Characterization of Construction Materials
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Lecture - 45
Analysis of Cementitious system 2 - Part 2

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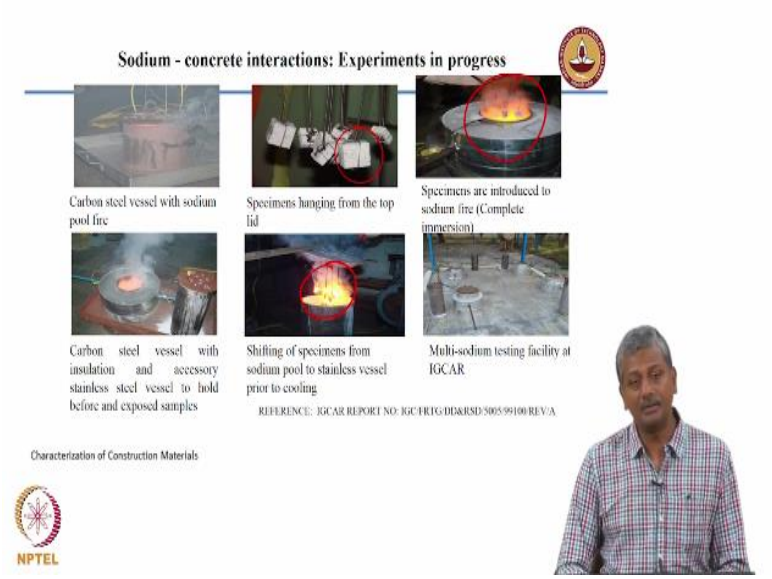

So when liquid sodium is coming at such high temperatures, there is a possibility that the pipes that are carrying liquid sodium may sometimes develop leaks or bursts. Because of sodium starts spilling on to the concrete structures. So to ensure that the damage to the structural concrete is avoided typically the structures which are in contact with the liquid sodium pipes have a sacrificial layer of limestone aggregate concrete that is on the surface.

Now why do we provide limestone aggregates concrete on surface? This because limestone is much more resistant to heat as compared to granite. Granite loses its elastic modulus rapidly after about 550 degrees Celsius. So it loses its strength and properties rapidly after 550 degrees Celsius, on the other hand limestone, you know that calcium carbonate decarbonates only at very high temperatures nearly 800 degrees Celsius is 700 to 900 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 to cement ratios for the sacrificial layer concrete? Only for the sacrificial concrete can we increase the life of the sacrificial concrete. So we did this experiment of liquid sodium exposure, not NIIT.

But IGCAR were they have a facility to test this. Because it requires a lot of care while handling this liquid sodium when it comes into contact with air creates some fire. You can either do it in an inert atmosphere where fire is not created. You can use the inert gases like xenon or neon but sorry, argon. But when it comes in contact with oxygen it creates the 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 where 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 degrees Celsius when it creates the fire the temperature automatically increases further so you can get a temperature as high as 800 to 900 degrees Celsius also which may still result in the decarbonation of lime stones. So limestone's aggregates was used to prepare these mortars.

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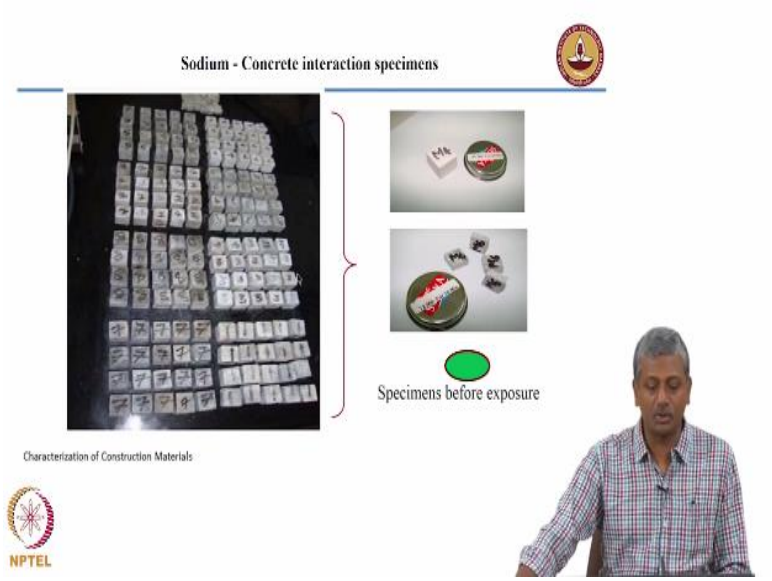

