Characterization of Construction Materials
Prof. Manu Santhanam
Department of Civil engineering
Indian Institute of Technology, Madras

Lecture - 45
Analysis of Cementitious system 2 - Part 2

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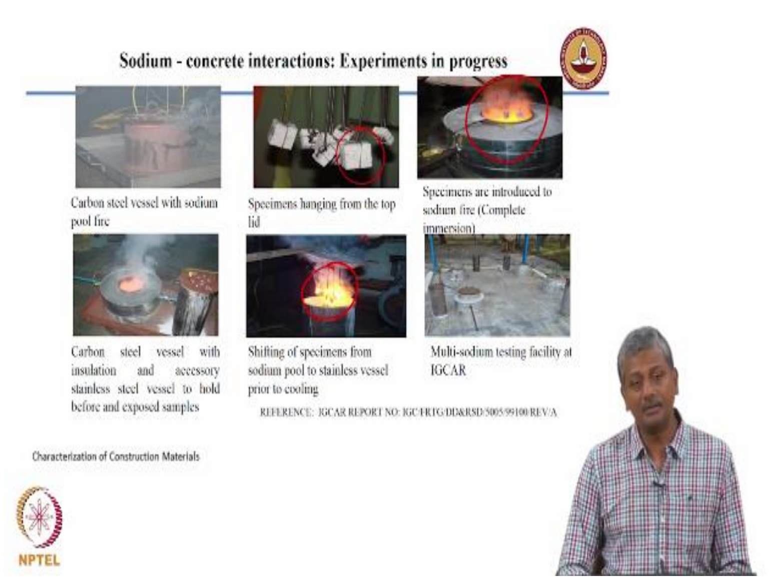

Sodium - concrete interactions: Experiments in progress

Carbon steel vessel with sodium pool fire

Specimens hanging from the top lid

Specimens are introduced to sodium fire (Complete immersion)

Carbon steel vessel with insulation and accessory stainless steel vessel to hold before and exposed samples

Shifting of specimens from sodium pool to stainless vessel prior to cooling

Multi-sodium testing facility at IGCAR

REFERENCE: IGCAR REPORT NO: IGC/FRTG/DD&RSD/5005/99100/REV/A

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So when liquid sodium is coming at such high temperatures, there is a possibility that the pipes that are carrying liquid sodium may sometimes develop leaks or bursts. Because of which the sodium may start spilling on to the concrete structures. So to ensure that the damage to the structural concrete is avoided, typically the structures which are in contact with this liquid sodium pipes have a sacrificial layer of limestone aggregate concrete that is on the surface. Now why do we provide limestone aggregate concrete on surface is because limestone is much more resistant to heat as compared to granite. Granite loses its elastic modulus rapidly after about 550 °C. So it loses its strength and properties rapidly after 550 °C, on the other hand limestone, you know that calcium carbonate decarbonates only at very high temperatures nearly 800 °C (700°C to 900°C typically). So it is able to withstand high temperatures.

So what we were trying to study here is what really happens in this interaction? And what is the significance of choosing different cementitious systems and different water-cement ratios only for the *sacrificial concrete.* The study was to see if we can increase the life of the sacrificial concrete. So we did this experiment of liquid sodium exposure, not in IIT, but at IGCAR where they have a facility to test this, because it requires a lot of care while handling, because liquid sodium if it comes into contact with air creates a fire. You can either do it in an inert atmosphere where fire is not created. You can use the inert gases like xenon or argon. But when it comes in contact with oxygen, it creates fire.

In this case, this was a liquid sodium fire that was created in the vessel. The cubical specimens of cement mortar that were prepared using different blends were then immersed into this liquid sodium pool which created a fire and extracted after different time intervals - 10, 20 and 30 minutes. 30 minutes is theoretically the maximum level of the fire, because by then all the water spray systems to get rid of the fire would have already been activated. You do not expect any fire to last more than 30 minutes.

But nevertheless the idea was to study what would happen in this accident scenario. So you can see here, the specimens are being taken out of the vessel and all of them are actually burning. Although the liquid sodium is at 550 °C, when it creates the fire the temperature automatically increases further. So you can get a temperature as high as 800 to 900 °C also, which may still result in the decarbonation of limestone. So limestone aggregates was used to prepare these mortars.

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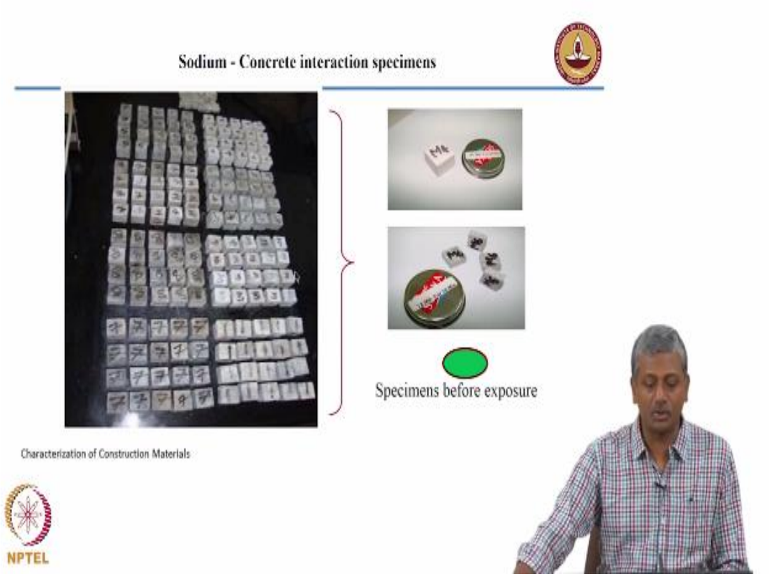

Sodium - Concrete interaction specimens

🟢 Specimens before exposure

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So, these are the specimens which were first cast with different combinations of cement and water-binder ratios.

