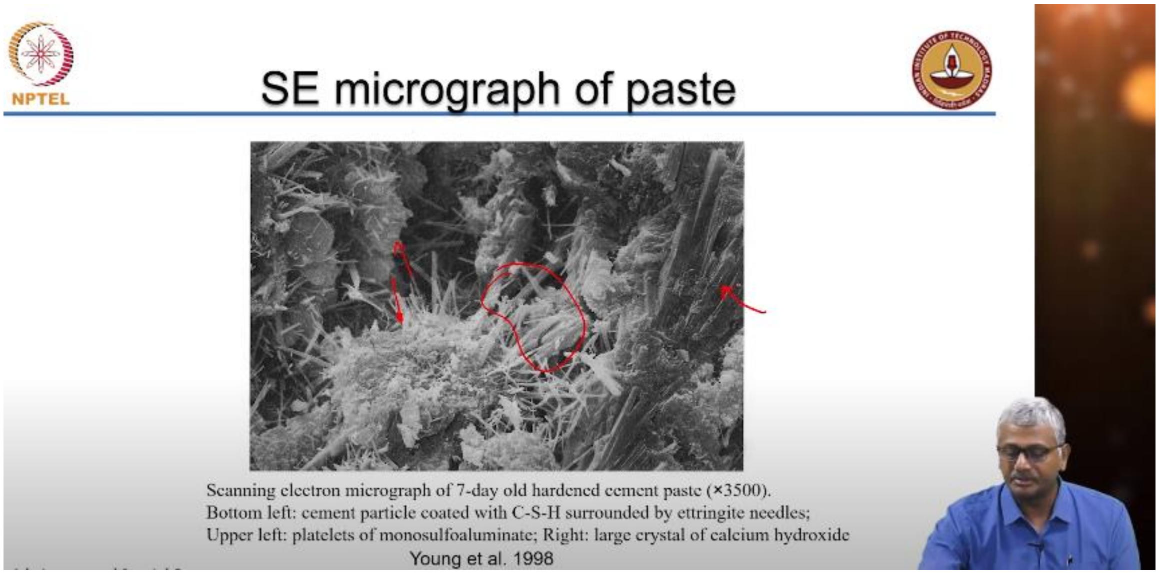

SE micrograph of paste

Scanning electron micrograph of 7-day old hardened cement paste (×3500).
Bottom left: cement particle coated with C-S-H surrounded by ettringite needles;
Upper left: platelets of monosulfoaluminate; Right: large crystal of calcium hydroxide
Young et al. 1998

Just to show you the structure of hydration products. Your CSH is basically these loosely defined structures. The well-defined crystalline structures could be that of ettringite. The large crystalline components could be that of calcium hydroxide. Large crystalline components are calcium hydroxide.

Another picture showing the fibrous loosely gel-like defined nature of CSH. More pictures in CSH.

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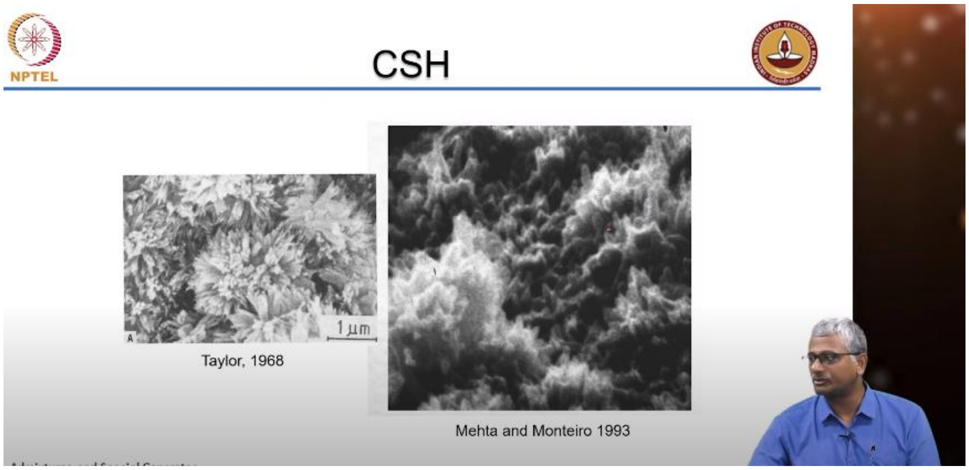

