Characterization of Construction Materials
Prof. Manu Santhanam
Department of Civil Engineering
Indian Institute of Technology – Madras

Lecture – 46
Application of Characterization Techniques to Assess Composite Binder with Limestone-Calcined Clay: What, Why and How? Part - 1

Welcome one and all to this NPTEL lecture on application of characterization techniques to assess composite binders with limestone-calcined clay. So, I am Yuvaraj, Ph.D. student working with Professor Manu. So, in this lecture, what I will try to talk about is, use of the techniques which we have discussed until this point in the class and look at ways in which we can apply these techniques to new cementitious systems and try to evolve understanding. So, by now, most of you would have understood use of characterization technique is supportive to finding answers to key questions in research. So, the first point is to understand or ask questions to find out what you want to analyze. There is a famous English proverb which says the proof of the pudding is in the eating. So, first you want to find out what you want to explain in terms of property, ask the question of what you want to characterize, then why you want to characterize like whether is it because of any significant difference in the property and then that will lead you to answers or precise answers in choosing the technique how you want to characterize.

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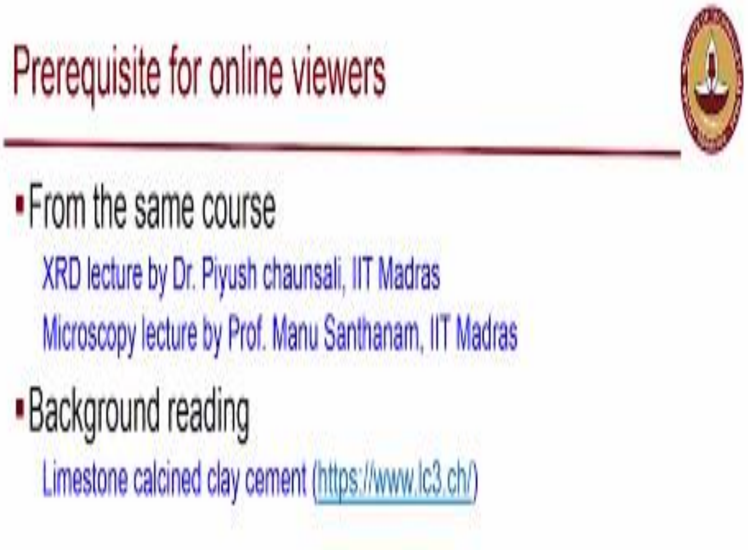

Prerequisite for online viewers

- From the same course
  - XRD lecture by Dr. Piyush chaunsali, IIT Madras
  - Microscopy lecture by Prof. Manu Santhanam, IIT Madras
- Background reading
  - Limestone calcined clay cement (https://www.lc3.ch/)

So, for the online viewers, prerequisite before taking this lecture would be to have covered the XRD lecture by Professor Piyush and the Microscopy lecture by Professor Manu and also some background reading on limestone-calcined clay cement which I will explain right now would be also required.

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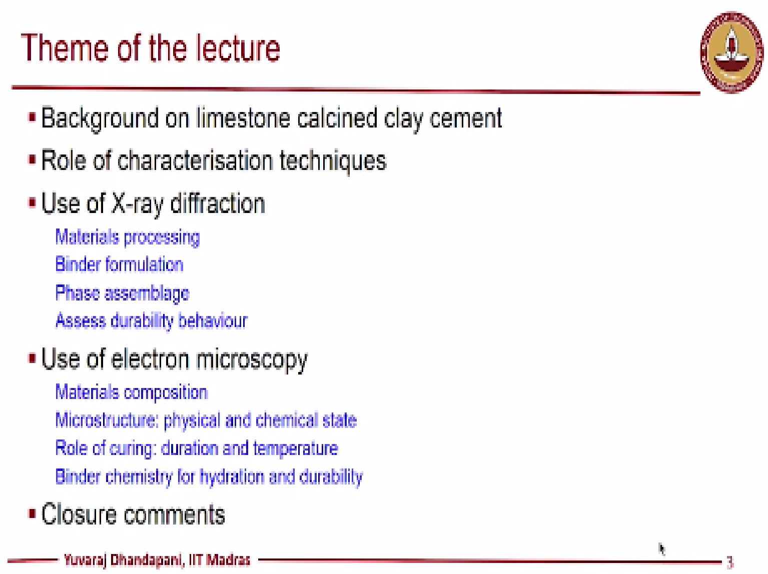

Theme of the lecture

- Background on limestone calcined clay cement
- Role of characterisation techniques
- Use of X-ray diffraction
  - Materials processing
  - Binder formulation
  - Phase assemblage
  - Assess durability behaviour
- Use of electron microscopy
  - Materials composition
  - Microstructure: physical and chemical state
  - Role of curing: duration and temperature
  - Binder chemistry for hydration and durability
- Closure comments

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So, this will be the scheme of things which will be covered in today's lecture. First, I will give you a background and introduce what is the new limestone calcined clay cement system, after which we will try to look at the role of characterization techniques, in particular XRD and SEM techniques to address a range of different problems when you are working with research questions. For instance, in XRD, it can be used to narrow down on material processing, formulations of binders to study, assess phase assemblage, and also to explain durability behaviors. Then we will move into microscopy and look how microscopy techniques can be used to assess material composition, microstructure, physical and chemical state, role of curing which involves assessing role of curing duration as well as curing temperature and role of binder chemistry which can be assessed using EDX to explain hydration and durability behavior.