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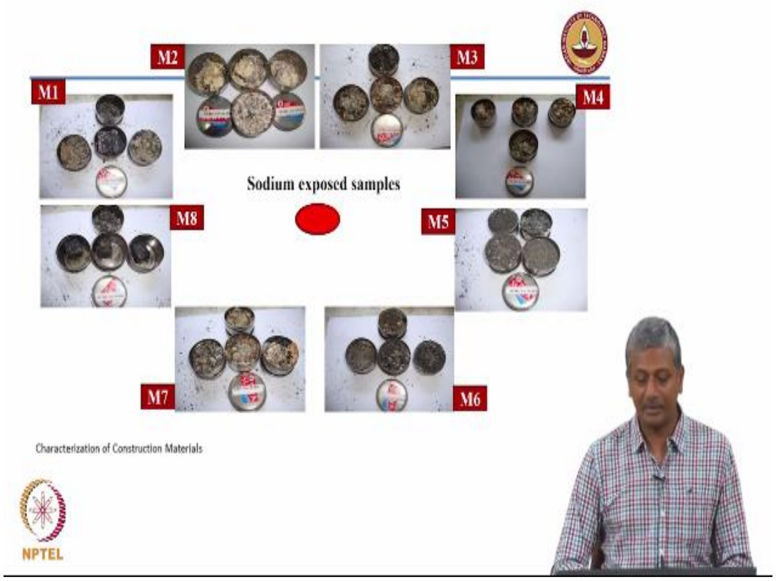

🔴 Sodium exposed samples

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But you can see what happens to them after you extract them from the liquid sodium. So none of them have preserved their shape, they are practically disintegrated.

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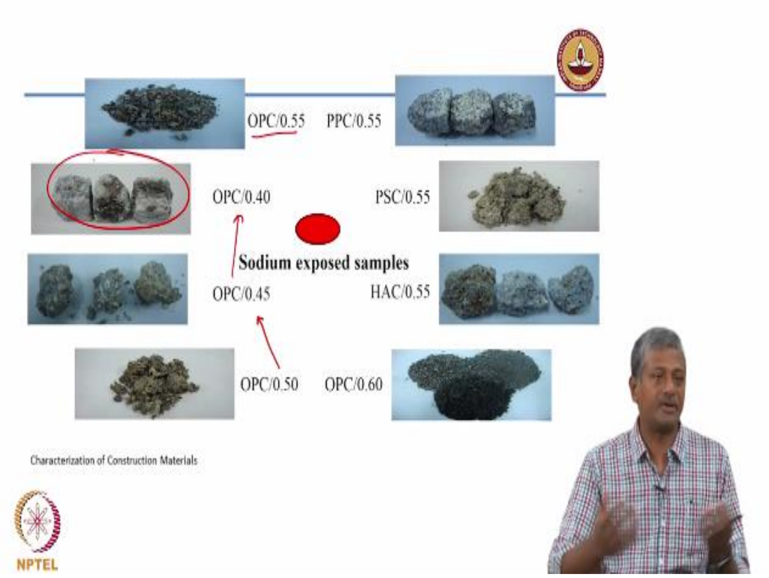

OPC/0.55
PPC/0.55
OPC/0.40
PSC/0.55
Sodium exposed samples
OPC/0.45
HAC/0.55
OPC/0.50
OPC/0.60

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Now, if you compare the different systems, this (left-side) is Ordinary Portland cement system with 0.55 water-binder ratio and you can see what happens to it. As you reduce the water-binder ratio to 0.5 and 0.45 and to 0.4, you start seeing that the disintegration is reduced significantly.

In a real nuclear accident, when the liquid sodium actually spills from the pipes there will be air in the system. So when it comes in contact with air, it will be fire basically. So, liquid sodium in contact with air at 550 °C will result in a fire.

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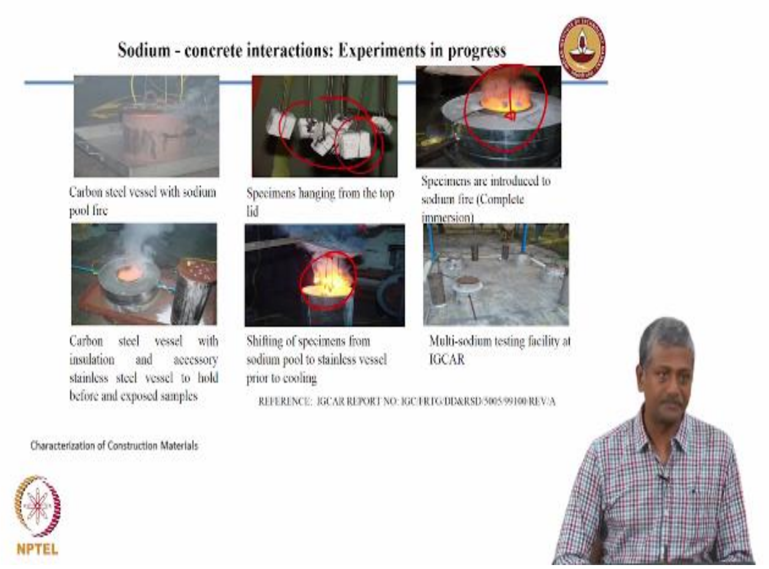

Sodium - concrete interactions: Experiments in progress

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So that is what is being created here in this picture that I've shown you. The specimens are being inserted into this vessel which has liquid sodium in it at 550 °C, but since it's open to the atmosphere, it is catching fire. So this liquid sodium is inside pipelines and when these pipes leak, sodium may come out and create a major fire, so there will be a pipe burst, for example, and that will create a major fire on the concrete and we want to see what the concrete does to withstand that fire, whether it can protect the structure still.

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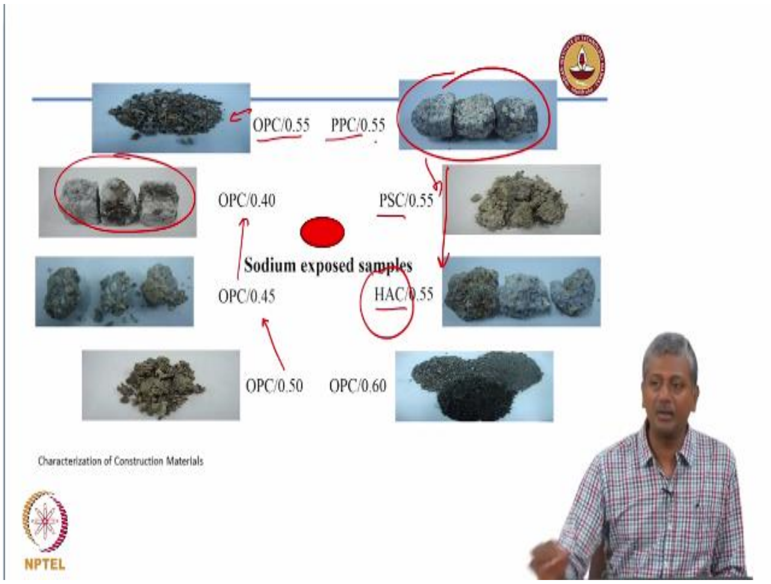

Sodium exposed samples

OPC/0.55
PPC/0.55
OPC/0.40
PSC/0.55
OPC/0.45
HAC/0.55
OPC/0.50
OPC/0.60

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So here you see, that when you actually reduce water-cement ratio, you tend to improve the stability of the system which is expected because you have lesser water to go out. When you have lesser water to go out, you form a much more stable system.