CSH

Taylor, 1968

Mehta and Monteiro 1993

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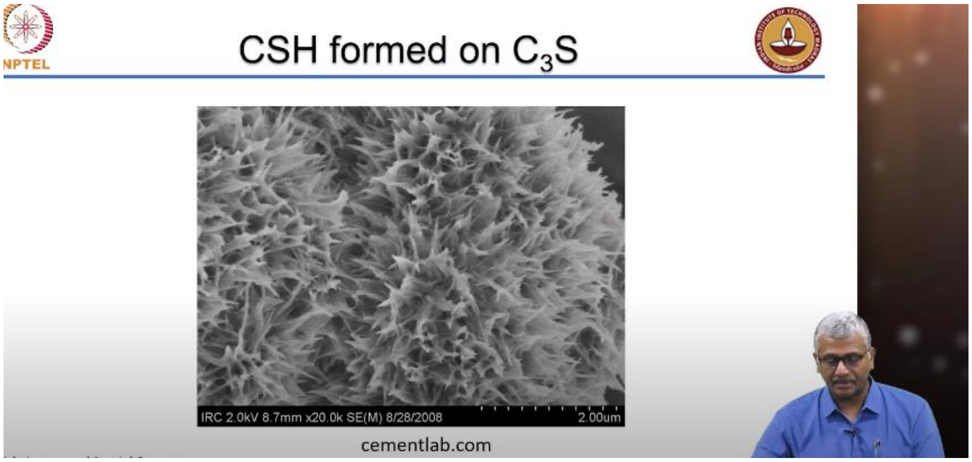

CSH formed on C_3S

cementlab.com

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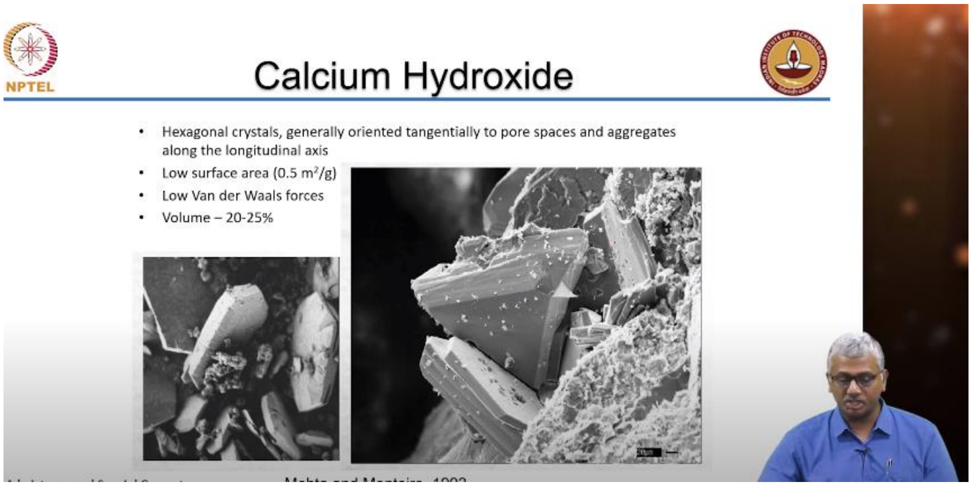

Calcium Hydroxide

- Hexagonal crystals, generally oriented tangentially to pore spaces and aggregates along the longitudinal axis
- Low surface area (0.5 m^2/g)
- Low Van der Waals forces
- Volume – 20-25%

Calcium hydroxide as I said is well defined crystalline phase.It has got a hexagonal crystalline shape and because of its well defined bulky shape it has got a low surface area. CSH on the other hand as you can see because of its fibrous shape it has got a very high surface area. So when you convert your calcium hydroxide to CSH your ability to occupy porosity increases. What does that mean? Now if I have a pozzolanic reaction I am converting calcium hydroxide to CSH that means more and more pores can now start getting blocked by CSH. That is the reason why durability goes up when I use pozzolanic materials because your pores become finer and finer. As your pores become finer water and other chemicals cannot easily enter the porosity. Permeability reduces. We will come back to that subject of course later. Ettringite, monosulphate are all highly crystalline components.

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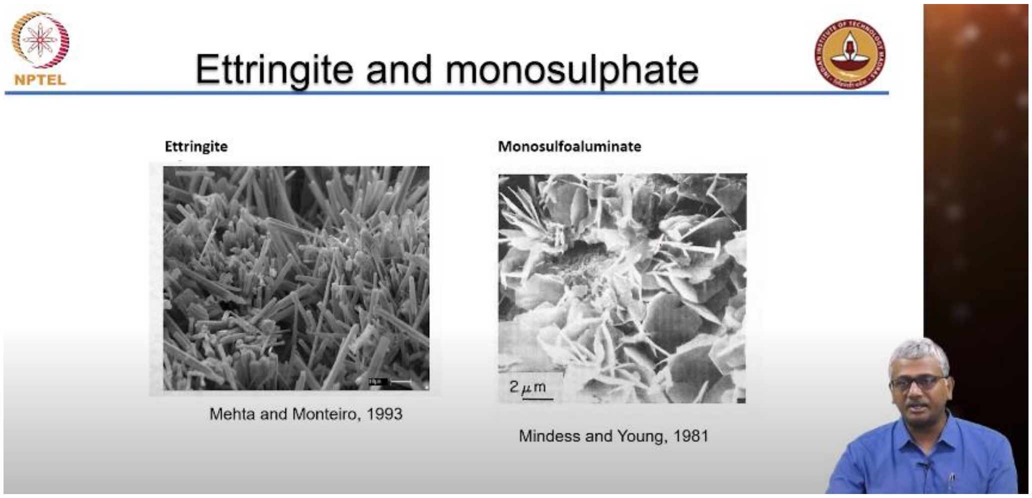