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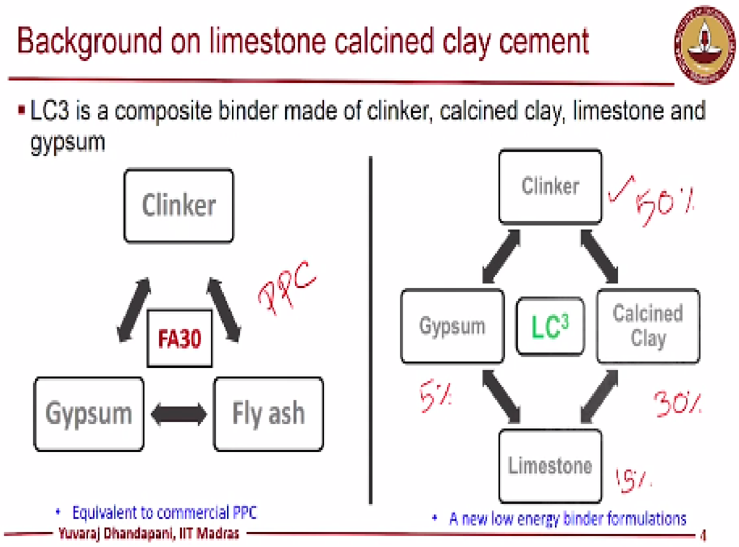

Background on limestone calcined clay cement

- LC3 is a composite binder made of clinker, calcined clay, limestone and gypsum

Clinker

FA30

PPC

Gypsum

Fly ash

Clinker ✓ 50%

Gypsum

LC^3

Calcined Clay

5%

30%

Limestone

15%

- Equivalent to commercial PPC
- A new low energy binder formulations

A brief background about the system before we start dwelling into different techniques - Limestone calcined clay cement is a composite binder which is made of clinker, calcined clay, limestone and gypsum. So most of you would be aware typical blended cement which is called Portland pozzolana cement, PPC cement, which is available in market is generally composed of clinker, fly ash and gypsum. So, in this binder which is called LC^3, we have clinker which is a major component which is brought down to about 50%. Then you have calcined clay, which is about 30%. So, these are empirical, we can work out with the formulations and then you have limestone which is about 15% and then you have gypsum which is typically about 5%. So, when you have range of different components within the binder, there are multiple reactions which happen. So, you need to address these interactions and understand what the implication of this composite structure on the final performance is.

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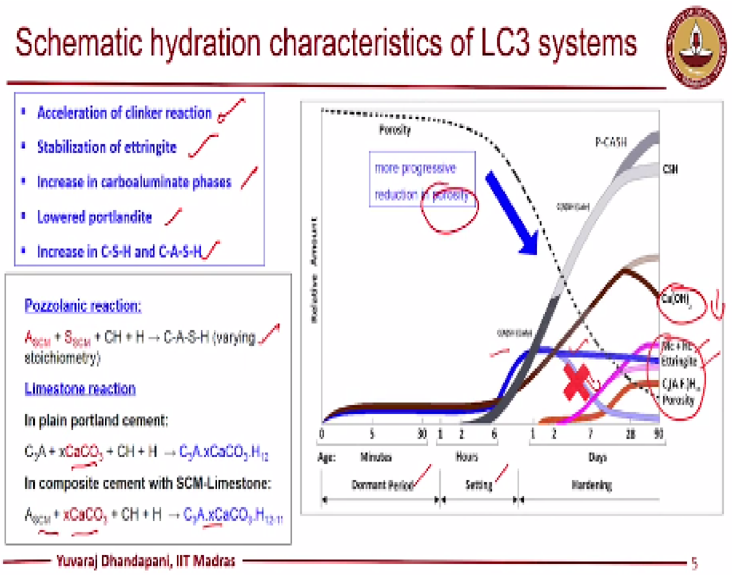

Schematic hydration characteristics of LC3 systems

- Acceleration of clinker reaction
- Stabilization of ettringite
- Increase in carboaluminate phases
- Lowered portlandite
- Increase in C-S-H and C-A-S-H

Pozzolanic reaction:

$A_{SCM} + S_{SCM} + CH + H \rightarrow C\text{-}A\text{-}S\text{-}H$ (varying stoichiometry)

Limestone reaction

In plain portland cement:

$C_3A + xCaCO_3 + CH + H \rightarrow C_3A.xCaCO_3.H_{12}$

In composite cement with SCM-Limestone:

$A_{SCM} + xCaCO_3 + CH + H \rightarrow C_3A.xCaCO_3.H_{12\text{-}11}$

So, for instance, this is a typical hydration curve of cementitious system. Generally what happens is initially you have a dormant period, hydration products start forming when setting occurs. Initially there is formation of C-S-H, so you call it early CSH, and along with which you also form ettringite and post the initial period if you do not have limestone in the systems, the ettringite amount start dropping, but when you have calcite particles within the system, the ettringite amount which is formed initially is sustained. It is because the calcite particle would react with the excess aluminates and form additional hydration products which are called mono and hemicarboaluminates, along with which, when you have calcined clay which is a pozzolan, you also have a traditional pozzolanic reaction which occurs in most of the blended cements.

