Characterization of Construction Materials
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Lecture – 47
Application of Characterization Techniques to Assess Composite Binder with Limestone-Calcined Clay: What, Why and How? Part - 2

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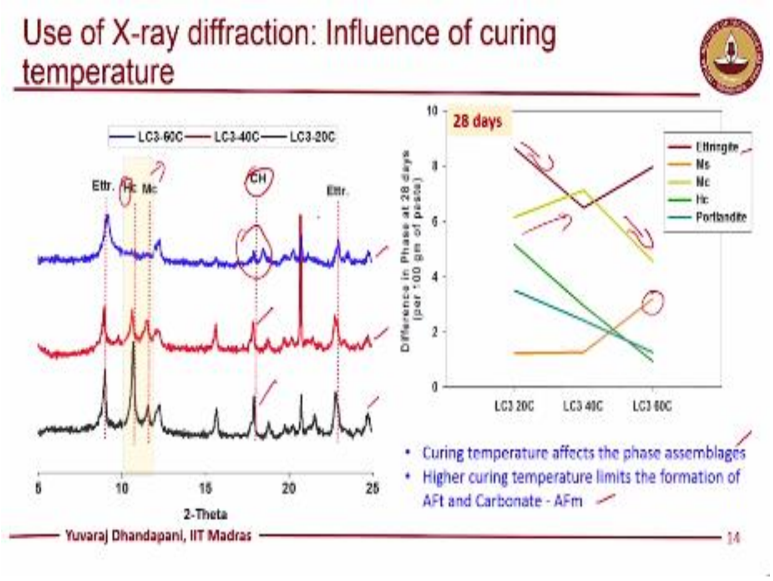

Use of X-ray diffraction: Influence of curing temperature

- Curing temperature affects the phase assemblages
- Higher curing temperature limits the formation of AFt and Carbonate - AFm

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The stability of the phases is important not only with respect to the long term curing condition, but also when you start using these binder formulations or when you want to have a research study where you want to address how the behaviour of the concrete or the new binder which you are investigating tend to vary with respect to curing conditions. For instance, you do concreting on a hot summer in Chennai or a cold winter in Delhi. So, you tend to produce varying levels of these phases.

So, X- ray diffraction can be a very useful tool in understanding the kind of hydrate phases that are formed with respect to curing temperature. So, here I have presented X-ray diffractograms of LC^3 binder systems which are cured at different temperatures at 20 °C, 40 °C, and 60 °C. What you tend to see is, the phases which are formed initially when system is cured at 20 °C, is reduced when you increase the curing temperature to nearly 40 °C, and at 60 °C, the phases are not present.

So, this leads to very interesting research questions to understand what is happening to these phases at high temperatures. And also in the XRD lecture, you would have been taught about quantification of the X-ray diffraction patterns. So, when you start quantifying the X-ray diffraction patterns, what you see is the ettringite amount which is formed initially, tends to reduce with curing temperature. The monocarboaluminate increases from 20 to 40°C, but however decreases at this temperature. So, instead of carboaluminate what you tend to start forming is the monosulphate which is more typical of this system. So, when you start having higher curing temperatures, so sulphoaluminates become more stable than carboaluminates. So in this way, X-ray diffraction will be a very useful tool to understand the effect of curing temperature on the final phase assemblage. The variations in the formation of hydrate phases such as ettringite and carboaluminates.

The influence of pozzolanic reaction can also be assessed. For instance, if you observe the calcium hydroxide peak at 20 °C, you still have a strong peak, at 40 °C, it is removed and at 60 °C, you do not see much of the peak, because when you increase the temperature, you accelerate the pozzolanic reaction. So clay reactivity is increased with temperature, which tends to consume more of the portlandite which is present in the system.

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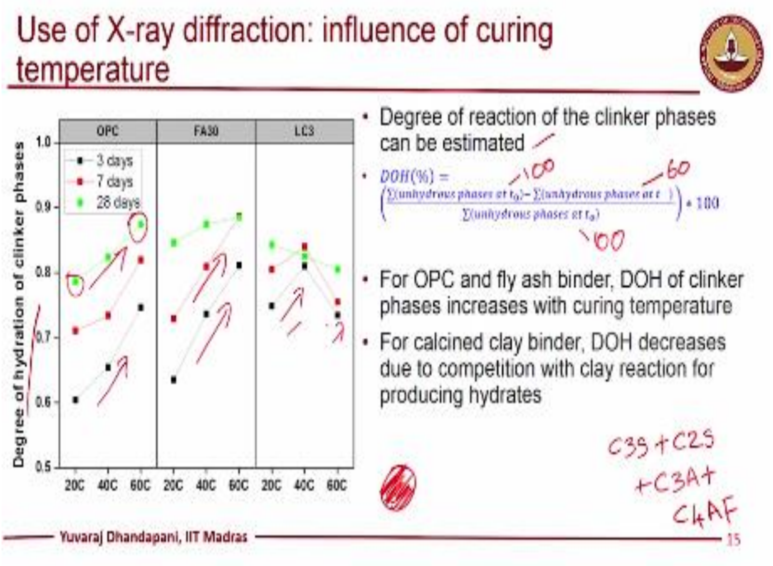

Use of X-ray diffraction: influence of curing temperature

- Degree of reaction of the clinker phases can be estimated
- $DOH(\%) = \left(\frac{\sum(\text{unhydrous phases at } t_0) - \sum(\text{unhydrous phases at } t)}{\sum(\text{unhydrous phases at } t_0)}\right) * 100$

100

60

100

- For OPC and fly ash binder, DOH of clinker phases increases with curing temperature
- For calcined clay binder, DOH decreases due to competition with clay reaction for producing hydrates

C3S + C2S
+ C3A +
C4AF

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So another aspect which we can understand with respect to curing temperature is what is happening in the binder as such? So, can we try to understand some mechanisms of how the different components present in the binder formulations is reacting. So, previously we discussed about the formation of carbonaluminates looking at the clinker itself. So, you have clinker and you have clay, we saw pozzolanic reaction of the clay was accelerated, but when we start observing just the clinker phases, there is some interesting behavior which we can identify.

