Characterization of Construction Materials
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Lecture - 44
Analysis of Cementitious system 2 - Part 1

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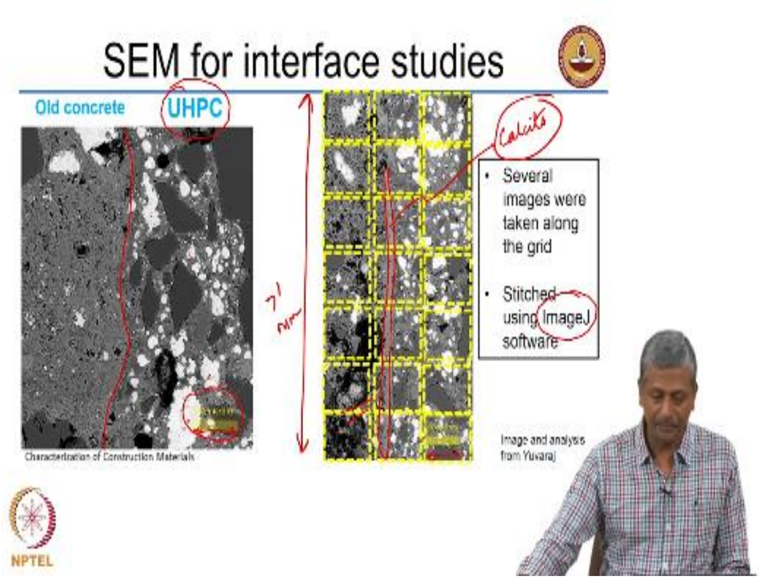

SEM for interface studies

- Several images were taken along the grid
- Stitched using ImageJ software

Image and analysis from Yuvaraj

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So we were looking at different types of examples of the application of scanning electron microscopy, and we saw how usefully it could be utilized to detect differences between different types of phases. So we were also talking about the fact that when you coat a substrate concrete with an ultra-high-performance overlay you can actually make out the distinction between these two types of concrete clearly an SEM micrograph. In some cases, the substrate concrete may have carbonated which leads to a surface layer of calcite forming and then you can clearly see this layer separating the overlay concrete and the substrate.

Now what will happen is as a result of this calcite layer formation, you may actually have a difference in the bond characteristics when you test the bonding strength of the overlay on top of the substrate. So we need to be aware of that, that one of the aspects that can actually affect the bond strength could be this layer of carbonated calcite that is forming on the surface. I also would like to mention that the image on the right is actually a complex collection of several images which were later stitched together using an image analysis software. So image analysis will be the focus of our next chapter. But for now I just want to tell you that these individual boxes represent individual images. So these are individual images which were then stitched together to get this composite image across a long dimension. So you see here that this field of width is 150 µm, so high magnification images were taken and stitched together. So, approximately we are talking about looking at an entire field of width of just over about 1 mm. This entire field of width is about 7 times 150 µm. So it is about 1.05 mm. So that gives you a methodology to actually put together a larger composite picture from very small high magnification images, and that is where the benefits of image analysis start coming in when used in conjunction with scanning electron microscopy, but we will get to that in the next lecture.

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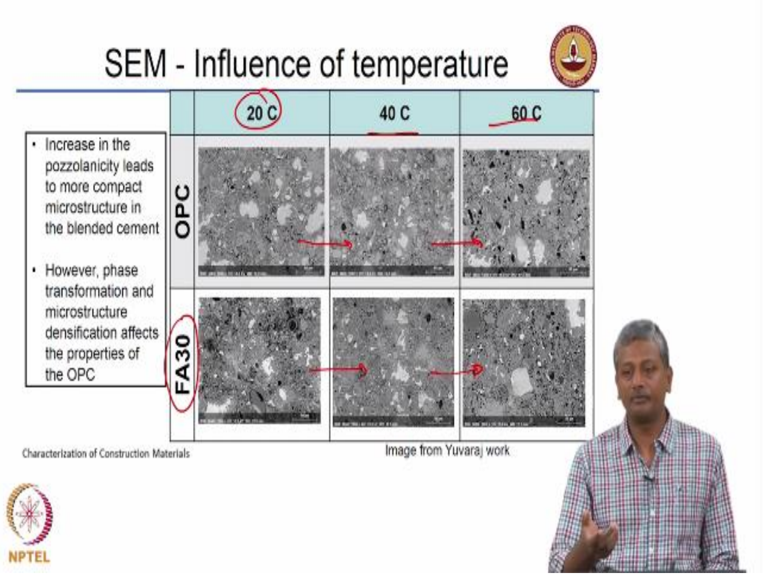