So, when you have multiple reactions happening in parallel, which is acceleration of clinker reaction because you have limestone in it, which tends to accelerate the reaction of clinker; stabilization of ettringite, which I have discussed here, when you have calcite particles, it tends to react with the alumina and form additional hydration products called carboaluminates, so you do not necessarily convert the ettringite to monosulfate; and lowered portlandite because you have calcined clay, which is a pozzolan, so portlandite amount tends to get lowered; and finally there is increase in pozzolanic C-S-H and C-A-S-H. So, characterization technique in particular can be used to assess range of different characteristics, for instance what is the change in these hydration products which are available and also what is the change in porosity, which is a physical structure.

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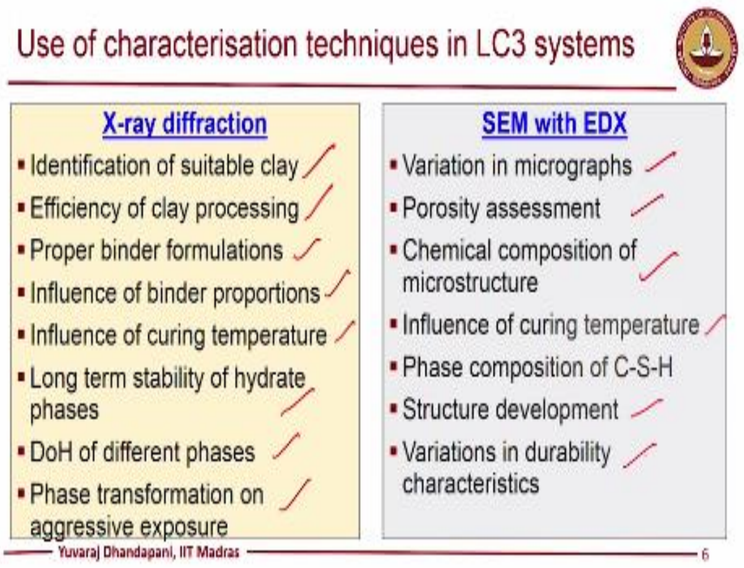

Use of characterisation techniques in LC3 systems

X-ray diffraction

- Identification of suitable clay
- Efficiency of clay processing
- Proper binder formulations
- Influence of binder proportions
- Influence of curing temperature
- Long term stability of hydrate phases
- DoH of different phases
- Phase transformation on aggressive exposure

SEM with EDX

- Variation in micrographs
- Porosity assessment
- Chemical composition of microstructure
- Influence of curing temperature
- Phase composition of C-S-H
- Structure development
- Variations in durability characteristics

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So, I have tried to list the range of different applications in which characterization technique can be used. For instance, if you look at XRD, it can be used to identify suitable clay which has to be used in the calcined clay based binder. What is the composition of the clay? How much is the kaolinite content in the clay and by heat treating the clay, that is, when you heat the clay and decompose it, how much of the clay is decomposed? What are the formulations which we have to come up with when you are having these multiple components? Is there a necessity to add or adjust the binder formulations? What is the influence of proportioning? When you have different proportions of these components, for instance difference in the limestone calcined clay ratio, how is it going to alter the final phase assemblage? How are these phases which are formed affected by curing temperature? And we are also looking at additional phases which are not necessarily available in typical blended cement. In typical blended cement, we always look at formation of additional pozzolanic C-S-H. Here, we are looking at different hydrates, whether these are stable over the period of time. Once it is formed, for instance after several years, whether these hydrates are going to be stable. So, there is no loss in property. What is the degree of hydration of the different phases which are there in the cementitious system? How are these phases responding when you expose it to aggressive environment, it can be sulphates, chlorides, carbonates; what is the tendency of it to transform and lead to any change in behaviors? So, these are different schemes in which XRD can be applied.

When you look at SEM, for instance, whether there is any difference in the microstructure itself? What are the characteristics of porosity? What is the chemical composition of microstructure? So, we discussed about pozzolanic C-S-H. So, when you have fly ash and calcined clay, is there any difference in the pozzolanic C-S-H which is formed. Again what is the role of curing temperature which is very critical in governing the performance in practical conditions? Whether there is any difference in the assemblage of these hydrates in the capillary pore space and what are the variations which occur due to exposure in durability environments? So we will go through each of these techniques and try to ask the question which tool is ideal or how the tool has been applied to understand the processing efficiency or the performance parameter in all these situations.