On the other hand when you use different cementitious components, here you have PPC, Portland slag cement, high alumina cement and see what happens in this case. The PPC system seems to give you the best performance. Portland Pozzolana cement system gives you the best performance at the same water-cement ratio as OPC or slag concrete on high alumina cement concrete. Now, that is interesting because we know that high alumina cement is a refractory material. We know that it is used for lining kilns at very high temperatures, for example, rotary kilns are sometimes lined with high alumina cement. So what is actually happening here, why does the fire performance of this system not reflect the same level of resistance as even a PPC? So there some questions need to be answered.

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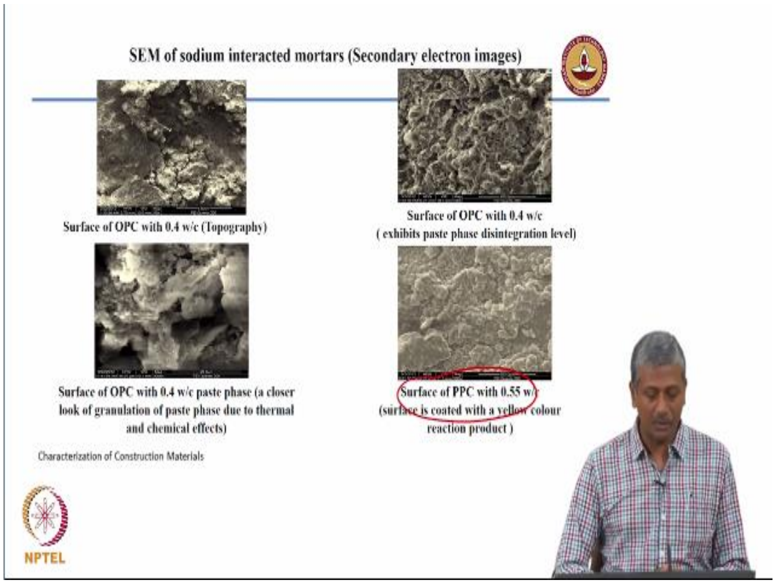

SEM of sodium interacted mortars (Secondary electron images)

Surface of OPC with 0.4 w/c (Topography)

Surface of OPC with 0.4 w/c
(exhibits paste phase disintegration level)

Surface of OPC with 0.4 w/c paste phase (a closer look of granulation of paste phase due to thermal and chemical effects)

Surface of PPC with 0.55 w/c
(surface is coated with a yellow colour reaction product)

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So we tried to look at the secondary electron images from these systems. Of course at the time that this study was performed, we had no way of starting off with a very good polishing that you see with the backscattered electron images, but nevertheless we have also attempted that in this case.

So here we were trying to look at the features that define the different types of systems and what we saw was the surface of the PPC at the same water-cement ratio as the other cementitious systems had a layer of products forming on the surface which we were actually never able to characterize very carefully. That is one of the shortcomings of the study that we were never able to actually fully capture what that layer forming was, which seemed to protect the insides significantly well.

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Exposed mortars

Vacuum impregnation

10 mm depth

Surface

Epoxy impregnated samples

Cutting

Polishing

Coating

Epoxy impregnated samples

BSE- Imaging

Specimen preparation of sodium exposed samples for SEM-BSE

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Now, of course to prepare the backscattered specimens, we had to deal with the extremely fragile and ready-to-break sort of cubes which were taken out from the fire, but nevertheless we did vacuum impregnation with low viscous epoxy and the epoxy impregnated samples were then polished and coated for backscattered electron imaging.

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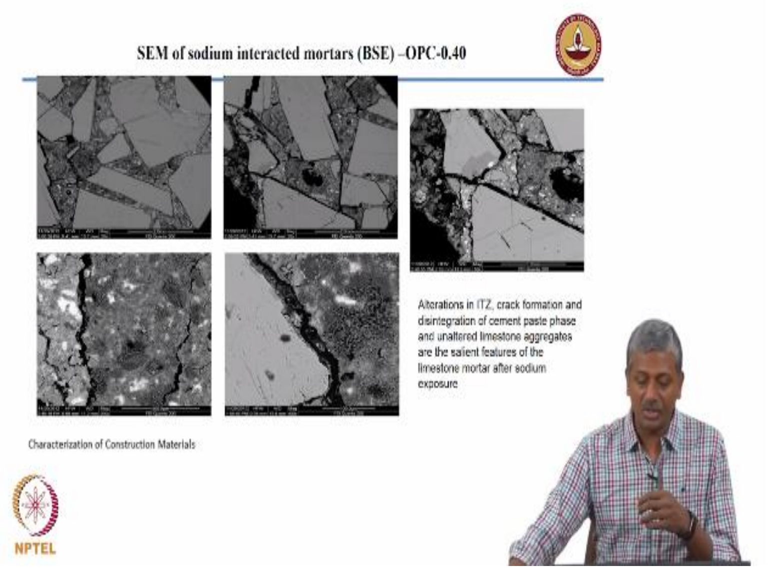

SEM of sodium interacted mortars (BSE) –OPC-0.40

Alterations in ITZ, crack formation and disintegration of cement paste phase and unaltered limestone aggregates are the salient features of the limestone mortar after sodium exposure

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So here you see examples of backscattered electron imaging. Now here, what you can make out quite clearly is that different systems seem to exhibit different levels of cracking at the interface with the aggregates. And that could happen because of the relative differences in the thermal expansion coefficients of the cementitious paste and the aggregate. Now it is interesting to note that while most structures showed cracking, the extent of cracking around the aggregate was maximum in the system which had high alumina cement.