SEM - Influence of temperature

- Increase in the pozzolanicity leads to more compact microstructure in the blended cement
- However, phase transformation and microstructure densification affects the properties of the OPC

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Image from Yuvaraj work

Another example here - the influence of temperature on hydration of cement was studied in this scanning electron microscopy study. So what happens is to accelerate the strength gain of concrete we sometimes enhance the curing temperature and this curing temperature enhancement is typically done with the help of steam. Now the issue that researchers have found with enhanced curing temperatures is that while it accelerates the early age strength development, there is often a decline in the later age properties - primarily strength and durability, with respect the normally cured concrete. Steam cured concrete can still have sufficient strength and durability in the long term, but in comparison with normally cured concrete it generally has lower strength and durability.

So, here you can clearly see from the SEM images at 20 °C, 40 °C and 60 °C, as to what happens in the microstructure to the porosity. So you can see here that the porosity is gradually increasing as temperature is increased from 20 °C to 40 °C to 60 °C. However, when I use fly ash as a 30% replacement for the OPC, I will find that my porosity actually seems to reduce or nearly stay the same as compared to 20 °C. So what is being shown in this SCM study is that, the use of blending materials like fly ash is able to overcome some of the ill effects of heat curing that is typically felt by ordinary Portland cement based systems.

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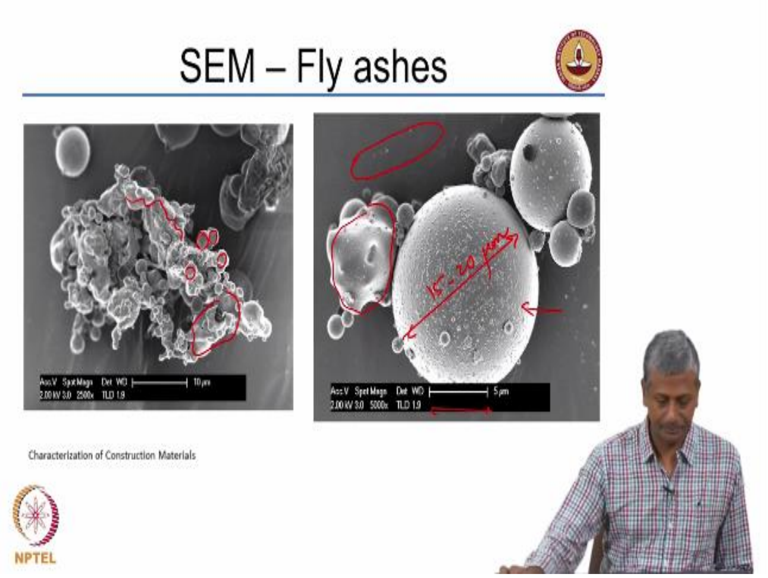

SEM – Fly ashes

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SEM has also been employed significantly to study the structure of different supplementary cementitious materials because you can get very clear cut understanding of the phases that are present in the system and also the morphological assessment of the particles that are present in the fly ashes. For example, here (image on left) you see that these are small spherical solid particles of fly ash which are connected somehow by this loosely held medium.

This on the other hand is a higher magnification image of a single solid particle - this entire width of the field is only 5 µm. So we are talking about something of the order of 15 to 20 µm in diameter. So 15 to 20 µm in diameter is the typical size of a fly ash particle. So that is a typical fly ash particle, which is spherical in nature.