For instance, here I have presented degree of hydration of the clinker phases. How this can be estimated is you can do an XRD, quantify the amount of clinker phases which is the cumulative of your C_3S + C_2S+ C_3A + C_4AF. So, when you take the summation of these phases at the initial time and at different intervals of time and normalize it with respect to the initial time. For instance, initially you have 100% clinker in your system, so normalized value, and at particular instance of time at 3 days, you have 60% which is remaining. So, your degree of hydration of your system would be at around 40% percent, 40% of your initial clinker phases have reacted.

So, when you start observing with respect to temperature, you can see the reaction of the clinker phases is accelerated. So, this is for the OPC system, where you can see at 3 days, 7 days and 28 days, there is a steady rise in the degree of reaction of the clinker phases. So, when you cure at 60 °C, around 85% of clinker has reacted. When you are curing at 20 °C, about 75 to 80% of your clinker has reacted, right. Again when you start moving towards your blended cements with fly ash, you again see a rise in the degree of reaction of your clinker. But interestingly when you start using highly reactive pozzolans, for instance here, calcined clay, what happens is your degree of reaction of your clinker increases initially from 20 to 40 degrees Celsius, but there onwards it start decreasing. So, this can lead to variation in behavior, for instance stagnation of strength development in your concrete when you start using highly reactive pozzolan. So, when you use silica fume or calcined clay, strength tends to increase much faster at the early age, but you do not see much rise in the strength post some time.

So, you need to understand what is happening when all these phases are present together. So, what happens is because the pozzolanic reaction is accelerated at high temperature, both the reaction of clinker as well as the reaction of pozzolan is competing for the space or formation of hydration products. So once the reaction products have formed and filled up all the pore volumes, you have pore volume, it is all filled up with the hydration products, and you do not necessarily tend to react more of the initial unhydrated phases. So, when system is cured at a higher temperature, the porosity gets filled up much faster, so the clinker does not necessarily react when it is cured at very high temperature. So, interesting analysis like this on the different phases can be done to understand the use of the technique or the driving factor between the reaction happening in a composite binder system.

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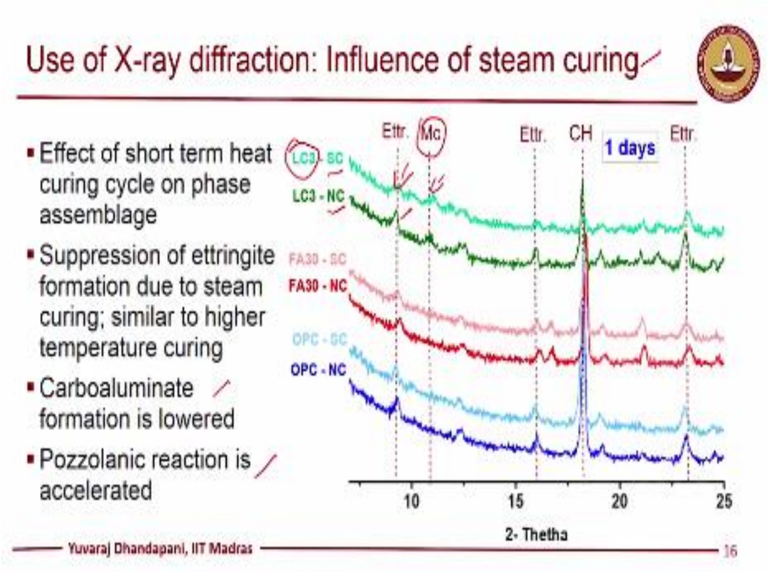

Use of X-ray diffraction: Influence of steam curing

- Effect of short term heat curing cycle on phase assemblage
- Suppression of ettringite formation due to steam curing; similar to higher temperature curing
- Carboaluminate formation is lowered
- Pozzolanic reaction is accelerated

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16

Another interesting point of application is when you consider practical scenarios where different curing conditions are applied, for instance, steam curing condition in a precast yard. So, when you try to formulate concretes or binders which can be used in such conditions and you want to use a new binder formulation such as LC^3 formulation in such conditions. So, we already discussed it is having varying levels of chemical phases. So, how these phases can react.

So, the SC are the steam cured concrete at 1 day and the NC of the normal cured. So, when you accelerate and cure it, what you can see is the ettringite phases which is present in the normal curing tend to get suppressed. So, the ettringite phases are suppressed and the carboaluminate phases are not seen very prominently in such conditions. So, this has to be dealt with and we can formulate our research studies based on the fundamental characteristics of the changes rather than direct application oriented scenario. So, for instance, why the carboaluminate phases are lowered? What is the role of pozzolanic reaction in such conditions?

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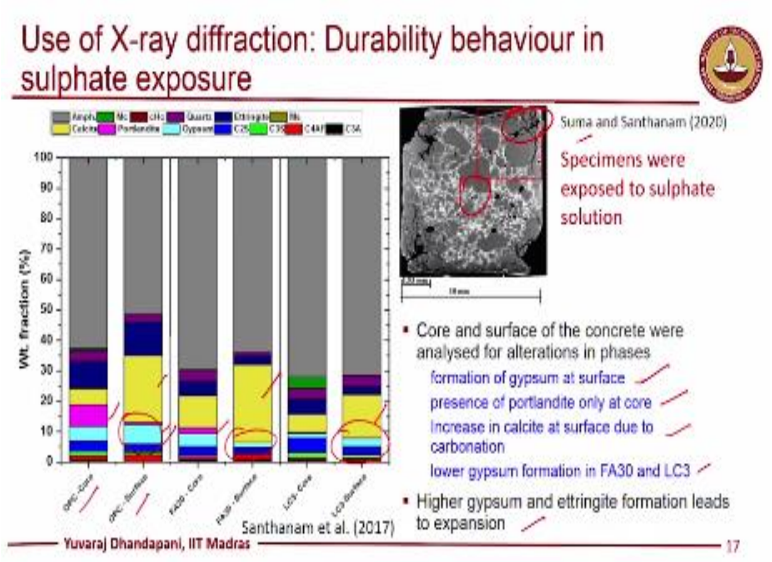