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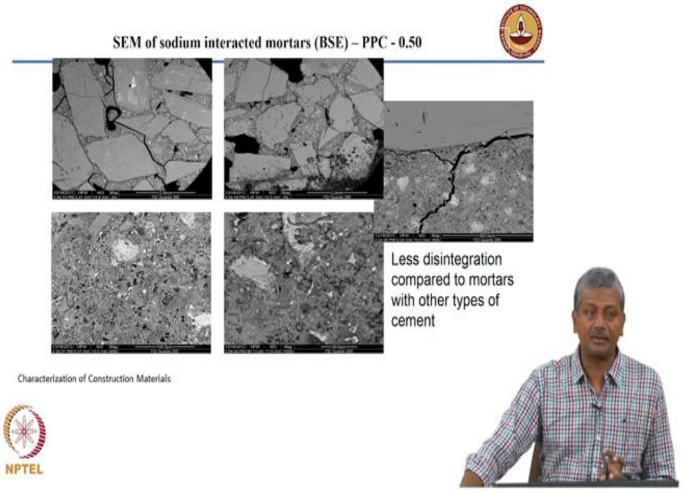

SEM of sodium interacted mortars (BSE) – PPC - 0.50

Less disintegration compared to mortars with other types of cement

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So it was OPC shown in previous slide. This (present slide) is your PPC and we can see in PPC, the cracks are limited.

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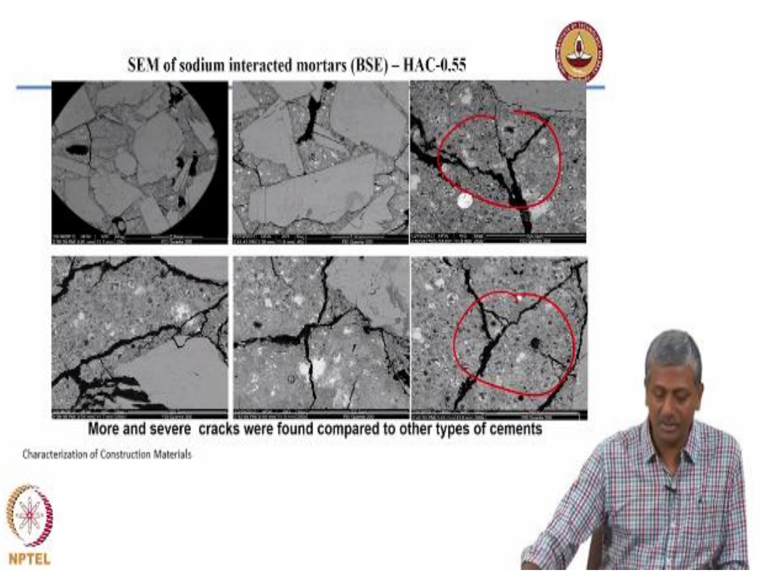

SEM of sodium interacted mortars (BSE) – HAC-0.55

More and severe cracks were found compared to other types of cements

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When you go to high alumina cement, the cracking was extensive not just between paste and aggregate, but within the paste itself the cracking was extensive. So there was some level of incompatibility which we did not really go into much more detail because of lack of time and we just concluded that at high temperatures the system between the high alumina cement and limestone aggregate seems to have some level of incompatibility, which causes more extensive cracking in the system which leads to more disintegration as opposed to other cementitious systems. So again I am not going to conclude this in more detail.

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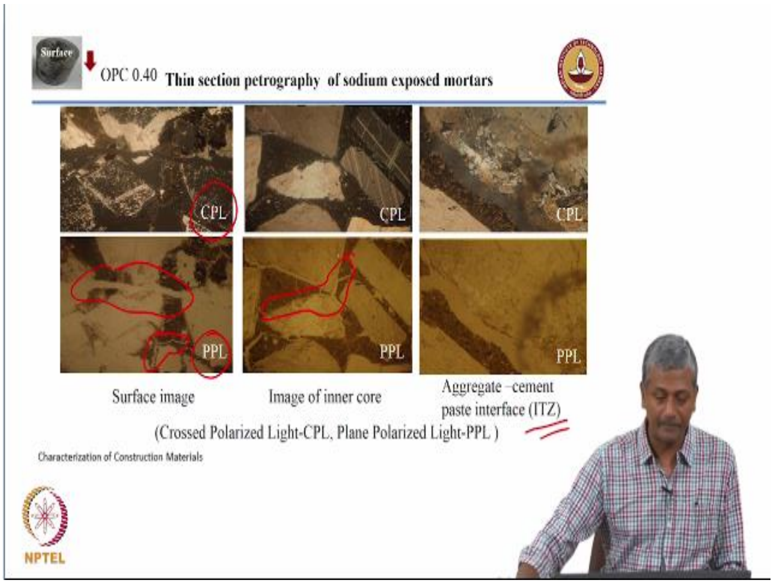

OPC 0.40 **Thin section petrography of sodium exposed mortars**

Surface image

Image of inner core

Aggregate –cement paste interface (ITZ)

(Crossed Polarized Light-CPL, Plane Polarized Light-PPL)

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I just wanted to also show you the comparative studies done with optical microscopy. So here we prepared thin sections of these epoxy impregnated samples and tried to monitor the extent of cracking that happens inside these system.

So now here the images are presented in crossed polarized light as well as plane polarized light. What do you mean by plane polarized - when the polarizer and analyzer are at the same angle. Cross polarized is when polarizer is at 0 degree angle and analyzer is exactly perpendicular to it - at 90 degrees. So what you see as a result of cross polarized light is that you are able to accentuate the difference between the different phases much more. Only thing is if you want to observe just the cracking, the plane polarized can give you a much nicer estimate of the cracking that is happening in the system. So again, you can see the ITZ cracking, you can see the cracking around the full system and so on.

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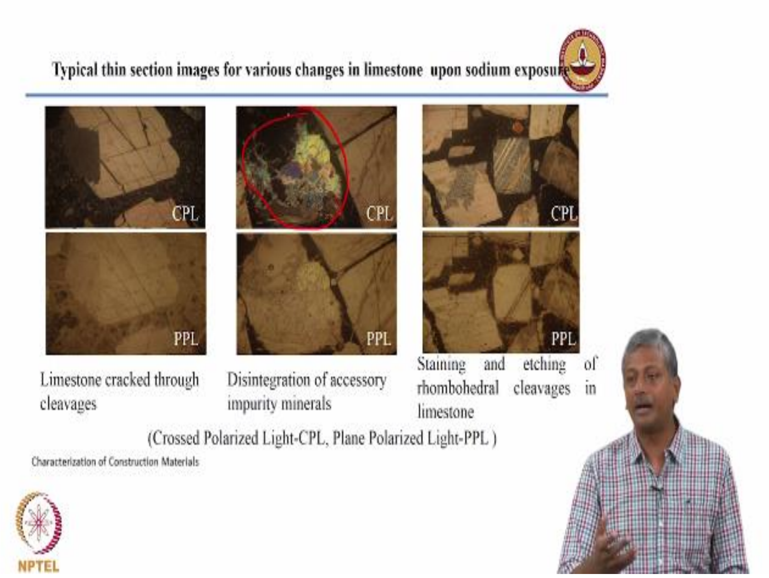
Typical thin section images for various changes in limestone upon sodium exposure

Limestone cracked through cleavages

Disintegration of accessory impurity minerals

Staining and etching of rhombohedral cleavages in limestone

(Crossed Polarized Light-CPL, Plane Polarized Light-PPL)

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These are thin section images for various changes in limestone upon sodium exposure and what you see is there are these accessory minerals, which are present in limestone. What we saw is even if limestone is stable at high temperatures 700 to 900 and °C, it may have some impurity minerals which start getting disintegrated at earlier temperatures, and that could be the reason why in spite of having limestone as an aggregate in the cementitious mortar we are still getting a high level of deterioration.