Now this is a secondary electron image because we could clearly see the spherical particles and you can see the depth of field that is shown by the secondary electron image. This is also fly ash (image on the left); it is just that the condensation of the gas along with the fly ash can sometimes create irregular shape particles also. Sometimes you can also get obloid particles. So, some of these spherical particles of silica in fly ash may get trapped between larger agglomerates, which may have gas inside also. So it is just the way that the condensation of the gas happens along with the fly ash that leads to the formation of different types of phases. So the other irregular shapes which are seen around this spherical particle may also be attributed to the impurities that you have in fly ash. If you look at Class F or siliceous fly ash, it is generally composed of 50 to 60% silica. So you still have remaining 30 to 40% of mostly impure phases.

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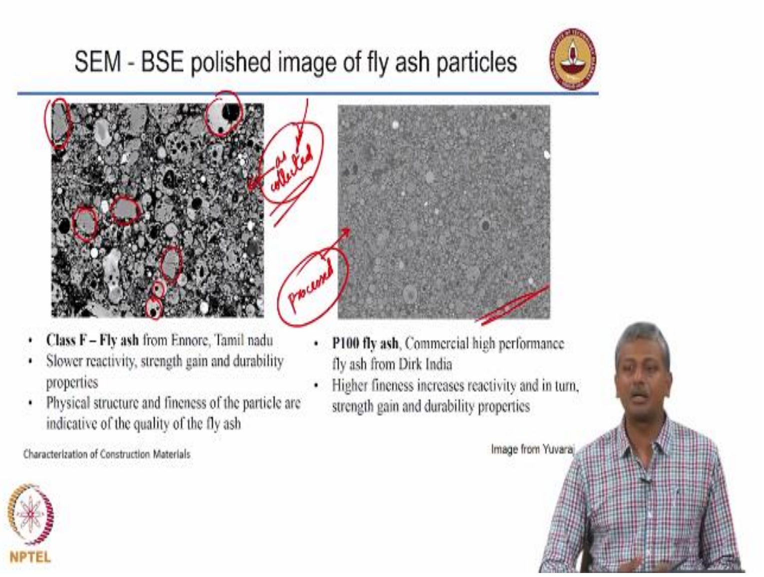

SEM - BSE polished image of fly ash particles

- **Class F – Fly ash** from Ennore, Tamil nadu
- Slower reactivity, strength gain and durability properties
- Physical structure and fineness of the particle are indicative of the quality of the fly ash

- **P100 fly ash**, Commercial high performance fly ash from Dirk India
- Higher fineness increases reactivity and in turn, strength gain and durability properties

Image from Yuvaraj

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This is a polished sample of a fly ash. So when you take fly ash, embed it in an epoxy and then polish it, you get a slightly different sort of an image. You obviously would not be able to make out the full sphere. What you will be getting are the projections of the spheres on a horizontal plane, which is nothing but a circle. So you see these circular features here (image on left). That is basically resulting from the polishing of the spherical particles of fly ash. So these are all fly ash samples, and you can see that fly ash also has these irregular features here. And those could be mostly the impurities like quartz. If you take an X-ray diffraction of fly ash, you will find that there are some crystalline phases like quartz and mullite, which may be present in the system. So those irregular particles could be well made of quartz or other crystalline siliceous components.

Now what you are seeing here are two different fly ashes. One is an as-collected fly ash from a thermal power plant. The other is a processed fly ash, which means the ash is collected from the power plant and brought to a factory and processed to control its chemical composition and physical properties. What you see here is that the size distribution - the particle size of the fly ashes on the left are varied between a very large range. On the other hand, on the right, the image shows that the particles of fly ash are more controlled to the smaller ranges. So if you buy the processed fly ash, typically you see that the performance in concrete is much more well-defined. Whereas when you get the as-collected fly ash, which is practically free of cost, you only have to arrange for the transportation to collect this material, it gives you highly variable properties in the cementitious matrix.