Ettringite and monosulphate

Ettringite

Monosulfoaluminate

Mehta and Monteiro, 1993

Mindess and Young, 1981

You can find these distributed across the overall microstructure. Again more pictures of ettringite and monosulphate. These are all taken with the help of scanning electron microscopy because you need the resolution defined by SEM to really get to this level. Optical microscopy cannot do this extent of imaging.

Pores and Air voids:

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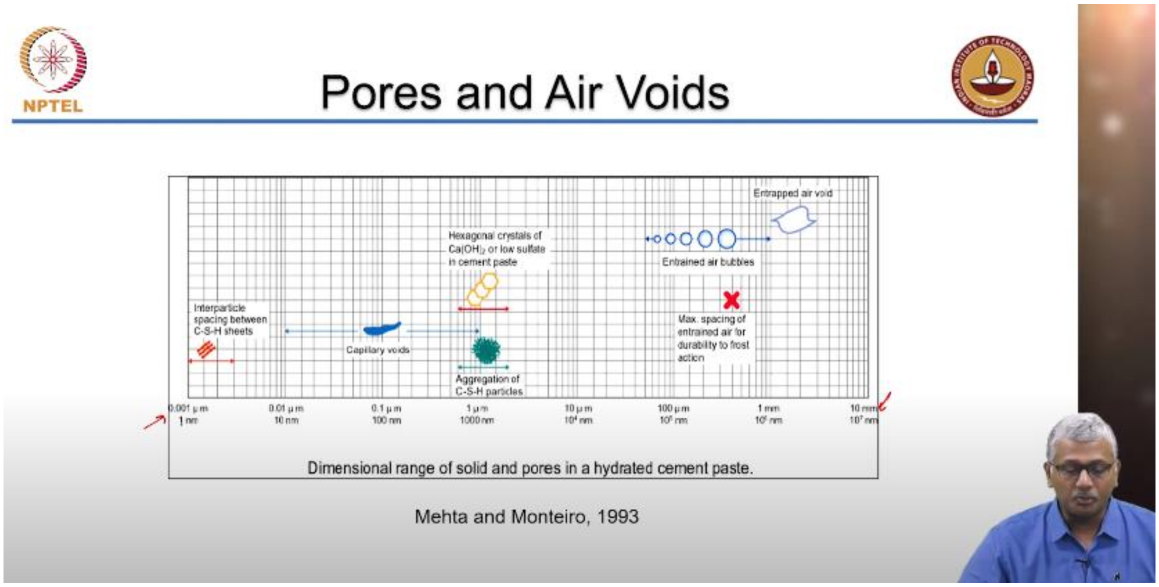

Pores and Air Voids

Dimensional range of solid and pores in a hydrated cement paste.

Mehta and Monteiro, 1993

So this is very important. What is the nature of porosity in concrete and porosity in air voids in concrete? So if you take a scale all the way from 10 mm to 0.001 micron or 1 nanometer, various mixtures within concrete are at that range. Your fine aggregate is up to about 150 microns and coarse aggregates are 5 mm and more. Entrapped air voids. So you mix concrete, you vibrate it but it is not possible to completely eliminate all the air from the mixture. So some air will get trapped. Some air can also get trapped because of bleeding.

What is bleeding? Water rises to the surface because it is lightest in weight. Sometimes it may get trapped under the aggregate and lead to a formation of what we call a bleed lens and that is exactly later going to become a void. But that is not an air void it is a bleed lens but nevertheless it will be of the same size as a typical entrapped air void several millimeters in size.

And then you have entrained air bubbles. What is entrained air? Air that is wantedly introduced into the system because of performance in specific environments like freezing and thawing. You put in these chemical admixtures which will entrain air. We will talk about that later. The size of the entrained air bubbles you can see is from several tens of microns up to about 1 mm.