So, these are the specimens which were first cast with different combinations of cement and water bind the ratios.

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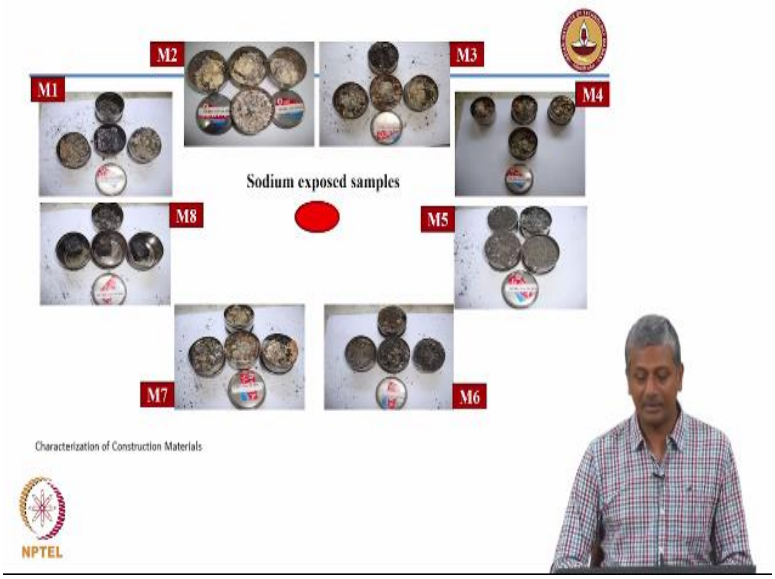

But you can see what happens to them after you extract them from the liquid sodium. So none of them have deserved their shape their practically on disintegrated.

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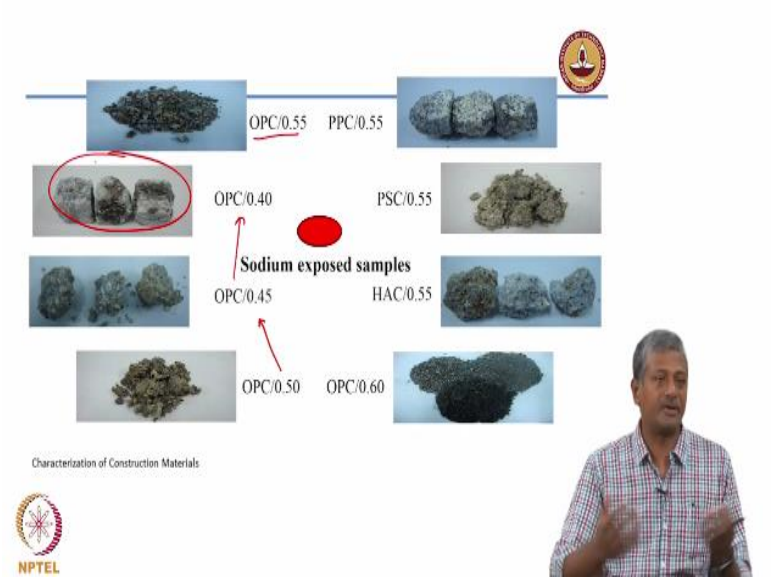

Now, if you compare the different systems this ordinary portend system with 0.55 water binary ratio that you can see what happens to it. As you reduce the water binder ratio to 0.1 to 0.45 and 0.4 you start seeing that it is integration is reduced significantly. In a real nuclear accident when the liquid 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 degrees Celsius will result in a fire.