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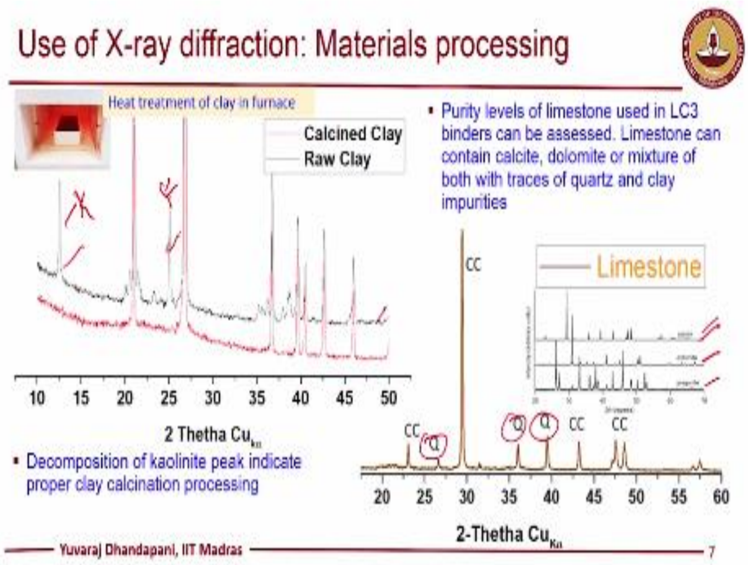

Use of X-ray diffraction: Materials processing

- Purity levels of limestone used in LC3 binders can be assessed. Limestone can contain calcite, dolomite or mixture of both with traces of quartz and clay impurities
- Decomposition of kaolinite peak indicate proper clay calcination processing

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For example, if you take material processing, I have given you X-ray diffractograms of raw and calcined clay. So in raw clay, you see this peak here in XRD. So this belongs to kaolinite peak. So when you heat treat kaolinite, the kaolinite tends to decompose and form an amorphous material which is an ideal pozzolan. So, if you want to test whether the clay has been calcined properly, XRD can be used very efficiently to check the kaolinite peaks. So for instance, these two peaks which you see here belong to kaolinite content. So if the peaks of kaolinite are completely decomposed after heat treatment, then the calcination efficiency has been proper.

Also the other component in the limestone calcined clay cement binder is calcite. When you look at calcite or the raw limestone which is available as deposits near the cement plant, it can have range of different calcium carbonate phases. So, for instance, you can have a calcite phase, you can have a dolomitic phase which is magnesium calcium carbonate, not necessarily pure calcium carbonate, and you have an aragonite phase which is a different phase of calcium carbonate. So, I have listed the peak intensity of these three different phases of calcite itself. So, when you are trying to come up with formulations for new binder, you want to have limestone in it, you tend to see what are the phases present in limestone? What form it is present in? So, for example, when you have calcite and dolomite, the reaction or the expansion in your systems can be completely different - because magnesium can tend to produce expansion in your system. So, you need to characterize the raw material before being used, also the purity of the material which is used. For instance, I have given you a diffractogram of limestone here. If you look at the diffractogram, you can see presence of quartz in it, which shows that the limestone which is presented here or assessed is not pure per se. So, then you need to assess what is the quality of the limestone? So, that can alter the reactions or extent of reaction of limestone with your calcined clay.

So, basically the question was when you heat treat the clay, what are the changes in the XRD peak? So, the black line which you see here is raw clay where you see the kaolinite peak. When you heat treat the clay, kaolinite tend to decompose and form amorphous aluminosilicate, so you do not see the kaolinite peak.

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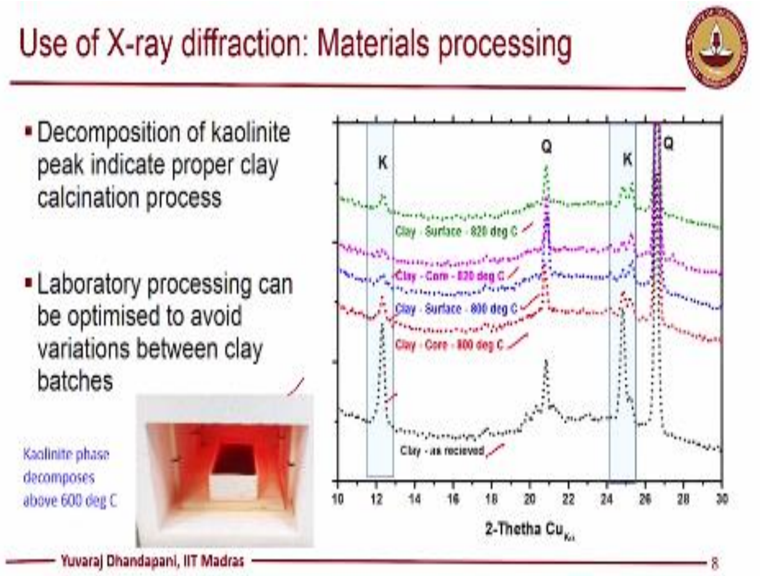

Use of X-ray diffraction: Materials processing

- Decomposition of kaolinite peak indicate proper clay calcination process
- Laboratory processing can be optimised to avoid variations between clay batches

Kaolinite phase decomposes above 600 deg C

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So, when you are doing a laboratory processing for instance, why material processing is important is, so when you are trying to formulate such materials or process the material in different conditions, in laboratory conditions, how do you identify what is the suitable temperature to be used or the dwelling time which has to be used.