Then in cement paste itself the hydration products could be at different scales.Your calcium hydroxide crystals are of the order of a few microns. Aggregation of CSH particles again of the order of a few micrometers. Your capillary voids are from 1 micron all the way up to about 10 nanometers. The large range for capillary voids. What is capillary void?

Capillary voids are not the same as entrained or entrapped air voids. Capillary voids or capillary pores, these are pores. Pore is basically more of a long continuous void that exists within the paste. Whereas entrapped and entrained air voids are more discrete voids that are present. Whereas capillary voids are more called capillary pores. If you go still further the inter particle spacing between CSH sheets is of the order of a few nanometers. So this range is what is called gel pores. The pores that are present within the CSH gel pores. These are capillary pores and then you have gel pores. So the sizes of your air voids and porosity within your system are varying significantly all the way from 1 nm to several mm. So this heterogeneity is what makes concrete very complicated. This heterogeneity is the problem and because of which we are not able to perfectly predict the properties well enough.

Workability of concrete:

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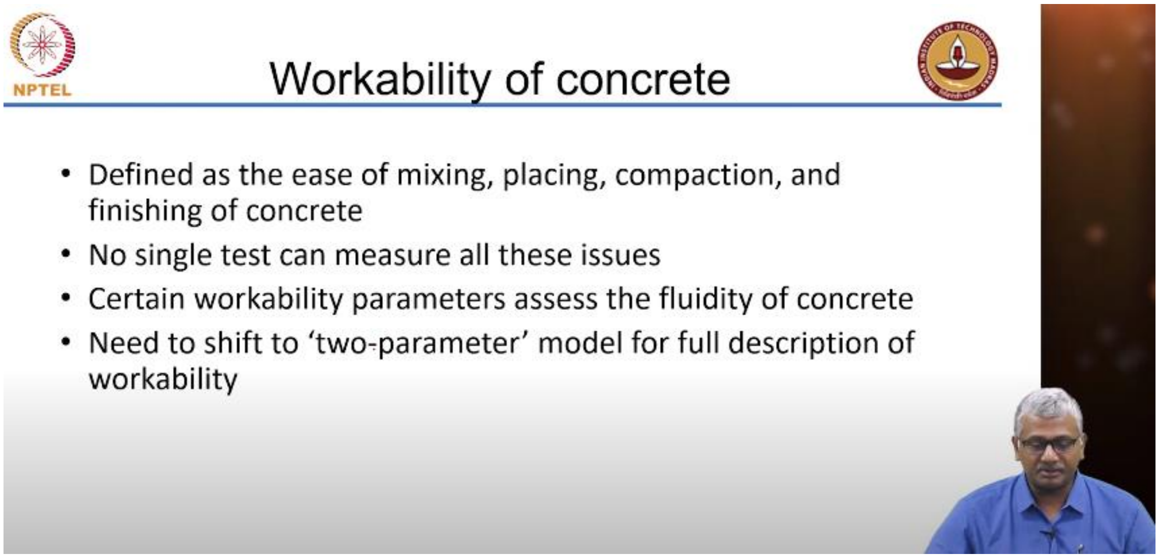

Workability of concrete

- Defined as the ease of mixing, placing, compaction, and finishing of concrete
- No single test can measure all these issues
- Certain workability parameters assess the fluidity of concrete
- Need to shift to 'two-parameter' model for full description of workability

Now this is an easy review in terms of properties of concrete. Workability you know very well is defined as the ease of mixing, placing, and compaction and finishing. There is no single test that measures all of these aspects. We use slump tests but that is not really giving you a complete picture. Concrete having a good slump need not be a concrete that can be pumped easily. Usually you can design mixtures in that way but it need not always be correlated. So there are different ways of testing workability but nobody bothers about the compaction factor anymore of course. But for stiffer mixtures you can use the flow table test or the VB test, for stiffer mixtures because slump cannot be measured slump is 0 for stiff mixtures so you can use the flow table or the VB test. Your IS guidelines give you some correlations between what you can get for different types of mixtures in between these tests.