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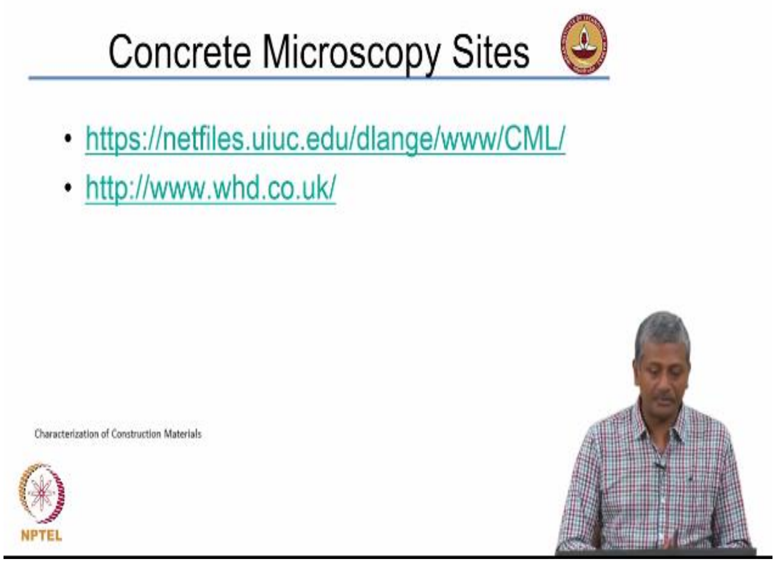
Concrete Microscopy Sites

- https://netfiles.uiuc.edu/dlange/www/CML/
- http://www.whd.co.uk/

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So that was a gyst of that study that was done. Actually it was coupled with several other investigations also to try and understand this problem wholly and suggest a remedy for accidental scenarios to IGCAR. Of course, there is a lot to see as far as concrete microscopy is concerned; there are a couple of interesting websites, which you'll really benefit from. So these two websites are quite good to see the different types of concrete microscopy examples that have been given by these authors on these websites. Of course there are a whole lot of papers that you can actually go through to appreciate this lot better. So I wanted to also show you examples of microscopy from other systems.

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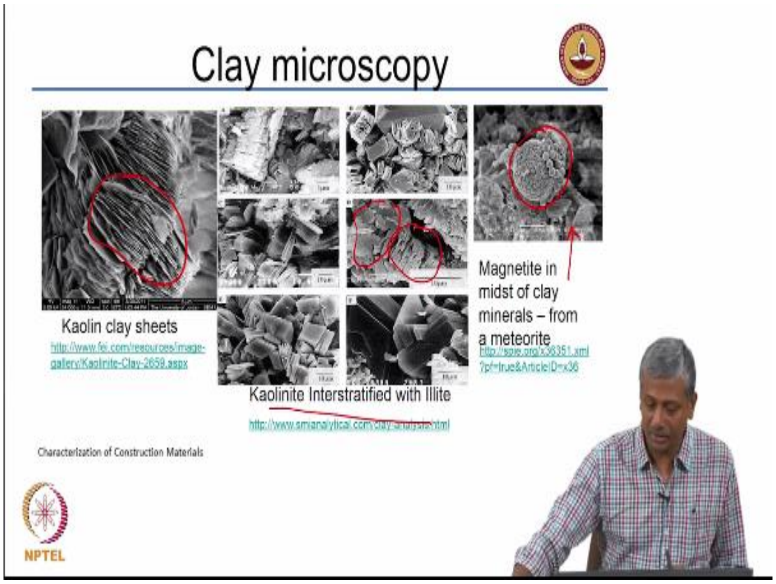

Clay microscopy

Kaolin clay sheets

http://www.fei.com/resources/image-gallery/Kaolinite-Clay-2659.aspx

Kaolinite Interstratified with Illite

http://www.smianalytical.com/clay-analysis.html

Magnetite in midst of clay minerals – from a meteorite

http://spie.org/x38351.xml?pf=true&ArticleID=x36

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Clay is a very exciting structure to be looked at under the microscope, because it has these plate-like features. You can very clearly see how well you can see these sheets in a secondary electron image. Now interesting example here is the presence of magnetite in the midst of clay minerals from a meteorite sample, so this is a sample that's come from space to Earth. You see how well we can actually monitor this.

And here you have an example of kaolinite clay, which is interstratified with Illitic clay. So you can see that there are differences in the morphological features of these units you see in the scanning electron microscopic image. So it's a very powerful tool to study the structure of clays. Microscopy is very good for studying structure of clays.

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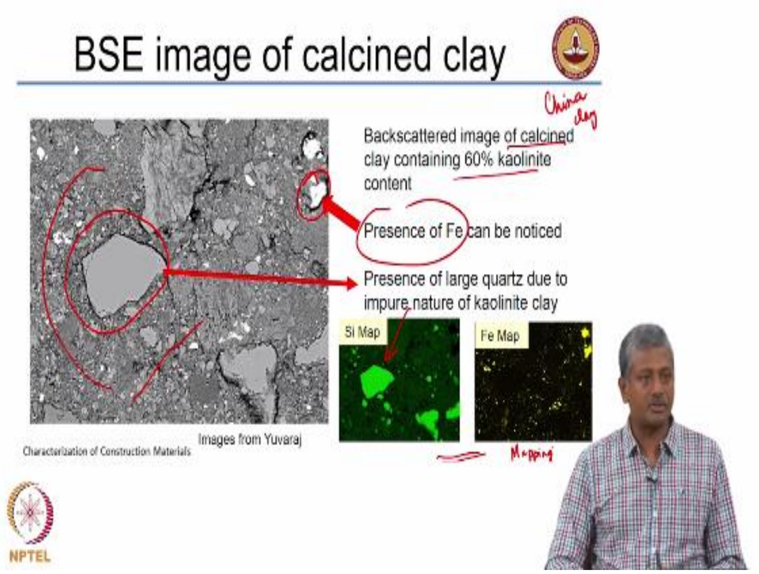