So, for instance, I have presented here decomposition of the kaolinite peaks in different conditions. So, the clay - as received, you can see very strong peaks of kaolinite, and then when we try to process it, we want to heat treat it. So, it is been heat treated in a furnace where you can tend to take it to anywhere between 600 to 800 °C. Theoretically at 600 °C kaolinite should decompose, but when you start having large volumes of material, the decomposition will not be uniform. In that case, what we should do is assess the material, like for instance here the sample has been taken from the surface of the furnace and from the core. So, when you start taking material from core and surface, what you can see is at the surface, the kaolinite peak is almost fully decomposed; but at the core, because he has to be transmitted till the core of the material, you still have a strong kaolinite peak. So, when you start seeing such behavior, what you need to ensure is you increase the temperature or dwelling time. In this case, the temperature was increased to nearly 820 °C to reduce the amount of kaolinite peak which is present. So, you tend to calcine the clay properly in those cases. So, laboratory process like this can be optimized by suitably using the characterization technique at right point in time, you do not want to end up using an un-calcined clay directly into your concrete or binder formulations which may lead to absorption of water or expansion cracking for example.

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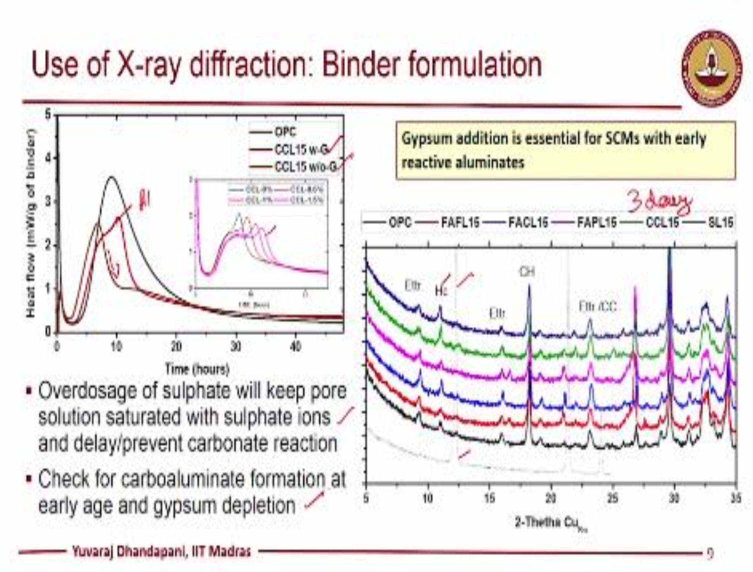

Use of X-ray diffraction: Binder formulation

Gypsum addition is essential for SCMs with early reactive aluminates

- Overdosage of sulphate will keep pore solution saturated with sulphate ions and delay/prevent carbonate reaction
- Check for carboaluminate formation at early age and gypsum depletion

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So, the other process is, once the material has been processed, coming up with formulations also will require characterization at suitable requirement. For instance, you have calcined clay, which is basically an aluminosilicate. So you tend to have excess alumina into your binder. So when you start having excess alumina, what I have presented here is a calorimetry curve of calcined clay binder with different dosages of calcium sulfate hydrate, which is gypsum. So when you start increasing gypsum dosage, you tend to push the aluminate peak (the second peak belongs to the aluminate), after the consumption of sulphate. So, when you start adding excess sulphate to the system, you tend to push the aluminate peak.

So you can see here, I have presented calorimetry curve of system without gypsum and with gypsum. So, when you look at the difference, the one with the gypsum produces a much broader silicate peak, and one without gypsum tend to have a very abrupt drop after the initial hydration curve, because when you do not provide sufficient gypsum to your systems, it can hamper with your tricalcium silicate reactions, so it can bring down your reaction extent. So, in these cases, when you are dealing with such binder formulations, you need to increase the gypsum dosage.

However, when you start overdosing gypsum to systems, what it does is it keeps the sulphate ions saturated in your pore solution. So, when you still have the sulphate ions, so I was talking about reaction of limestone into your systems. So, when you start adding sulphate ions, it will hamper or suppress the reaction of your carbonates into your system. So, you do not necessarily produce the ideal kind of binder formulation which is desired. You come up with a mixture of calcined clay limestone or clinker, but if you overdose sulphate by some extent, it will not allow the limestone to react.