So most ready-mix concrete suppliers would collect fly ash directly or get it through suppliers who are collecting fly ash and distributing to the RMC manufacturers. The problem there is you get high variability. When you actually get fly ash like that, you get very high variability. On the other hand, when you use processed fly ash you can control to a very significant level the quality and performance of the concrete. In textbooks we often read that the use of fly ash as a cement replacement increases workability of concrete, but when you work with some as-collected fly ashes, you will find that the workability is actually not increasing, sometimes it is even reduced, because the as-collected material may also have a high degree of unburnt carbon present in it which you do not have a control of. Whereas in a processed fly ash, all that is very well controlled. That is why the cost increases, but at the same time you get a much better performance.

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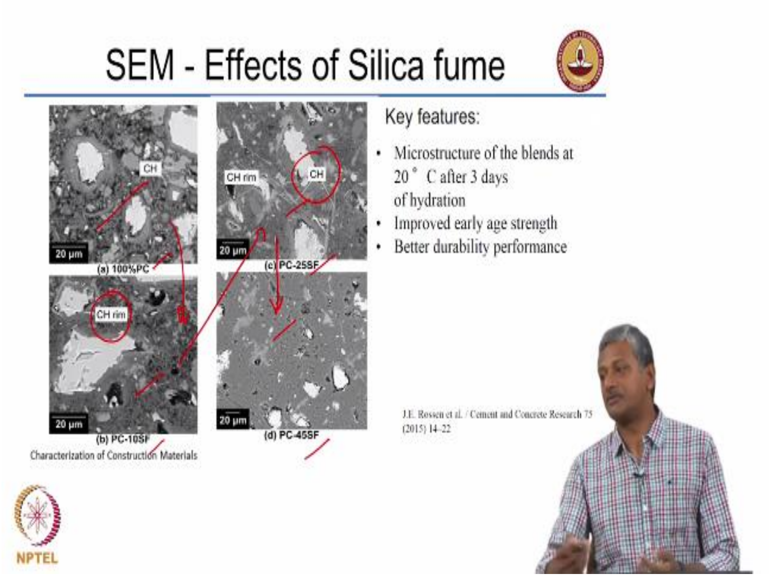

SEM - Effects of Silica fume

Key features:

- Microstructure of the blends at 20 ° C after 3 days of hydration
- Improved early age strength
- Better durability performance

J.E. Rossen et al. / Cement and Concrete Research 75 (2015) 14–22

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Now silica fume is another mineral admixture, which is known to densify the cementitious matrix and increase the strength and durability in the long run. So these are some examples of silica fume at varying levels of replacement. So this is 100% PC - that means no silica fume, this is 10%, this is 25%, and that is 45% silica fume. Of course nobody would be using silica fume at 25% and 45% unless it is for something like an ultra-high-performance composite or a reactive powder concrete. Only in those cases will we use such high levels of silica fume - 25% is what we use. 45% - probably never, because dispersion of silica fume into a cementitious matrix will be a challenge, since silica fume's particle size is of the order of tenths of microns. Cement is 15μm and silica fume is of the order of 0.1 to 0.5 μm, so at that particle size trying to disperse this uniformly in a cementitious medium is a big problem.

So nevertheless in this study, since they were doing this study on paste they could very well formulate the right mechanisms for dispersion and they found very clearly that, the porosity keeps decreasing as I go from 100% PC to increasing levels of silica fume. The paste is becoming more and more dense, and basically decreasing porosity. And the amount of calcium hydroxide that you see is going on reducing. So, as I put more reactive silica in it, it will start consuming more and more calcium hydroxide.