BSE image of calcined clay

China clay

Backscattered image of calcined clay containing 60% kaolinite content

Presence of Fe can be noticed

Presence of large quartz due to impure nature of kaolinite clay

Images from Yuvaraj

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This is an example of calcined clay which we use for our research studies to make the limestone calcined-clay systems that go as replacement for cement. So here, this is an example – backscattered image of calcined clay containing 60% kaolinite content. So please remember when we extract clay from the Earth, it will be present with a lot of impurities. The ceramic and paint industries typically take the very high purity clay, which they also call as China clay. China clay is the extremely white kaolinitic clay - almost 95% pure kaolinite that they extract from the mines, for the semiconductor industry and the paints and ceramics industry. They need that high purity clay and they burn it at very high temperatures: 1000 °C plus, because they want an inert material that acts like a filler; a white filler is what they want.

Whereas for cementitious materials, we can burn it at around 750 to 800 °C, because that activates the clay, which is akin to the activation of clay that happens in the rotary kiln of cement manufacture. So at 750-800 °C, we do not produce a crystalline kaolinite, we produce a metakaolin, which is not crystalline. Now in such cases, sometimes we can even use the clay from these mines, which has lot of impurities in it. So for example, if the clay has a lot of iron in it, when you extract it from the mines, it will have a red color and these ceramic and paint industry people, do not want it because they do not want the red color. So when we get the clay, you can actually extract significant pozzolanic qualities out of that clay itself, even with 60% kaolinite.

So here you can see the presence of iron in these calcined clay systems. And you can also see other impurities that are present. Now what is this impurity? We did an Energy Dispersive Spectroscopy mapping to see that these impurities are actually just quartz (silica). This is obviously crystalline silica which is not going to be of any use as far as reactivity is concerned. But nevertheless, the remaining part of the system which contains your reactive aluminosilicate from the calcined clay, will give you high degree of pozzolanicity.

So this is the mapping feature associated with Energy Dispersive X-Ray Analysis. So not only can you take spot scans of X-rays, you can actually take a map along the line or along an area, which gives you the elemental distribution across the entire region.

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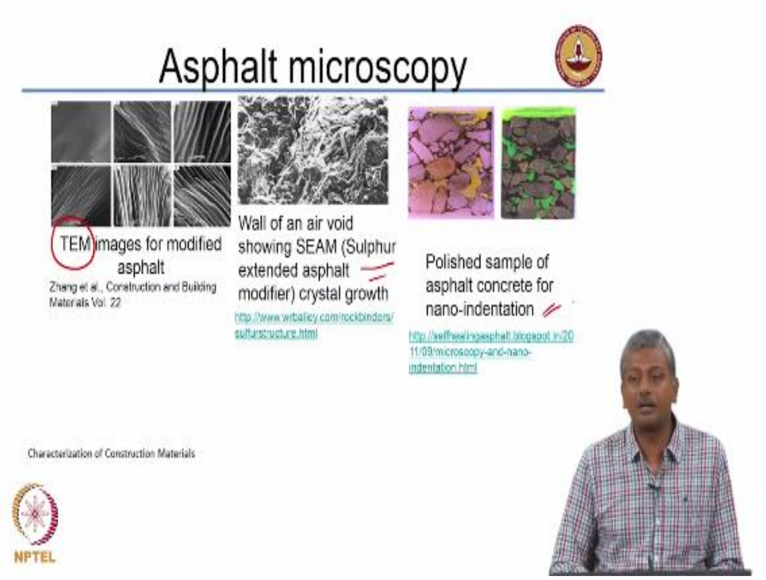

Asphalt microscopy

TEM images for modified asphalt

Zhang et al., Construction and Building Materials Vol. 22

Wall of an air void showing SEAM (Sulphur extended asphalt modifier) crystal growth

http://www.wrbailey.com/rockbinders/sulfurstructure.html

Polished sample of asphalt concrete for nano-indentation

http://selfhealingasphalt.blogspot.in/2011/09/microscopy-and-nano-indentation.html

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These are images from asphalt. You have transmission electron images for modified Asphalt. Now of course, much of the recent developments as far as asphalt is concerned is with the use additives in the binder like crumb rubber or you have other polymers which are modifying the asphalt characteristics to obtain much better performance across a range of temperatures.

So here Sulphur Extended Asphalt Modifier (SEAM) is being shown and you can see the crystal growth happening in the system in the secondary electron image. This is a polished sample of asphalt concrete for nano-indentation just to understand the distinction in the hardness of different phases.

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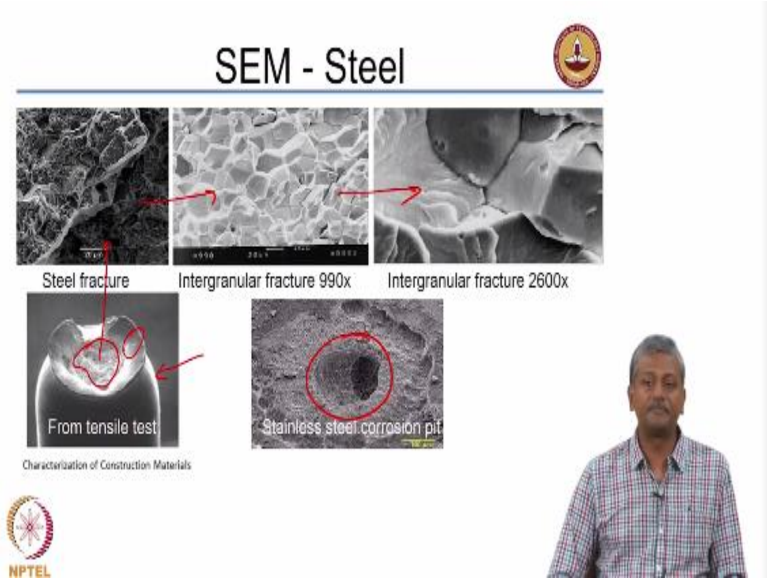

SEM - Steel

Steel fracture

Intergranular fracture 990x

Intergranular fracture 2600x

From tensile test

Stainless steel corrosion pit

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Now with steel you can produce excellent images of steel fracture for instance. Here you have a steel specimen that has been pulled in tension and you can clearly see the cup formation in this case (bottom-left image). You see the lip here and you see the grain boundary where the fracture has actually happened. And this steel fracture, if you expand you can see the features much clearer (top-middle image). So as you increase the magnification (top-right image) you can see the features of the broken grains or the separated grains much clearer. And this (bottom-right image) is actually a pitting corrosion example from steel, which has been very clearly monitored using scanning electron microscopy.