Use of X-ray diffraction: Durability behaviour in sulphate exposure

Suma and Santhanam (2020)

Specimens were exposed to sulphate solution

- Core and surface of the concrete were analysed for alterations in phases
  - formation of gypsum at surface
  - presence of portlandite only at core
  - Increase in calcite at surface due to carbonation
  - lower gypsum formation in FA30 and LC3
- Higher gypsum and ettringite formation leads to expansion

Santhanam et al. (2017)

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So, coming into durability, here I have presented some quantitative X-ray diffraction results on samples which are exposed to sulphate conditions from one of my colleagues - Fathima Suma. So, this is a microscopic image of the sample which is exposed to sulphate. So, you tend to see a lot of damages at the surface and the core is intact. So, when you try to understand why the damage happens at the surface, so for instance, if you look at the quantitative measurement at the core and surface, you can observe that there is formation of gypsum at the surface. So, gypsum for instance, the blue here (in graph), you can see higher amount of gypsum which is formed in the surface. Presence of portlandite can be seen only at the core. So, portlandite which is here, it is present at the core, it is present at the core in this system as well (OPC). Increase in calcite amount at the surface because it tends to get carbonated. So, the calcite amount are higher at the surface, and what you can also observe is in the case of fly ash and calcined clay binder, you do not have higher amount of this gypsum which is formed in the plain Portland cement. So, in plain Portland cement, you have higher amount of gypsum, in these systems you have lower amount of gypsum. So, this can be a very ideal way to explain the difference in the behavior of these binders when you expose to sulphate conditions. So, initially gypsum gets formed and then lead to formation of ettringite, and when you have lower amount of sulphate moving in, you do not produce gypsum and ettringite. So, that can explain the expansion, which is caused due to gypsum and ettringite formation in these binder systems.

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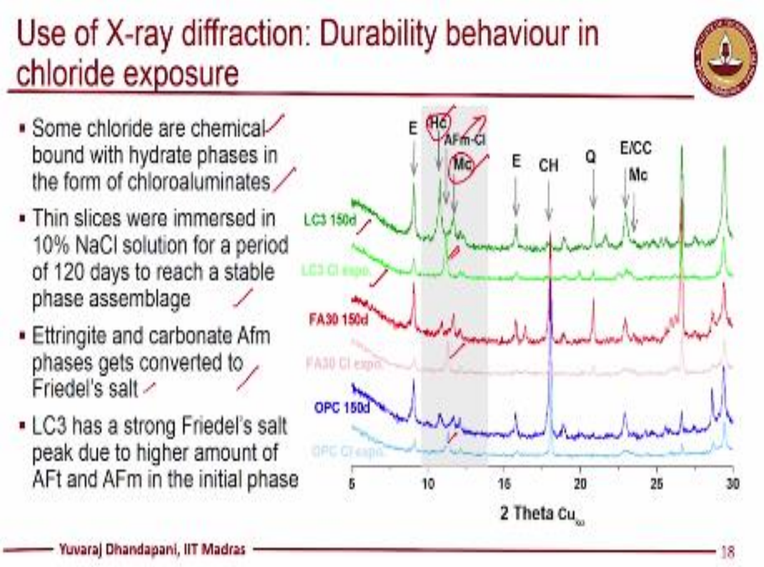

Use of X-ray diffraction: Durability behaviour in chloride exposure

- Some chloride are chemical bound with hydrate phases in the form of chloroaluminates
- Thin slices were immersed in 10% NaCl solution for a period of 120 days to reach a stable phase assemblage
- Ettringite and carbonate Afm phases gets converted to Friedel's salt
- LC3 has a strong Friedel's salt peak due to higher amount of AFt and AFm in the initial phase

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Similarly, when you start looking at the other problems, such as chloride for instance, so, these are X-ray diffractograms of different systems exposed to chloride conditions. So, what happens is some chlorides are chemically bound within the hydrates. So, to assess the potential stability of these hydrate phases on exposure to chloride, we just immersed a thin section of sample in chloride condition, about 10% NaCl for 120 days, and assess what is the progressive conversion of this phase, for instance, something called as Friedel's salt gets formed in this phase.

So, when you start observing the X-ray diffraction pattern, you can see the one which is just cured and after exposure to chloride conditions. You can see the peak which is present for hemicarbo- and monocarbo-aluminate disappears and tend to produce a peak which is characteristic of AFm phase which has chloride, which is called calcium chloroaluminate or Friedel's salt. So, such phase transformation happens and you can see a stronger peak in the case of calcined clay binder because you have higher amount of the hemicarboaluminate phases. So, you form Friedel's salt in fly ash concrete as well as in OPC concrete, but the amount of Friedel's salt formed in the composite binder with calcined clay and limestone is much higher because the initial phase composition with the hemicarboaluminate and monocarboaluminate is also higher in the system. So, it helps conversion of these phases to Friedel's salt, which implies that there is higher amount of chemical binding of your chlorides on exposure to chloride environment in such systems. So, durability behavior in different exposure conditions can also be assessed by use of these techniques.

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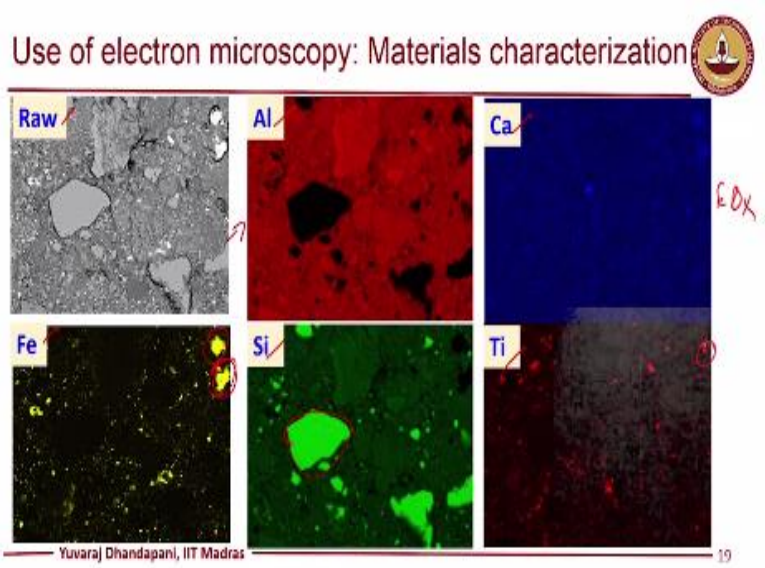
Use of electron microscopy: Materials characterization

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Next, we will move into microscopy, where microscopy can be used to understand the material characteristics, for instance, here I have presented micrographs of clay. So, when you have micrographs, these are something called as EDX images, mapping images you tend to map for different elements. You want to understand what is present in this raw clay. So, whether the clay is pure or there is some impurity.