So, very simply what you can do is, check in XRD, so what I have given here is, dotted line is an XRD peak of gypsum. This was done at 3 days. So, when you check XRD at 3 days, what we tend to see is almost the consumption of gypsum which is not present, gypsum tends to dissolve initially, also the formation of carboaluminate peak, here in this case hemi-carboaluminate which is half molecule of carbonate. So, once you see formation of carboaluminate that just confirms that you have not overdosed gypsum to such an extent that you are suppressing the carbonate reaction. So, this can very easily help you to come up with formulation which are more ideal in the case of limestone calcined clay and clinker. So, you have to check for the carboaluminate peak at the early age to ensure that gypsum is not overdosed and sulphate is not kept saturated in pore solution.

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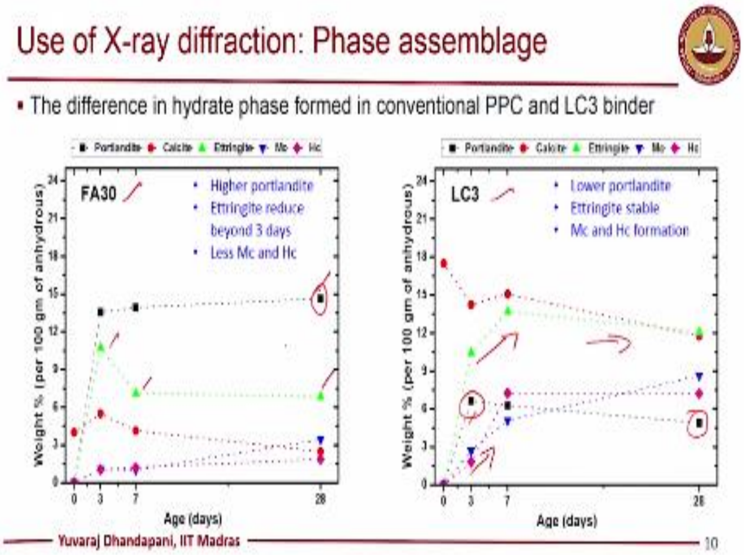

Use of X-ray diffraction: Phase assemblage

- The difference in hydrate phase formed in conventional PPC and LC3 binder

FA30
- Higher portlandite
- Ettringite reduce beyond 3 days
- Less Mc and Hc

LC3
- Lower portlandite
- Ettringite stable
- Mc and Hc formation

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The next zone once you have processed the material, you have tried to confirm the binder formulations are right, the next characteristics which we can try to address or understand is what is the change in the phase assemblage. So when we say phase assemblage, what are the compositions of the phases which are formed? So, for instance here, I have presented the phase assemblage of a fly ash binder, which is more typical, most of you would understand what a fly ash binder is and LC^3 binder.

So, let us go through the differences for instance here you tend to see portlandite content and portlandite content is stable almost at 15% until the age of 28 days. And then if you look at the ettringite amount, initially ettringite amount reaches about 10 %, later it tends to drop which is more or less expected because you do not have limestone in such system. So, as I told before, the ettringite amount tends to get reduced because it gets converted over the period of time to monosulfate.

But if you look at the calcined clay limestone based system, you can see the ettringite amount increasing and almost remaining stable from that point at around 10-12 %. This is because when you have limestone, the ettringite amount tends to remain stable. Also interesting observation would be - you can see the portlandite content which is almost at 6%, ultimately at around 4% in the case of calcined clay binder, whereas in fly ash you tend to see very high amount of portlandite. This also confirms the reactivity of the material. So, since calcined clay is highly reactive, it tends to consume lot of portlandite which is present at a very early age. And you can also see the amount of carboaluminate reactions which are forming. So, for instance here (graph on the right), the carboaluminates which are forming which is hemi-carboaluminate tends to rise from nearly 1% to 7 % and remain stable. So, in this way, you can characterize the material and make sure the formulations are in line with the theory which is expected behind the interactions.

The portlandite will be consumed by fly ash over the period of time. So, here what I have presented is up to 28 days. So, we know that fly ash is a less reactive pozzolan. So, it tends to react much slowly after the 28 days. At the early ages, you tend to have only the dilution effect, and clinker is reacting over the period of time. So I will show you later some diffractograms of fly ash concrete at 150 days and 4 years, where we tend to see a complete consumption of portlandite.

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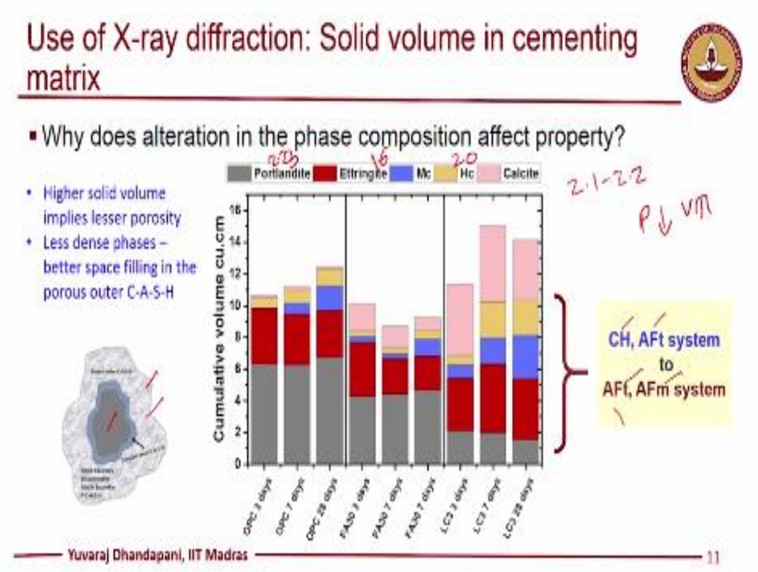

Use of X-ray diffraction: Solid volume in cementing matrix

- Why does alteration in the phase composition affect property?