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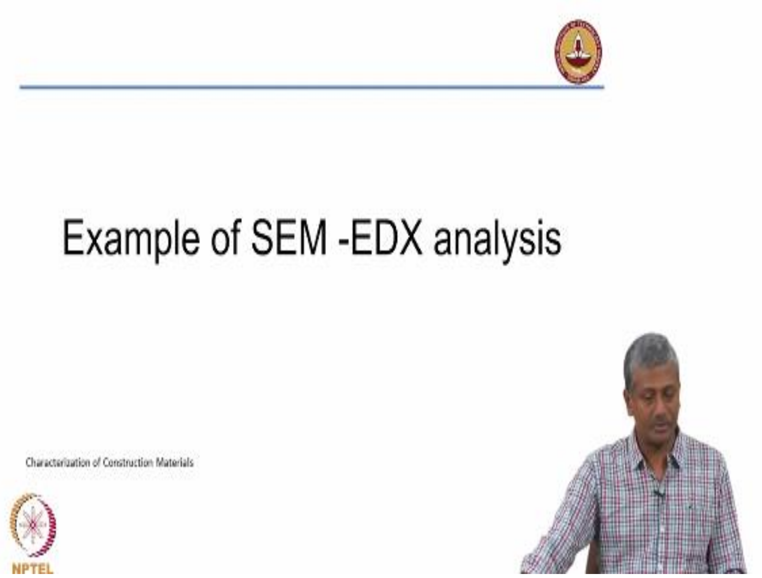

Example of SEM -EDX analysis

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I will also show you a couple of examples of SEM-EDX analysis, so that you can appreciate how the information from X-Ray can be actually used to supplement the information you are getting from the images.

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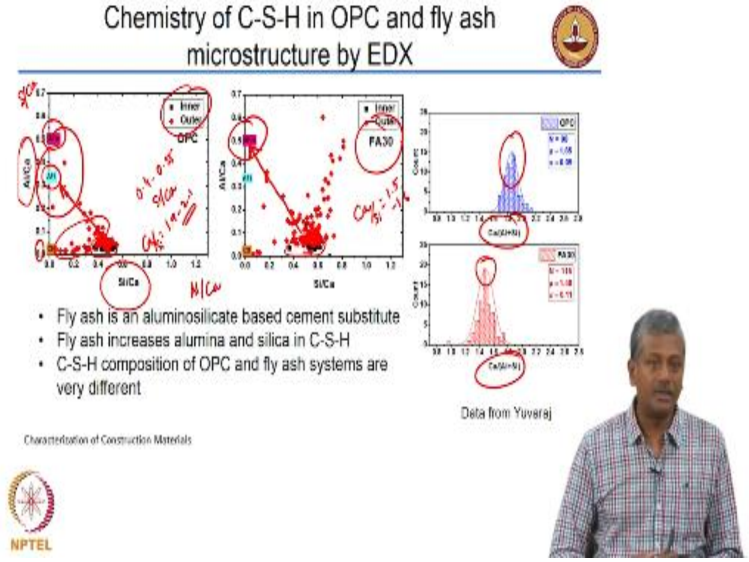

Chemistry of C-S-H in OPC and fly ash microstructure by EDX

- Fly ash is an aluminosilicate based cement substitute
- Fly ash increases alumina and silica in C-S-H
- C-S-H composition of OPC and fly ash systems are very different

Data from Yuvaraj

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So, this is an example of C-S-H understanding in OPC and fly ash microstructure by EDX. So what is typically done is several points are taken, as I told you earlier, you would need to take multiple points across the C-S-H and analyze the atomic ratios of the different elements that are coming out in your X-ray analysis. Typical ways of plotting that is to plot either the Si/Ca ratio on the X-axis versus Al/Ca ratio on the Y-axis. Or sometimes you can also plot Al/Ca on the X-axis and S/Ca (sulphur to calcium ratio) on the Y-axis. These are just different ways of representing it.

Now, why do we need to present it like this? What it does is, help us group these points differently. For example here, you can see that the analysis has been done for inner C-S-H and outer C-S-H; the black points represent the inner C-S-H and you can clearly see the black points are all in a very narrow band here. The black points are mostly in a narrow band of let us say about 0.4 to 0.55 Si/Ca ratio. What does that mean in terms of Ca/Si ratio? We just divide by 1 by these numbers, so you get Ca/Si ratio. So we are talking about 1.9 - 2.1 generally. So, that is the composition of the inner C-S-H and you can see the amount of aluminium in the inner C-S-H is limited we are talking about 0 - 0.1 or 0.0 to 0.05 is the amount of aluminum, inside the inner C-S-H.

When you go to the outer C-S-H, there is a vast range of composition that you see. What is the reason for this vast range of composition? It is because the outer C-S-H is intermixed with several other phases. You can probably hit calcium hydroxide phases; you can hit ettringite or monosulphate phases also in the system. And you can see this line is going towards the Al/Ca axis or Al/Ca ordinate, you have AFt and AFm marked there, that means AFT is ettringite aluminoferrite trisulphate, AFm is aluminoferrite monosulphate, and you can see that, some of those points that you are showing there might be representative of ettringite and monosulphate. That is why you can clearly distinguish now the difference that happens with the inner and outer C-S-H.

In the case of fly ash system, again you get the inner C-S-H, which is in this range, but you see here that the overall Si/Ca ratio in the inner C-S-H is also moved to the right. It is now closer to 0.6 as compared to 0.5. So the Ca/Si ratio which was 1.9 to 2.1 in Portland cement systems, in the case of fly ash systems it will come down about 1.5 to 1.6. The outer C-S-H which is an amalgamation of different components seems to point out that your tendency is to form more AFm phases, rather than AFt phases which are seemed to form in Ordinary Portland cement systems.

So, you get the differences in compositions analyzed by doing spot analysis on the inner and outer C-S-H. So what is also shown here is a Ca/(Al+Si) ratio in OPC and in fly ash and what you are seeing here is that this ratio is centered around 1.8 in the case of OPC system and 1.5 in case of fly ash systems. So you can understand the distinction between the Pozzolanic reaction produced C-S-H and the cement reaction produced C-S-H.