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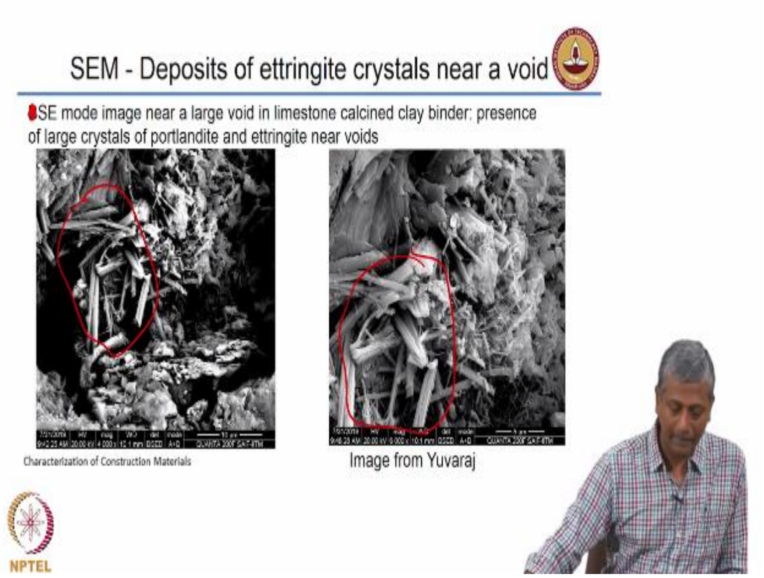

SEM - Deposits of ettringite crystals near a void

- SE mode image near a large void in limestone calcined clay binder: presence of large crystals of portlandite and ettringite near voids

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Image from Yuvaraj

Now again one of the common understandings of cement paste hydration that has been achieved by SEM is in understanding the structure of the hydration products that are forming. So here this is example of deposition of ettringite crystals near a void in a cement paste system. Now in this case, of course what we are seeing is a secondary electron image of a large void in a limestone calcined-clay binder (not BSE). This is SE mode - secondary electron mode image near a void in a limestone calcined-clay binder. So limestone calcined-clay binders are where we replace cement with a mixture of limestone and calcined clay. Now what happens when you replace with limestone calcined-clay is that the chemistry works in such a way that the ettringite that forms the initial phases of cement hydration remains stable and does not convert to monosulfate. So, when you look at LC^3 binders, you will expect to find more ettringite in system and indeed you can see these needle-like features which are basically your ettringite deposits that are forming inside the system.

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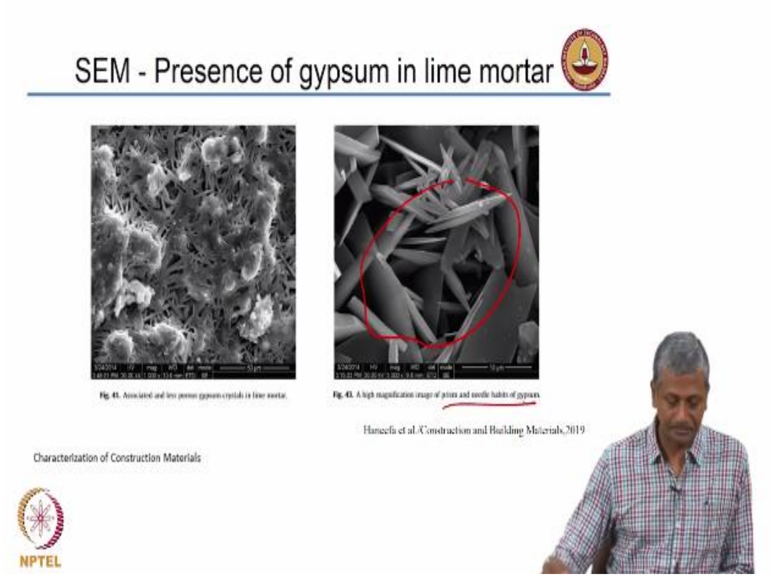

SEM - Presence of gypsum in lime mortar

Fig. 41. Associated and less porous gypsum crystals in lime mortar.

Fig. 43. A high magnification image of prism and needle habits of gypsum.

Haneefa et al./Construction and Building Materials,2019

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Now SEM can also be applied to study heritage materials. So in this case, this is an SEM study of lime mortar from a heritage structure, but what was also seen is there is presence of these well-defined crystals of gypsum, these are needle and prisms of gypsum that are formed in the lime mortar.