So, when you start looking at the ionic or elemental map of all these phases, you can observe the alumina and silica which are more generally seen or expected to be present in clay. For instance, this large particle which is present here is purely silica, which implies it is a quartz particle. Also what you can see is large amount of these bright phases in iron indicates that there is higher amount of iron in the clay. So, in this condition the clay which was used here have a color of reddish tint in it. So, pure metakaolin will be whitish in color. The clay which was studied here had a red color. So when you want to understand why the changes occur in the color of the clay, it is because of the presence of iron in the clay as impurities. So, if you want to understand different materials which are used and look at maybe impurities such as titanium and other materials present in it, microscopy can be a very useful technique to identify local distributions of these phases.

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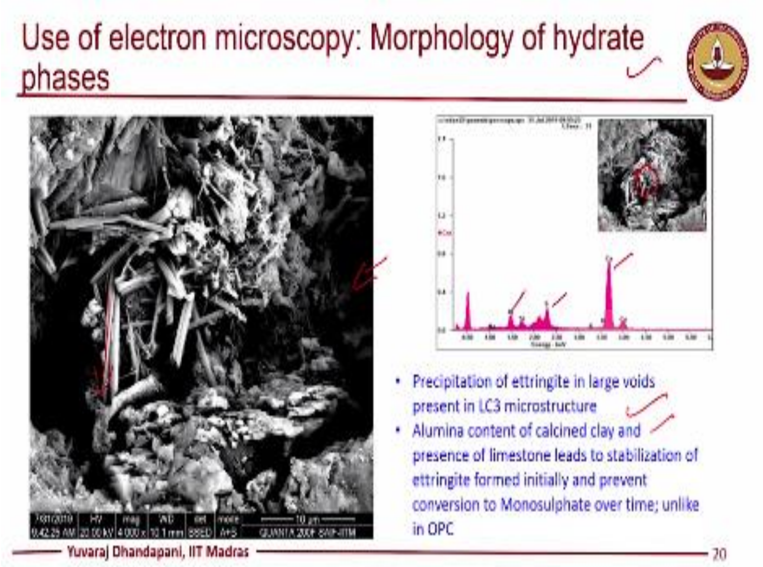

Use of electron microscopy: Morphology of hydrate phases

- Precipitation of ettringite in large voids present in LC3 microstructure
- Alumina content of calcined clay and presence of limestone leads to stabilization of ettringite formed initially and prevent conversion to Monosulphate over time; unlike in OPC

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The next important characteristic where the SEM is often used is to understand the morphology of the hydrates. We tend to see higher amount of ettringite formed, but where is the ettringite formed? So, here I have presented a micrograph of an ettringite precipitated in large voids of an LC^3 system. So, naturally we tend to believe that ettringites are long needle-like structure and because when you have a higher amount of alumina and limestone, you tend to have large amount of ettringite which is formed. Interestingly, you can also tend to look at the changes between all these binders and try to come up with the understanding why a large chunk of these ettringite is formed in the large voids. So, when ettringite is formed at later ages, it tends to precipitate where there is free space. So, because you have a large void in these conditions, you tend to form a chunk of ettringite. Similarly, there are also theories which suggest that there will be deposits of portlandite just along the interfacial transition zone of your aggregate and cement. So, to confirm ettringite, you can simply do an EDX at one of these needles and it tends to confirm calcium, sulphur and alumina, which confirms that it is the ettringite phase which is present.

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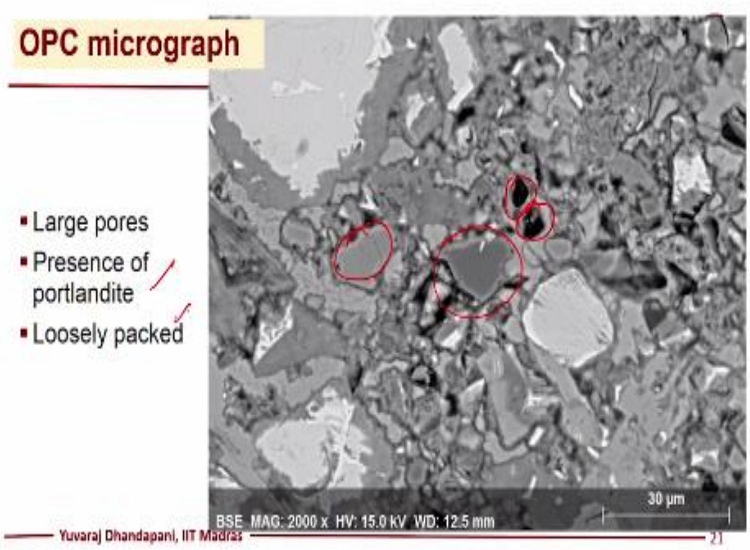
OPC micrograph

- Large pores
- Presence of portlandite
- Loosely packed

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21

The other feature apart from morphology is the micrograph itself. So, what all characteristics we can observe from micrographs. So, for instance, this is a micrograph of an OPC binder, plain Portland cement. So, you can see these large crystals here and also large voids which are present, because you have these large crystals of hydrate phases which are formed and presence of portlandite, you tend to see the structure is kind of loosely packed, and you can assess it to come up with the estimates of porosity, which I will discuss in a short time.