- Higher solid volume implies lesser porosity
- Less dense phases – better space filling in the porous outer C-A-S-H

CH, AFt system to AFt, AFm system

So, why is this important? Why do we want to assess what is the governing phases or the amount of phases which is produced? So, for instance, here what I have presented is the cumulative volume of the solid phases. So, we have different phases produced. So, when you have phases, what it finally ends up doing is, it all forms solid and all the solid which is produced or the hydrates which is produced tend to fill up the porosities. But what is different between the different hydrates is the density of the phases. So when the density of the material is lower, the volume filling capacity is high. So, for instance, you can observe here the volume of ettringite, monocarbonate, and hemicarbonate, which comes to round about 6 cu. cm., in the case of LC^2 binder. So, when you look at portlandite and the other phases in these cases, the overall volume of these phases tend to be around 4 cu. cm. So, when you have higher volumes of these phases because of the density of the phases (these phases tend to have lower density, for instance, ettringite has a density of around 1.6, carboaluminates have a density around 2, C-S-H has a density around 2.1 to 2.2 and calcium hydroxide has a density of around 2.23). So, when you have phases with lower density, for instance you have more amount of ettringite, it tends to fill up the solid volume much better than the other phases.

So, what happens is you have a cement grain; you tend to produce C-S-H around the cement grain. So, when you have these phases which are having lower density, the convergence of these reaction products in the capillary region will be much more. So, this can be used to address such behavior like when you have conversion of a system which is dominated by calcium hydroxide and ettringite and later it is getting dominated by your ettringite and carboaluminates. So, you can have a completely different level of property development because of the difference in the solid volume.

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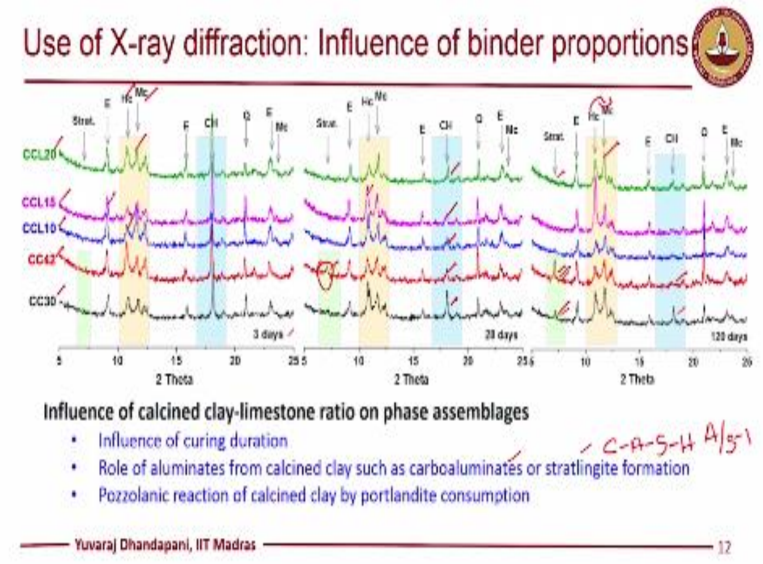

Use of X-ray diffraction: Influence of binder proportions

Influence of calcined clay-limestone ratio on phase assemblages

- Influence of curing duration
- Role of aluminates from calcined clay such as carboaluminates or stratlingite formation
- Pozzolanic reaction of calcined clay by portlandite consumption

C-A-S-H A/S-1

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So, we have seen that it can change the solid volume, but how it can help us theorize a lot of knowledge, in terms of fundamental research questions. So, for instance here, I have presented X-ray diffractograms of calcined clay binder. So, this is binary calcined clay at 30% and calcined clay at nearly 42%. You have calcined clay limestone at 10%, 15% limestone and 20% limestone. So, what you can observe is in the cases where you have limestone, you tend to see a rise in the ettringite peak because limestone preserves this ettringite which is formed. Also when you start adding higher amount of limestone to your systems, you tend to vary the amount of monocarboaluminate and hemicarboaluminate which is formed. So, when you have more calcite, you tend to form directly monocarboaluminate. When you have less calcite, you tend to form hemicarboaluminates which gets converted progressively to monocarboaluminate.

So, when you consider it along with curing conditions, for instance, this is at an early age which is at 3 days. When you look at 28 days, you can see a rise in the hemicarboaluminates peak for some systems, but when you start looking at later ages with higher amount of limestone in it, the phase which is more stable is monocarboaluminate. So, when you have more calcite particles in your system, it tends to progressively convert all the hemicarboaluminate into monocarboaluminate. So, this leads to changes in the phase assemblage with respect to curing.