So why would gypsum form inside the lime mortar? It could be because of external moisture or rain carrying sulfates into the system. So when sulfates enter the system, obviously they have a chance of converting the lime present to gypsum. So you can get gypsum deposition inside lime mortar either due to acid rain, which could be one of the reasons or maybe the groundwater itself may have penetrated (seeped up) with the sulfates inside which led to the formation of gypsum.

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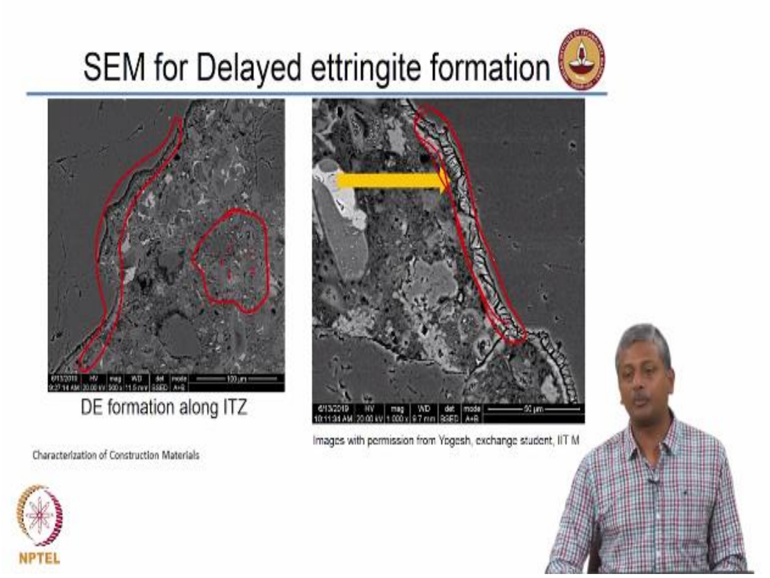

SEM for Delayed ettringite formation

DE formation along ITZ

Images with permission from Yogesh, exchange student, IIT M

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Now Delayed Ettringite Formation (DEF) is a specific circumstance where you have the suppression of ettringite formation at the early stages and this ettringite which is suppressed at early stages maybe because of very high temperatures of curing will reappear at later stages in the hardened cementitious matrix causing cracking.

Now very often we miss the point where it appears inside the cementitious system. But we only start looking at these features of ettringite deposition which form around the aggregate. And initially when DEF was examined by scanning electron microscopy, researchers came to an erroneous conclusion that you needed to have voids and cracks in the system for DEF to happen. What they surmised was that if you have voids and cracks present in the system, only then would the ettringite recrystallize and cause expansion and cracking.

But later, subsequent research proved that this ettringite that was forming was in the dense cementitious matrix itself. It is only reasonable that it forms in very small pores inside this cementitious matrix, because when it does, it will exert a large amount of pressure, because ettringite is expansive, if it forms inside a small pore, it will exert a much larger pressure than if it forms at such locations where already high porosity is available. So what researchers were able to conclude is that the ettringite formation typically started off in the very small pores of the C-S-H itself, created lot of expansive stresses that resulted in cracking and subsequently this ettringite redeposited in the regions where cracks and voids were present, because it was able to nucleate and grow into larger crystals. So again, if you look at the zone around the aggregate you see a lot of ettringite there, but that is only an after-effect, the cracks have already appeared and the ettringite has simply gone and redeposited in these pores.

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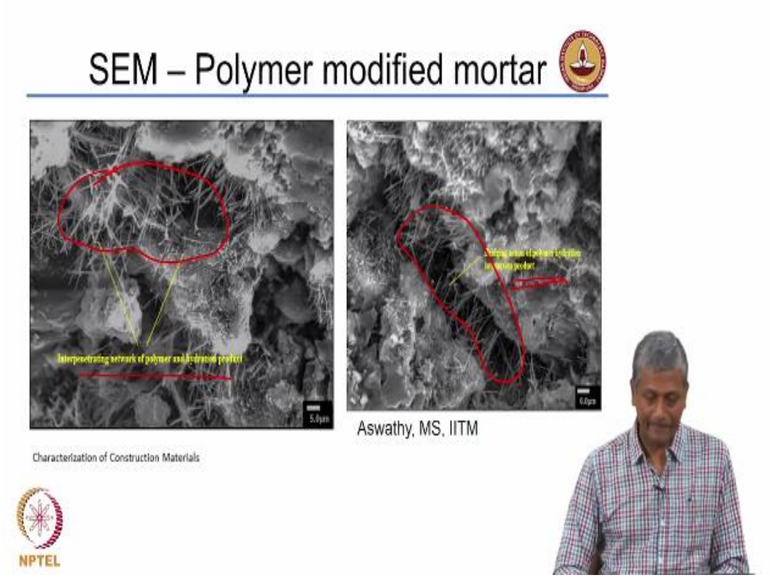