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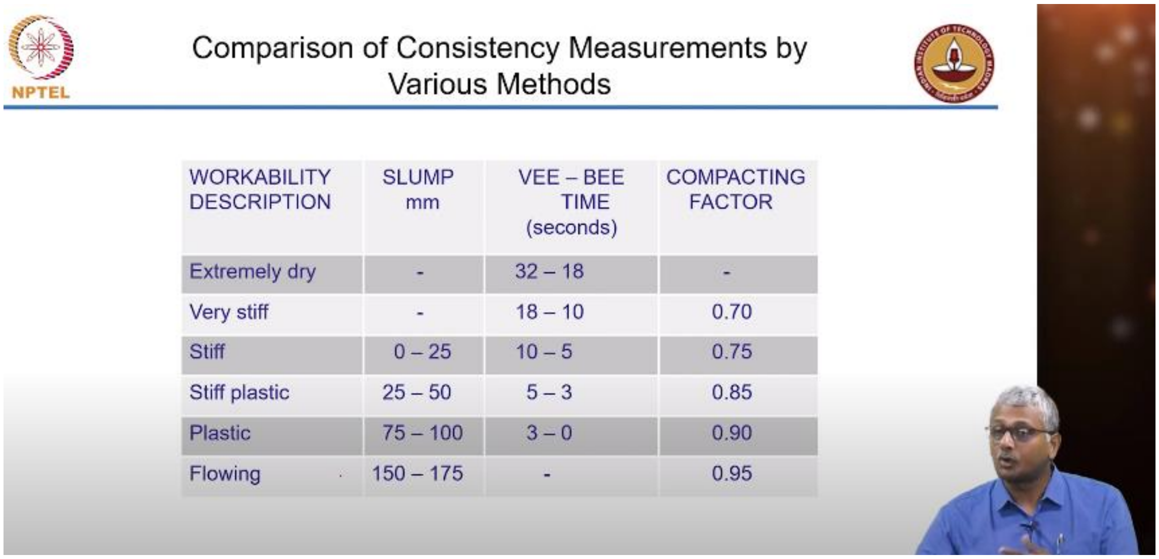

Comparison of Consistency Measurements by Various Methods

WORKABILITY DESCRIPTION	SLUMP mm	VEE – BEE TIME (seconds)	COMPACTING FACTOR
Extremely dry	-	32 – 18	-
Very stiff	-	18 – 10	0.70
Stiff	0 – 25	10 – 5	0.75
Stiff plastic	25 – 50	5 – 3	0.85
Plastic	75 – 100	3 – 0	0.90
Flowing	150 – 175	-	0.95

But these days all of this is actually almost going out of the window because more and more people in job applications are shifting towards flow-able concrete. There are of course applications where zero slump concrete is also required for instance roller compacted concrete but most applications involving concrete in regular structures is moving towards self-compacting concrete because it eases the application significantly.

Placement of concrete:

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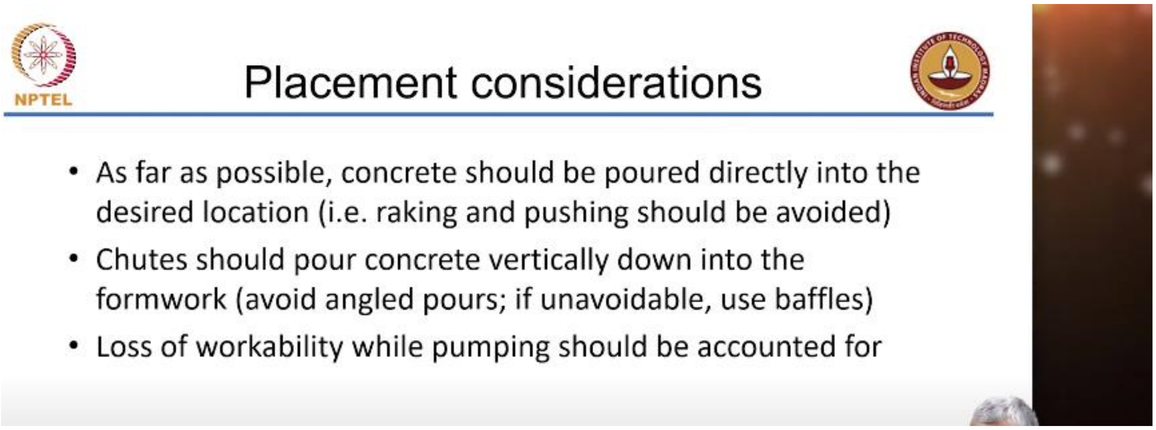

Placement considerations

- As far as possible, concrete should be poured directly into the desired location (i.e. raking and pushing should be avoided)
- Chutes should pour concrete vertically down into the formwork (avoid angled pours; if unavoidable, use baffles)
- Loss of workability while pumping should be accounted for

Now placement of concrete has to be done directly in position rather than keeping it in one location and trying to rake it because you do not want to cause any segregation. So you need to ensure that concrete is poured almost vertically down rather than coming at an inclination again to avoid segregation of the aggregate from the concrete. So again segregation and bleeding need to be paid attention to. Segregation is simply separation of paste and aggregate, bleeding is separation of water from the mix. All this happens when you do not design your mix well. Sometimes when you over vibrate your concrete also it can happen. When you over vibrate you can lead to segregation and bleeding.