Also, this can help us analyze what the role of aluminates or silicates is, for instance. The aluminates tend to react and form C-S-H or form hydration products like carboaluminates. So, what I want to bring to your attention is, if you look at the binary binder system which has only calcined clay, you start seeing a peak in this zone at around 7 degrees, which indicates the formation of stratlingite. Stratlingite is C-A-S-H, where Al/Si ratio is 1. So, when you have Al/Si in the ratio of 1 in the C-A-S-H, that phase is called stratlingite. So, when you do not add limestone to your system, there are excess aluminates which are available. So, naturally the aluminates start reacting and start moving into your C-S-H and end up finally forming a stratlingite phase. So, slowly aluminates are moving, for instance, you can see here, when you have higher amount of calcined clay 40%, even at 28 day, you start seeing signs of stratlingite. When you have only 30% calcined clay, strätlingite amount is lesser. When you have 40% calcined clay at 120 days, you can see a very stable strätlingite phase. So when you start adding limestone to it, you do not see any formation of strätlingite, because all the aluminates are consumed in the formation of carboaluminates.

And also what we can observe is the role of pozzolanic reaction which is the reaction of the silicates as well as aluminates. So, what you can see is the dominant consumption of portlandite at different region. So, it can be quantified to explain how much of portlandite is consumed or how much of calcined clay is reacted. So, for instance, when you have only 30% calcined clay, because you have higher amount of clinker in it, you see signs of portlandite present even at 120 days, in the other cases you do not see signs of portlandite. This can also help us understand why strätlingite is forming in some conditions. So thermodynamically, strätlingite is stable only if the system is defective of portlandite, there is no portlandite in the system. So when portlandite is completely consumed, you start forming a higher amount of strätlingite in the system.

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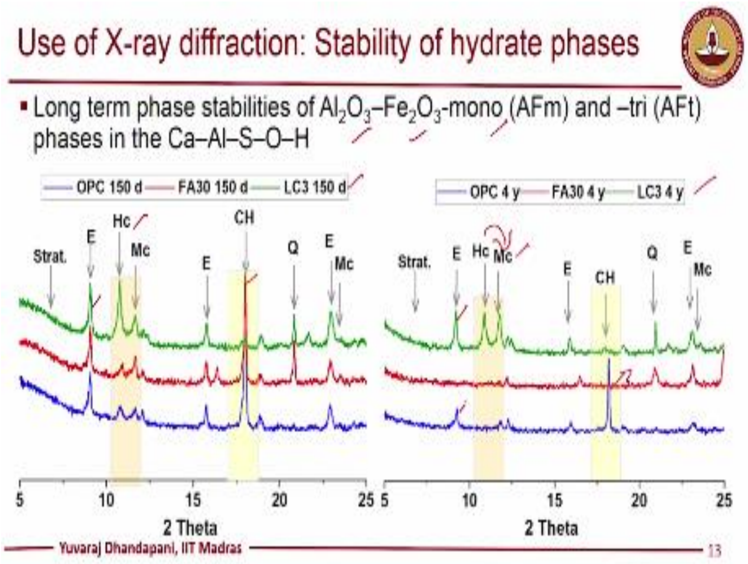

Use of X-ray diffraction: Stability of hydrate phases

- Long term phase stabilities of Al_2O_3–Fe_2O_3-mono (AFm) and –tri (AFt) phases in the Ca–Al–S–O–H

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The next aspect - we can understand how the structure is developing, different phases are forming. The other is to ensure that these phases are stable over the period of time. So, you make concrete, you make critical infrastructure with such new binder formulation and expose it to natural environment for a long period of time. So, the phases which are formed should be stable in those conditions. So, in case of research when you are coming up with new formulation, trying to address it, it is necessary to ensure that the phases remain stable or what is the change in phases, that become an interesting point of contention. So, long term stability of the AFm indicates Al_2O_3-Fe_2O_3-mono phases or tri phases, AFt is ettringite and AFm is monocarbonate, hemicarbonate and monosulfate.

So, here I have presented X-ray diffractograms of plain Portland cement, fly ash cement and LC^3 cement at about 150 days. So, what you can see is higher amount of hemicarboaluminates compared to monocarboaluminate. So, these are X-ray diffractograms at about 4 years when the system was not cured, just sealed, just like your concrete and kept in Chennai conditions. So, at 4 years, when you tend to see, the hemicarboaluminates have progressively converted to monocarboaluminates, but the hydrate phase as such formed in this new binder system tend to be stable. So, this ensures that the hydrate phases tend to have certain level of stability in such conditions. Also, you can observe, this is calcium hydroxide peak in fly ash, but when you start looking at around 4 years, you do not see much calcium hydroxide because fly ash would have reacted by now and consumed most of the portlandite which is available. Also you can see ettringite also, which is nearly at stable and much higher amount in the case of calcined clay system.