SEM – Polymer modified mortar

Aswathy, MS, IITM

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This is an SEM image of polymer modified mortar, sometimes we use latex modified concrete, we use styrene and butadiene rubber or latex which is added in a liquid medium into the concrete and as the cement sets and hardens the monomeric features of styrene butadiene end up forming a polymer and this polymer film ensures that you get a very dense structure which is impermeable to water. And it also affords some degree of elasticity to the concrete, flexibility to concrete, because obviously it is rubber.

So here this is an interpenetrating network of polymer and hydration product that is seen to be forming inside the cementitious system that is hydrating and this polymer hydration interaction product is basically bridging particles of cementitious matrix to ensure that there is good degree of denseness into the overall structure that actually forms.

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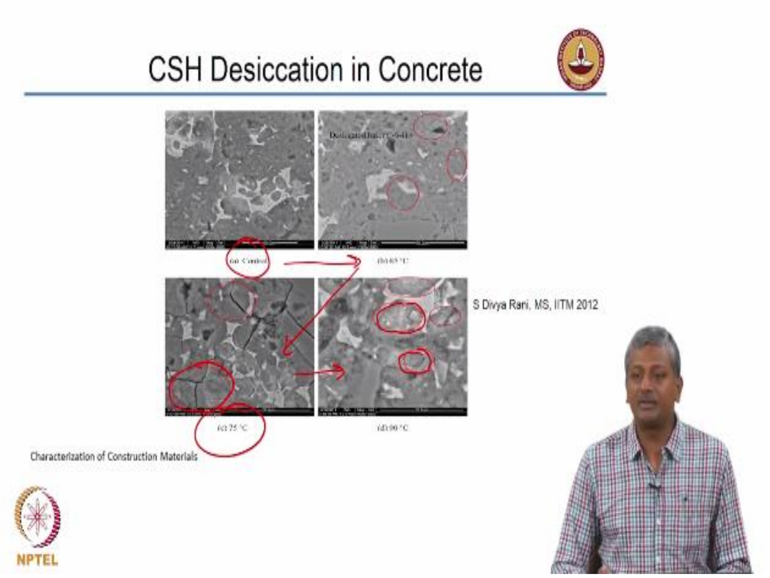

CSH Desiccation in Concrete

S Divya Rani, MS, IITM 2012

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Now this is another example of a study which we had done here to look at what happens when concrete is cured at moderately elevated temperatures. So this was a study that we had performed for Indira Gandhi Center for Atomic Research, where they wanted to find out the concrete outside the nuclear vault which may have a high temperature, because of the nuclear reactions there is obviously Gamma rays and X-rays which try to come out, which are shielded by the high density concrete on the top. But because of the reactor vessel increasing in temperature, you need to have a cooling system around it to ensure that the temperatures are kept down and then the concrete is there surrounding this nuclear reaction vault to provide the structural stability.

The only problem is, you have to invest a lot in getting the cooling system to cool down the system from very high temperatures to less than about 100 °C. Now the issue is the cooling system can be made a lot more economical, if they understand that concrete can withstand higher temperatures. Typically the ACI code for nuclear structures says that the concrete temperature should not exceed 65 °C in the outer vault - the protecting concrete which is surrounding the vault, the temperature should not exceed 65 °C. Because of that they have to invest a lot in the right level of cooling systems. The study here was to show that you can increase this permissible temperature limit up to 75°C without really causing much damage to the concrete, and to understand that, we did a vast range of tests including mechanical properties. One of the aspects was to study what happens to the internal structure of the paste when you heat it across this temperature range.