Consolidation of concrete:

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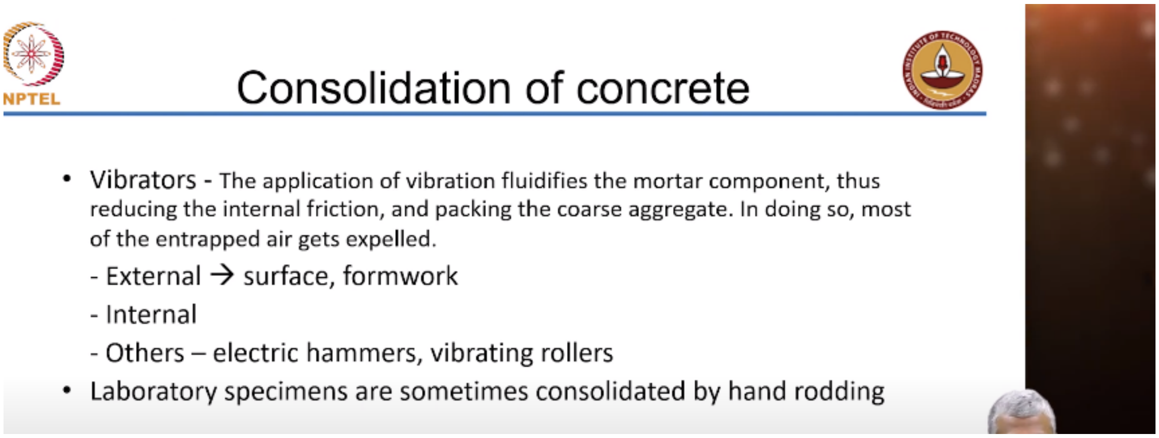

Consolidation of concrete

- Vibrators - The application of vibration fluidifies the mortar component, thus reducing the internal friction, and packing the coarse aggregate. In doing so, most of the entrapped air gets expelled.
  - External → surface, formwork
  - Internal
  - Others – electric hammers, vibrating rollers
- Laboratory specimens are sometimes consolidated by hand rodding

Vibration is absolutely important from the point of view of obtaining the right compaction level in the concrete because if you do not compact well you do not get the properties that you have. You have different types of vibrators, external, internal, surface vibrators, formwork vibrators and so on and so forth.

Finishing:

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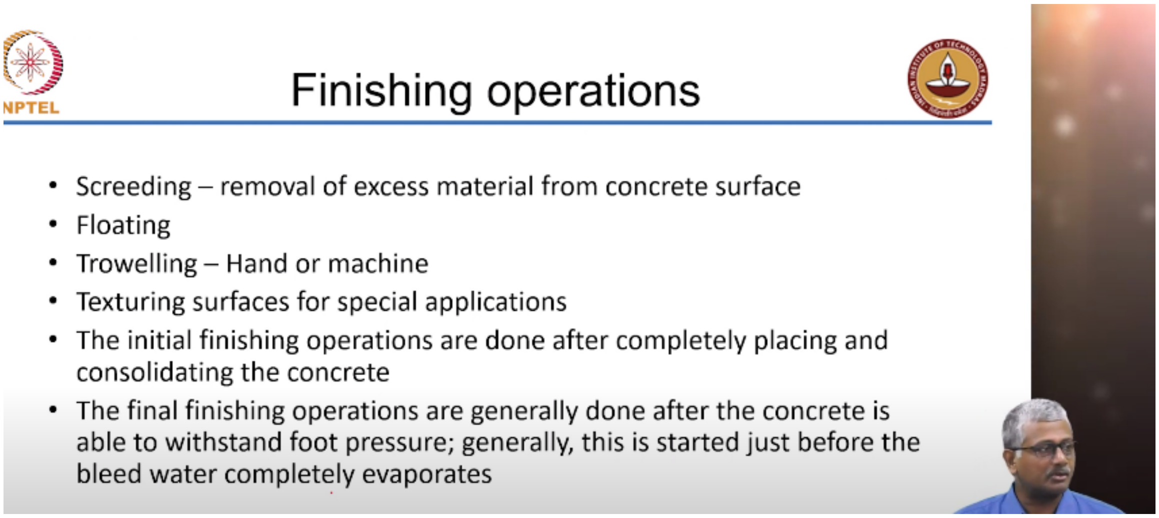

Finishing operations

- Screeding – removal of excess material from concrete surface
- Floating
- Trowelling – Hand or machine
- Texturing surfaces for special applications
- The initial finishing operations are done after completely placing and consolidating the concrete
- The final finishing operations are generally done after the concrete is able to withstand foot pressure; generally, this is started just before the bleed water completely evaporates

Finishing follows compaction and there are various ways of finishing. These days of course finishing is leading to an entirely new science of concrete technology that is textured concrete. You get a lot of textured concrete, in fact now texturing has reached the level of actually even putting photographs on the surface of concrete just like what they do on the top of cakes. Icing on the cakes just like that they have icing on the concrete with people's photographs also on top of the concrete. So all these are very specialized applications of concrete today. But there are various different tools that are available.