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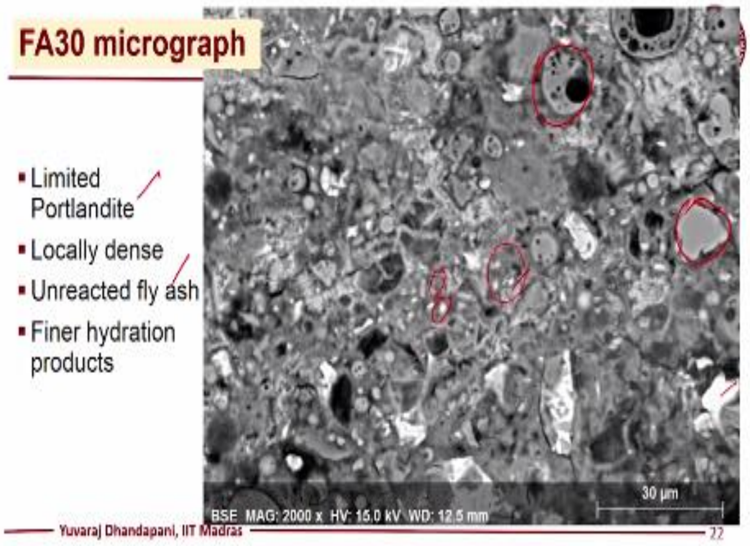
FA30 micrograph

- Limited Portlandite
- Locally dense
- Unreacted fly ash
- Finer hydration products

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22

So, when you start moving towards blended binders, for instance with fly ash, you do not tend to see a greater amount of these large crystals which are portlandite and also we can observe lot of these circular phases which are very typical of fly ashes. Interestingly, what you should also look at is the local densification which is there, for instance, a lot of finer amount of these hydration products which are formed, which are typical of the pozzolanic C-S-H, which is formed in the system. The bright phases are the unreacted phases and the hydrate phases are the ones which are present in this zone with gray scales.

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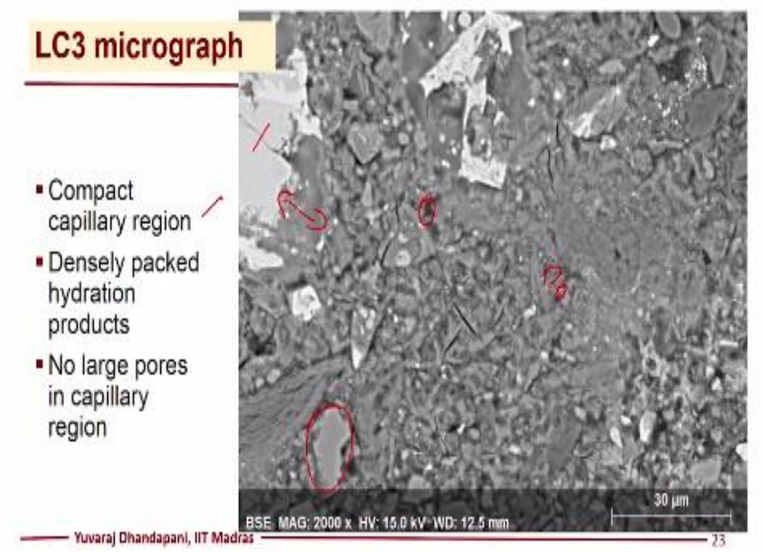

LC3 micrograph

- Compact capillary region
- Densely packed hydration products
- No large pores in capillary region

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When we start looking at micrographs with calcined clay binders, for instance, this is an unreacted clinker. You have the zone around the clinker which is your inner C-S-H and you can look at the capillary region, which is the inter-particle region and the amount of hydrates which is formed and the packing of hydrates. So, compared to the plain Portland cement system, where you tend to have lot of these large crystals, you find much of the fine-grained species or hydrates in the case of calcined clay binder, which tend to produce a very dense structure. So, physical comments like such, about the packing of the structure, the amount of voids which is present can be made by using micrographs extracted from SEMs.

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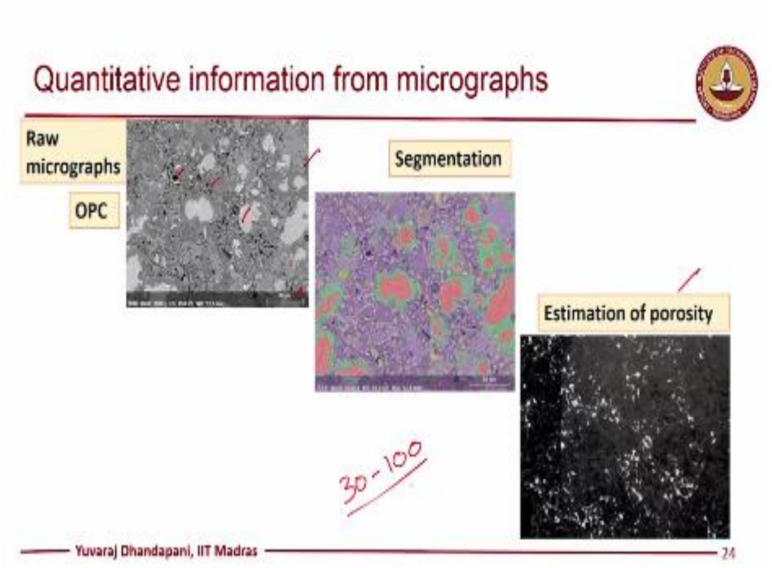

Quantitative information from micrographs

Raw micrographs

OPC

Segmentation

Estimation of porosity

30-100

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But can we extract quantitative information? For instance, this is a raw micrograph of an OPC binder. There is a process called segmentation, which will be covered in the image analysis lecture. So, when you do segmentation, you can split out phases which correspond to different grayscale. So, you have a brighter scale and a darker scale and a black spot which is porosity, you can segment all these phases. Once you segment it, you can separate out and extract only the porosities alone. So, you can get estimates of porosity by doing processing of these images.

Naturally, in such condition, you are looking at very minor scales; the scale is about 50 µm. So, in order to get a representative analysis, it is necessary to do at least 30-100 images and then take the overall assessment of porosity in such cases. So, it is basically when you want to come up with porosity assessment with micrograph, making sure it is representative of the system is very critical. So, you need a sufficiently large number of images to process.