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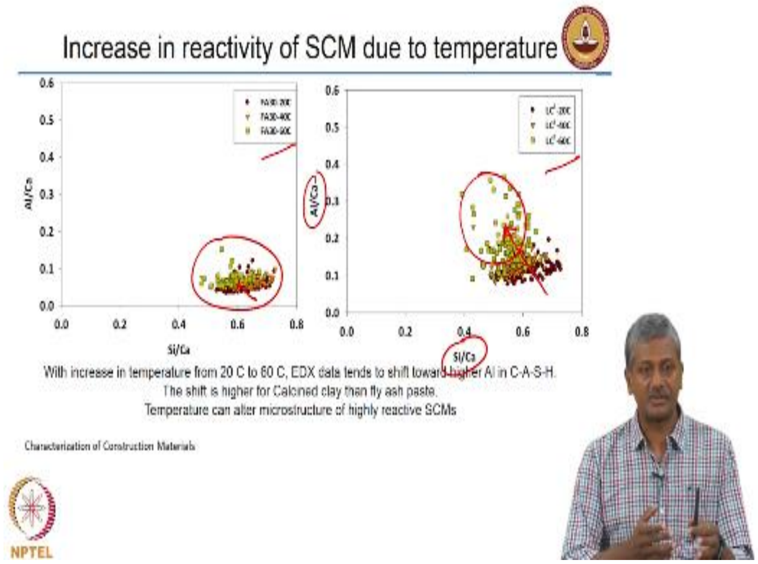

Increase in reactivity of SCM due to temperature

With increase in temperature from 20 C to 60 C, EDX data tends to shift toward higher Al in C-A-S-H.
The shift is higher for Calcined clay than fly ash paste.
Temperature can alter microstructure of highly reactive SCMs

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Now we saw the scanning electron microscopy images of ordinary Portland cement paste at different temperatures of 20 °C, 40 °C and 60 °C. Here this is just an example of fly ash and LC^3 systems at different temperatures as to what really happens to the composition. So what is again plotted here is the Al/Ca ratio versus Si/Ca ratio and what you see very clearly is that, as the temperature increases your plot is seen to move more and more to the left.

In this case (FA30) when they increase in temperature from 20 to 60 °C, you do not see such a large change, although still the tendency is to move towards the left. In case of LC^3 systems (limestone calcined clay system), the effect is much more significant. You see the shift is much more significant. So what we are trying to show here is that with the change in temperature, the compositions of phases seem to indicate a major change in the LC^3 systems as opposed to fly ash based systems.

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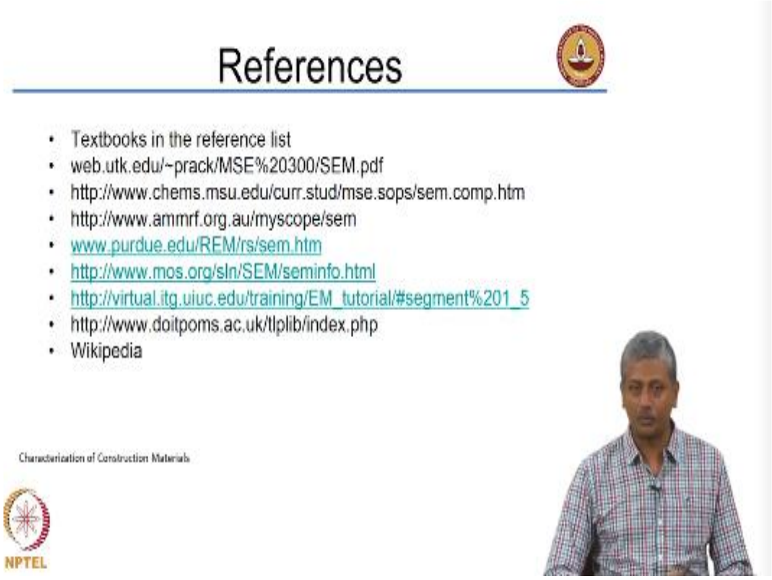

References

- Textbooks in the reference list
- web.utk.edu/~prack/MSE%20300/SEM.pdf
- http://www.chems.msu.edu/curr.stud/mse.sops/sem.comp.htm
- http://www.ammrf.org.au/myscope/sem
- www.purdue.edu/REM/rs/sem.htm
- http://www.mos.org/sln/SEM/seminfo.html
- http://virtual.itg.uiuc.edu/training/EM_tutorial/#segment%201_5
- http://www.doitpoms.ac.uk/tlplib/index.php
- Wikipedia

Characterization of Construction Materials

NPTEL

So with that I come to the conclusion of this segment of our course on optical and scanning electron microscopy. I have also presented here several other references which can actually add to the information that you can achieve from this lecture. There are lot of instances of description of microscopy given on the internet, but please remember that on the internet you get mixed sort of information. A lot of the information and internet is not peer-reviewed and that is why you need to be very careful. When you get information from papers and books, please remember that those are peer-reviewed; somebody has actually gone through and certified that that information is indeed reasonable. Nobody can say it’s accurate, because we are dealing with an experimental science, nothing is accurate here.

What fits in with expected theory is what is reasonable. Sometimes people make all kinds of claims with their assumed studies, sometimes people show all kinds of things focusing on the aspect that they want to show rather than a balanced view of the entire system. So what we need to understand is how to actually appreciate a balanced view of the whole system to form decisions about why the behavior is reflected by the internal structure or what aspects of the internal structure are responsible for the behavior.

So therein lies the challenge - we need to be balanced in our approach, at the same time we should not get carried away by features that maybe present only in 0.1% of our system. We need to ensure that we are doing a meticulous job of scanning the entire sample to get the image that we want to show the example of. So again, we are just trying to exemplify macro scale behavior by trying to understand the microstructural level details.

And once more, since when you are going to more and more sophisticated forms of microscopy, your analysis obviously becomes more and more expensive; not just more expensive, it becomes more confusing also. The more details that you seek, the more confused you can get. You have to be extremely lucky to get this right in the first go; right from getting the right level of sample preparation to focusing on the area that you really want to focus on, because very often you get lost in your specimen because your specimen is a few millimeters in size. Your area of interest is only a few microns. So sometimes you can get lost in the sample because millimeter to micron is 1000 times. You are reducing your size 1000 times; so sometimes you can get lost. That means we need to invest a lot of time; more time obviously implies more instrument usage time and that requires more cost. So justification of microscopy is obviously very important. You need to justify why microscopy is needed and what features from the microscopy can be actually used to show the reasons to show your macro scale theory.