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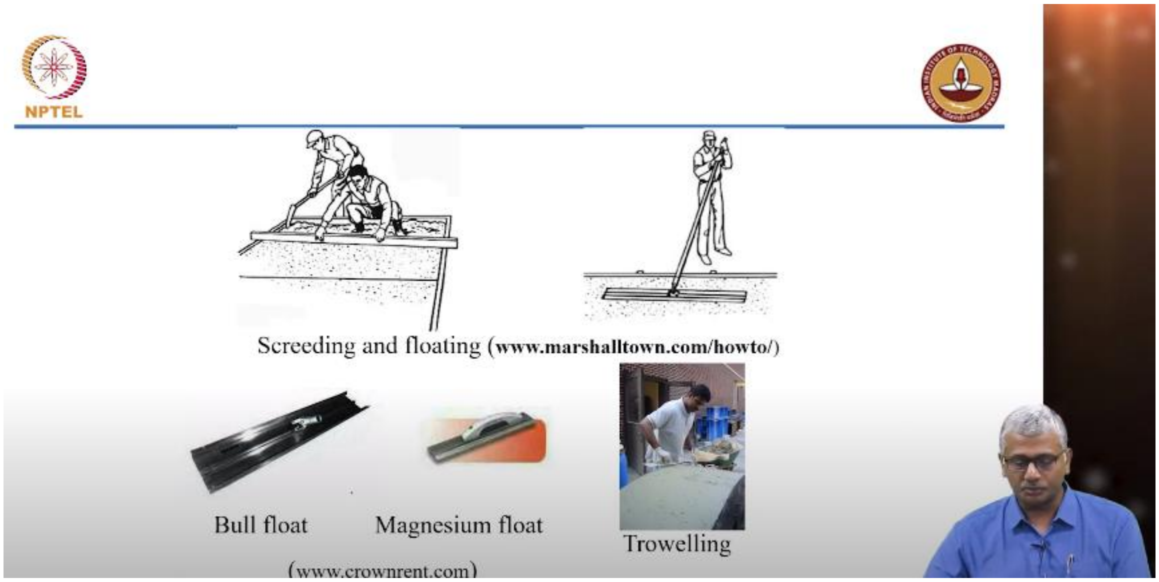


Screeding and floating (www.marshalltown.com/howto/)

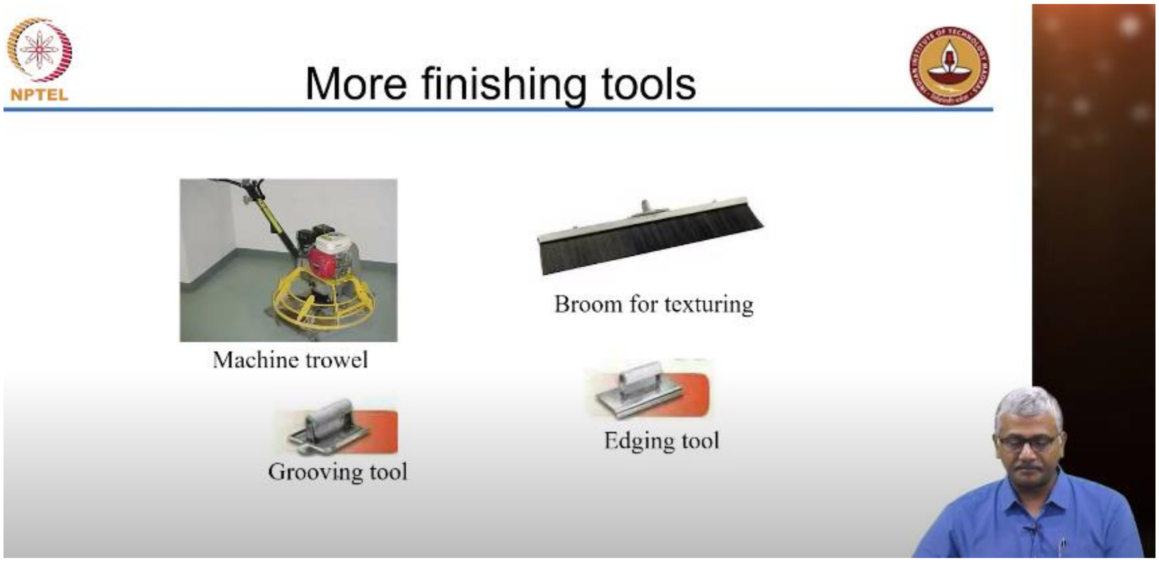
Bull float

Magnesium float

(www.crownrent.com)