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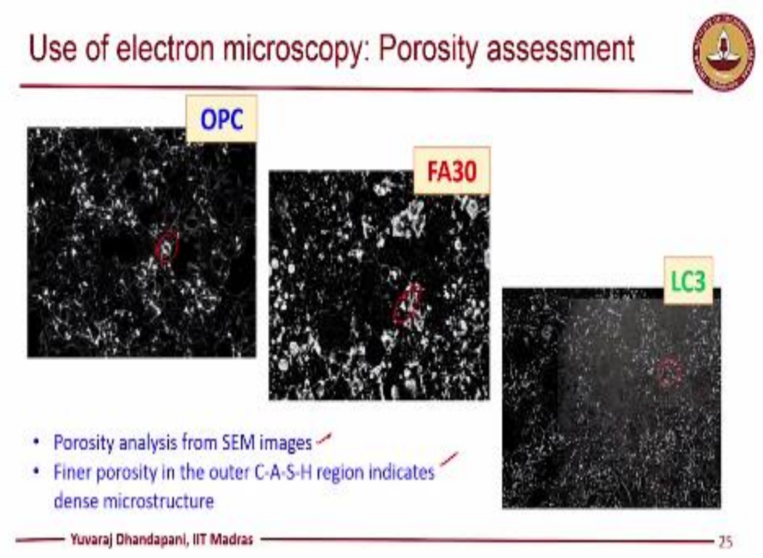

Use of electron microscopy: Porosity assessment

- Porosity analysis from SEM images
- Finer porosity in the outer C-A-S-H region indicates dense microstructure

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So here I am just giving a typical presentation of the kind of porosity which is present in different binders. So, you can see large amount of this white spaces and here a lot of fine grain porosity because of the packing.

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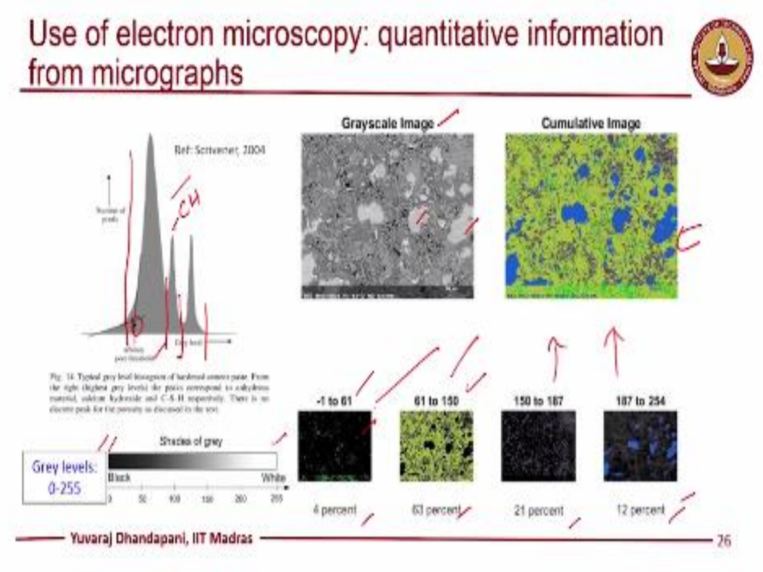

Use of electron microscopy: quantitative information from micrographs

Grey levels: 0-255

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So how is this processing done? Though this will be dealt separately, because I have introduced it, I will just cover it up a bit quickly. So, you tend to produce a grayscale image from the microstructure, which is having varying levels of greyscale. So, greyscale for an 8-bit image will vary from 0 to 255; 255 is bright white and 0 is black. So, you tend to get an image like that and then you can fit an arbitrary threshold for your porosity. So, in this case, it is fixed at 0 to 61 and segregate all the phases corresponding to that region and the remaining phases, for instance, you can separate your phase from here to here, which corresponds to your major dominant C-S-H, and then the second peak which is here which corresponds to your calcium hydroxide, and the last region which corresponds to your unreacted clinker phases. The brightest phases which are present in your micrographs are unreacted phases.

So, in that case, we can get estimates of your different volume fractions of the phases, 4% of porosity, C-S-H about 60% coverage, calcium hydroxide about 20% and 12% of unreacted clinker which is present. So, assessment like that can be made with the help of micrograph and understood the local distribution of hydrate phases. So, for instance, you can make a cumulative image of all those 4 phases together and produce a cumulative image which can be representative of the spatial distribution of different hydrates in your microstructure.

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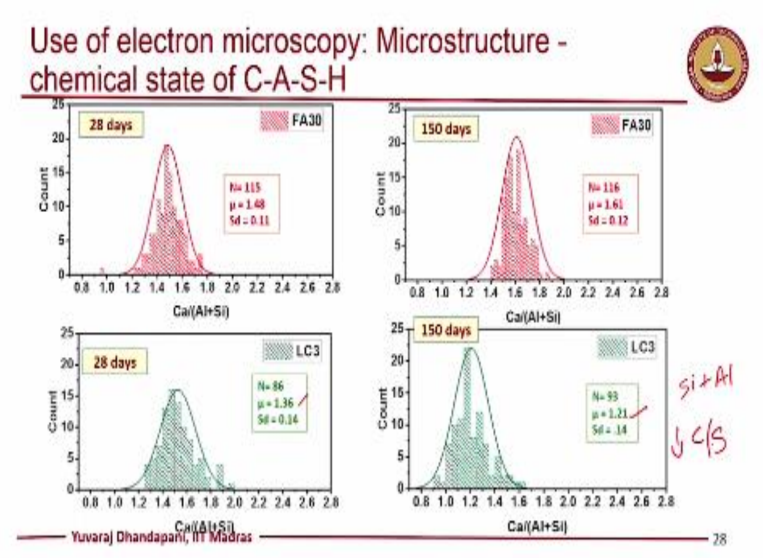

Use of electron microscopy: Microstructure - chemical state of C-A-S-H

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28

So, microscopy is to do the imaging and understand the characteristics of the physical structure and also there is a mode of operation in SEM called EDX, so which was covered during the theory part of the lecture. EDAX (EDX) will give you local chemical composition of your hydrates. For instance, if you go back to your micrograph, you pick a point here and do an EDX assessment; you will get an EDX assessment of the C_3S clinker. Here you will get the chemical composition of your C-S-H. So, when you want to understand if there is any variation in the C-S-H formed in the plain Portland clinker reaction and pozzolanic reaction. So, what I have done is I presented, here the C-S-H composition in terms of Ca/Si ratio. So, when you look at only plain Portland cement, the mean value, so this was done over about 100 points nearly, you can see the number of samples to be representative, the value is about 1.8. When you start using fly ashes, the value comes down. So with respect to curing ages, you do not see much difference with respect to standard deviation. The value comes down from nearly 1.8 to 1.4, which indicates that you have less calcium in your C-S-H or more silica from fly ash has gone into your C-S-H.