One of the common features that happen in cementitious materials as you heat it between 0 and 100 °C is that the free water that is available obviously starts getting removed. Now this free water is there in the capillary porosity obviously, which is larger compared to the gel porosity which is within the C-S-H. So what we are seeing here, as compared to the control concrete, when you increase the temperature to 65 °C to 75 °C and to 90 °C, what you end up doing is desiccating the C-S-H. This is the inner C-S-H forming in the system. And you can see the cracks inside the inner C-S-H. So what is happening there is that, there is a desiccation of the inner C-S-H. Because in C-S-H, you know that it has pores and the water in the gel pores is trying to migrate out, which is expected because less than 100 °C the water that is not chemically bound will start to migrate out. And this desiccation is resulting in cracking.

Apart from this, obviously we saw no macro level effects and ultimately the study led to the conclusion that up to 75°C, temperatures are not going to pose any problems with respect to any of the properties of the concrete. So, the advantage here is that the 10 °C additional temperature that you give to the concrete can actually help in reducing the extent of effort that you need to put into the cooling system.

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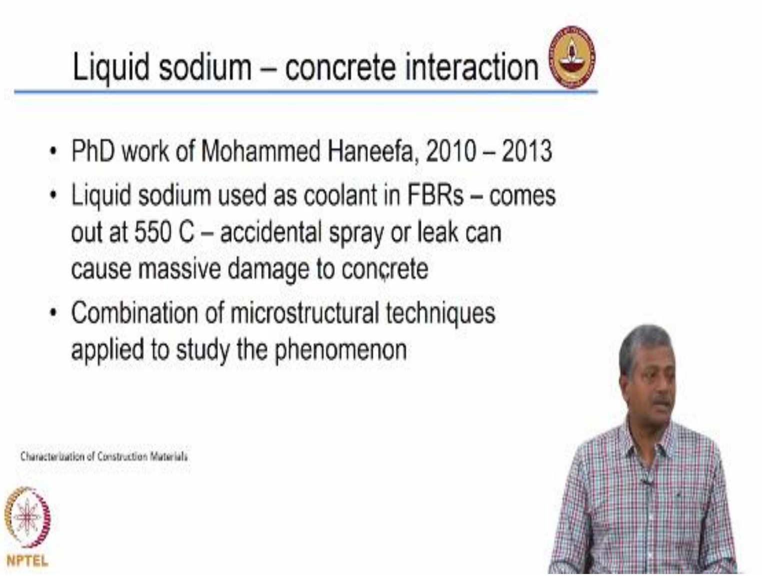

Liquid sodium – concrete interaction

- PhD work of Mohammed Haneefa, 2010 – 2013
- Liquid sodium used as coolant in FBRs – comes out at 550 C – accidental spray or leak can cause massive damage to concrete
- Combination of microstructural techniques applied to study the phenomenon

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This is another example of a study that was performed here in our lab by Mohammed Haneefa. He worked on another project for the Indira Gandhi Center of Atomic Research. So you might have heard about the BHAVINI reactor that IGCAR Kalpakkam has actually just recently inaugurated. It has not yet started producing electricity, but then it is soon going to start, starting to get critical. The idea is that this is a completely indigenous type of reactor that has been produced by India and they want to replicate it in several locations to start processing nuclear energy for electric power.

Now, this is a very different reactor as compared to the typical heavy water reactors that are available in most parts of the country. This is called a prototype fast breeder reactor. And this fast breeder reactor works with liquid sodium as a coolant. So you know that nuclear reactions increase the temperature, you need some sort of a cooling system to reduce the temperature. So, liquid sodium is here used as a coolant. Interestingly to produce liquid sodium, you need to heat sodium above 450 °C. So although it is a coolant, it is still at a high temperature and when it goes into the system and extracts the heat from the system and comes out, it is now at 550 °C.