Trowelling

(Refer to slide time: 27:31)



More finishing tools

Machine trowel

Broom for texturing

Grooving tool

Edging tool

Curing of concrete:

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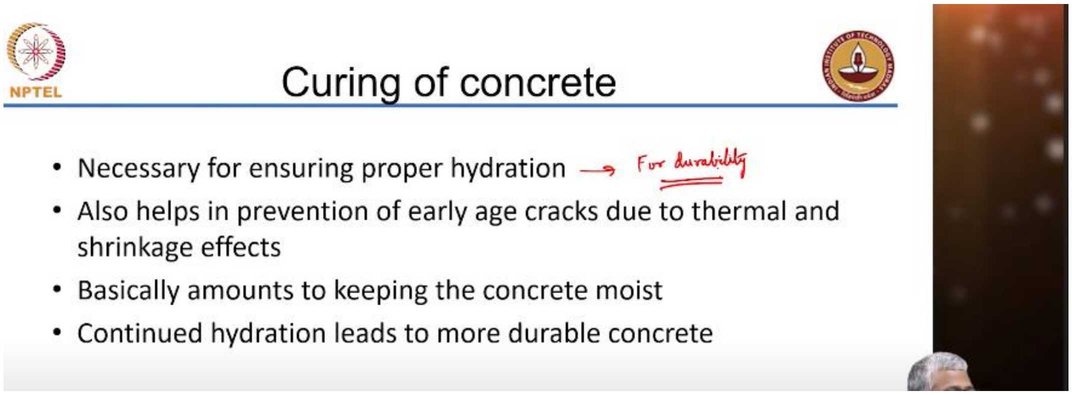

Curing of concrete

- Necessary for ensuring proper hydration → For durability
- Also helps in prevention of early age cracks due to thermal and shrinkage effects
- Basically amounts to keeping the concrete moist
- Continued hydration leads to more durable concrete

Curing concrete is important to obtain the required level of hydration but from the point of view of curing is done not so much for strength but more for durability. Always remember that curing is important for durability.

Now a lot of people seem to think that concrete is cured on the site to keep the concrete temperature low. It is not correct. You do not want to pour cold water on top of a hot concrete. It is a bad idea. So that is a false idea in the minds of people who are at the site. They think that they keep the temperature low by pouring water. It is not the idea. The idea is to ensure that a moisture source is available to ensure that concrete does not dry out during the process of hydration.

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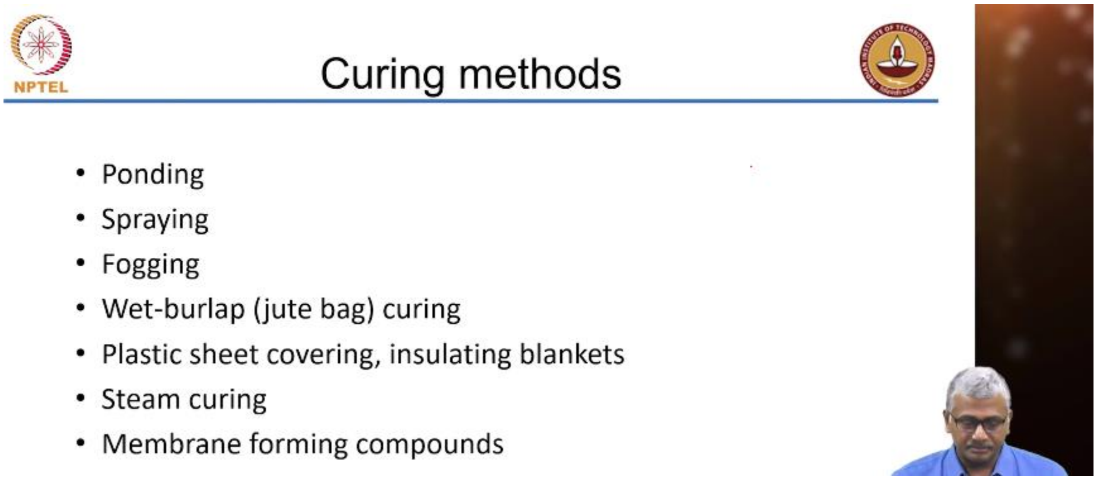

Curing methods

- Ponding
- Spraying
- Fogging
- Wet-burlap (jute bag) curing
- Plastic sheet covering, insulating blankets
- Steam curing
- Membrane forming compounds

Various methods of curing, an important discussion obviously which will come later is the use of membrane forming compounds or curing compounds that are applied in many job sites nowadays because water for curing is not easily available.