When you start comparing your fly ash system with your calcined clay system, you can see that the value has come down even further to nearly 1.3, which indicates that your C-S-H has even lesser calcium in it. Because of the reactivity of the clay, higher amount of your silica and alumina species have gone into your C-S-H. This can hold importance in explaining behavior in different exposure. For instance, when you have decalcification kind of mechanism, for instance removal of calcium on exposure to sulphates or on exposure to carbonates. In those conditions, you tend to have the systems with lower calcium to silica ratio, losing calcium much faster, because it has lesser amount of calcium buffering in the C-S-H itself. Such fundamental information can be understood by doing the chemical composition analysis.

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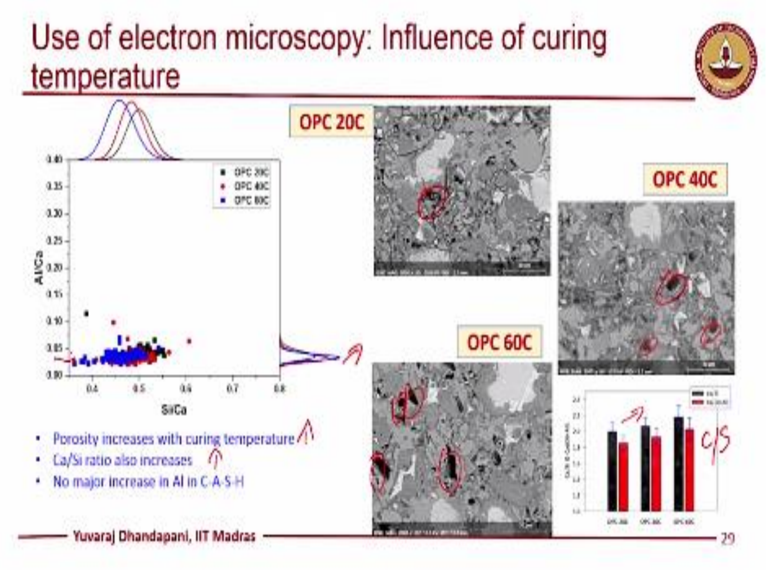

Use of electron microscopy: Influence of curing temperature

- Porosity increases with curing temperature
- Ca/Si ratio also increases
- No major increase in Al in C-A-S-H

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29

Again, going back to the curing, we discussed that there is difference in the phases, but there is also a difference in the microstructure which is formed. So, we saw previously by using XRD you can quantify the degree of reaction of your phases. So, when you look at the hydrate phases, this is OPC cured at 20 °C, you see less amount of these voids. At 40 °C, there are more of these voids. When you start curing at even higher temperature, you start forming large number of these voids, because the C-S-H is forming at a faster rate, the C-S-H composition tends to vary. It becomes more crystalline or it tends to have higher amount of calcium in the C-S-H, because of which you lose the dispersion of your C-S-H in your system, which increases the overall porosity.

So, when curing temperature is higher, the overall porosity of the system can be higher despite the increase in the degree of hydration. So, Ca/Si ratio tends to increase. But if you look in the OPC system, you tend to see in the Al/Ca ratio, that the distribution is almost concentrated in this zone itself. There is no change in the C-S-H composition, especially with respect to alumina in it.

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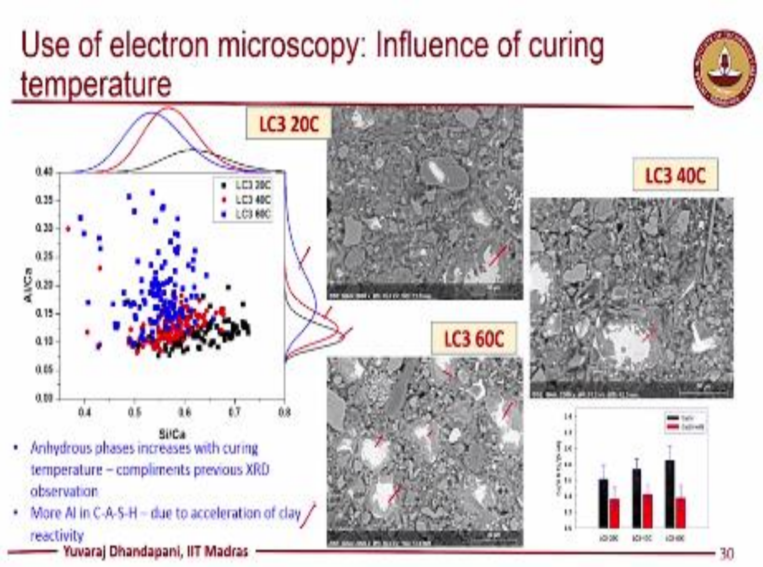

Use of electron microscopy: Influence of curing temperature

- Anhydrous phases increases with curing temperature – compliments previous XRD observation
- More Al in C-A-S-H – due to acceleration of clay reactivity

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When you start looking at calcined clay binders, because you have alumina, the clinker reaction is accelerated and clay reaction is also accelerated. When both are accelerated, what happens is because of the clay reactions, you tend to increase the alumina content in your C-S-H, and I was also talking about reduced degree of hydration of your clinker phases in calcined clay system. So, if you look at the micrographs, this is at 20 °C, at 40 °C, when you start looking at 60 °C at the same scale, you tend to see large amount of this unreacted clinker grains which are present in your system. So, more alumina goes into C-S-H because of the higher reactivity with respect to temperature.

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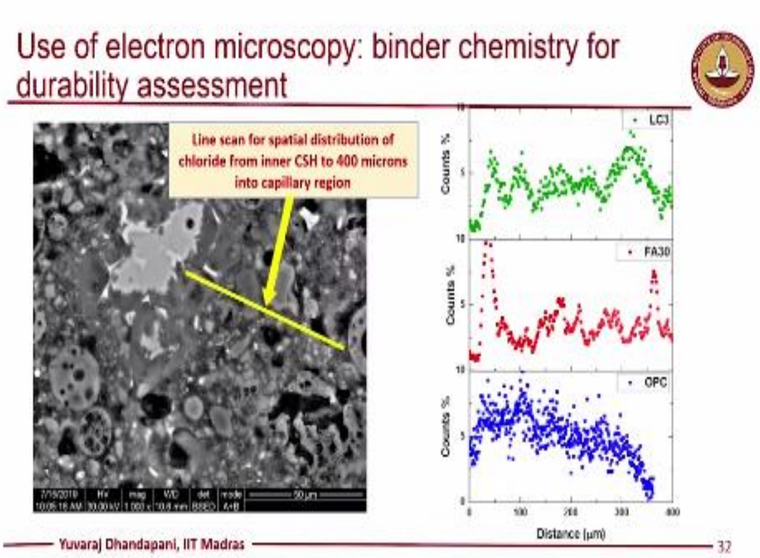
Use of electron microscopy: binder chemistry for durability assessment

Line scan for spatial distribution of chloride from inner CSH to 400 microns into capillary region

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32

Another case, the point of contention to explain is how is the C-S-H composition relevant? So, for instance, if you look at the ternary chart, you can make charts like this, which can explain the variation in microstructure. For instance, it is related to your pure phase diagrams of different hydrated phases that can be present when you have calcium, silica and alumina. So, you have Portland cement, which is present in this region. When you start forming C-S-H, typically in a Portland cement, the C-S-H will be in this region (Refer the ternary chart).

When you start adding pozzolans, which are rich with silica and alumina, the C-S-H phase tends to get shifted towards this region and in the case of LC^3, we saw you can start forming phases which are almost at the mid of this region which is strätlingite phase. So, one variation which this can cause is because you are producing different characteristics of C-S-H, you tend to control the property development unanimously on all the concrete which are made with such system. For instance here, I have presented one of the performance parameters called resistivity, which is a bulk response. So, the band indicates the response from 5 different sets of concrete. So, because the clay is reacting much faster, you can see the value has risen between 3 to 7 days itself and it is much higher across the age. When you start using fly ash binders or slag binders, the value tends to rise much lower.

These are varying levels of concrete produced with the binder which indicates the role of the material which is used to make concrete. So, when you understand what is leading to this major rise unanimously on all the concretes which are made, it is related to basically your microstructure which is formed because of the ingredients in the binder.

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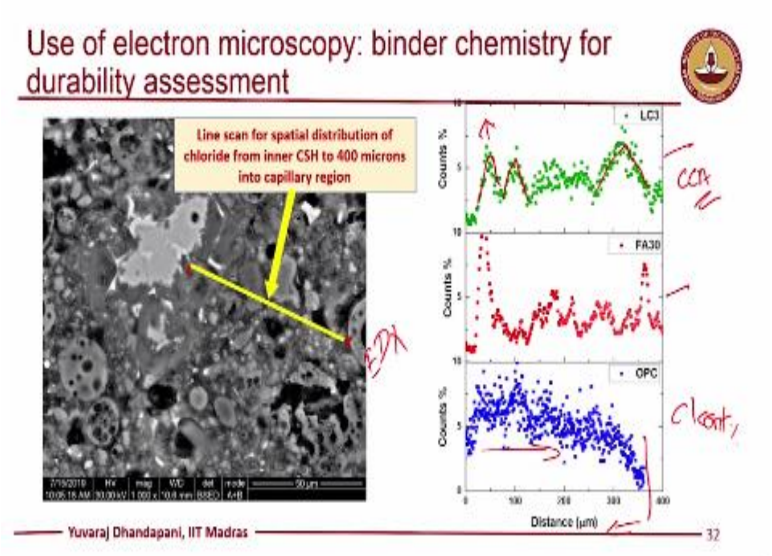

Use of electron microscopy: binder chemistry for durability assessment

Line scan for spatial distribution of chloride from inner CSH to 400 microns into capillary region

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The last point of discussion is to understand durability behavior. So, we saw XRD for chloride analysis, and this is SEM for chloride analysis. So what we have done is an EDX scan from your cement grain till your outer C-S-H point. So, this indicates the distance from your cement grain to your outer C-S-H point. You can see near the cement grain, there is not much chloride. The count indicates the chloride content percentage. You can see near the cement grain, there is not much chloride bound, but when you start coming far, into the outer C-S-H region, you have high amount of chloride which is bound.

In the case of calcined clay binder or fly ash binder, you can see local peaks like this in different zones. These indicate the reaction of chloride in the outer C-S-H region to form calcium chloroaluminate phases. So, when you have certain phases with chloride which is formed, you can have local increase in the chloride content which can be traced by using an EDX technique.

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Closure comments

- The use of what, why and how...
- Importance of rigorous analysis

Characterization techniques as a tool contains answers to critical knowledge gaps in research; It is not a answer by itself

"If I had an hour to solve a problem and my life depended on the solution, I would spend 55 minutes to determine the proper question."
- Albert Einstein

So, we have discussed about application of the characterization technique dealing with range of different problems with respect to one binder. What I have tried to do is explain to you the use of what, why and how. So, we have dealt in each slide a different practical problem, which is brought down in terms of scientific questions and explained by means of characterization tool by doing a proper analysis. So, when you are dealing with characterization, the major point is coming up with the right question. So, what is the change in the behavior which you want to explain by using the characterization tool? So, that will lead you to choice of proper characterization tool and use the characterization tool to bridge the critical knowledge gap in research. Merely a run of experiments alone cannot answer all the questions. Your questions should lead to your experiments which can answer the behaviors in some content.