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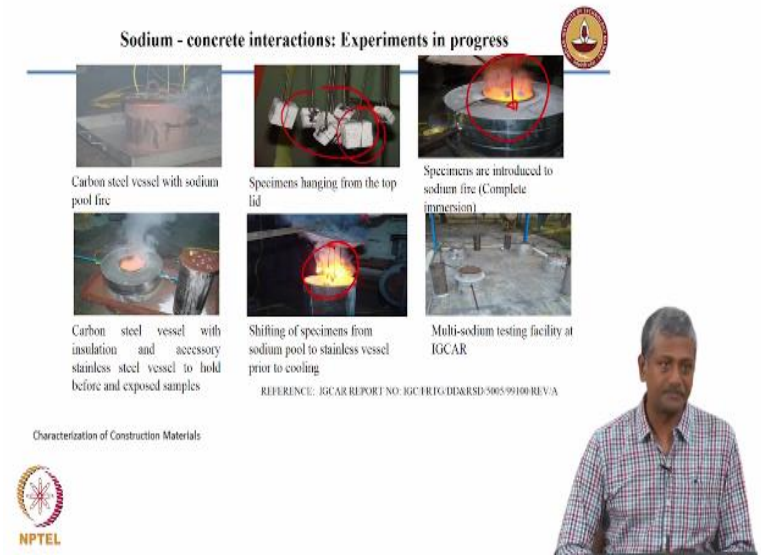

So that is what is being created here in this picture there is shown you the specimens are being inserted into this vessel which has liquid sodium in it at 550 degrees Celsius, but since its open to the atmosphere it is catching fire. Yes, so this liquid sodium is inside pipelines and when these

pipe 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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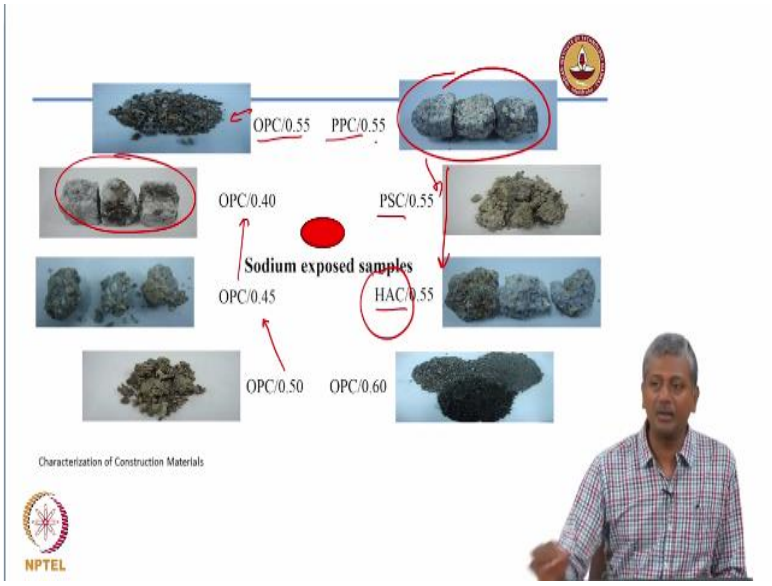

So here you see that when you actually reduce water cement ratio you tend to improve the stability of the system which is expected because you have lesser water to go out, when you have lesser of water to go out you form a much more stable systems. On, the other hand when you use different cementitious 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, there is interesting because we know that alumina cement is the refractory material. We know that it is used for lining at very high temperatures lining kilns, for example rotary kiln sometimes a line with high alumina cement.

So what is actually happening here, why does the fire performance of the system not reflected same level of resistency even a PPC? So there some questions need to be answered.

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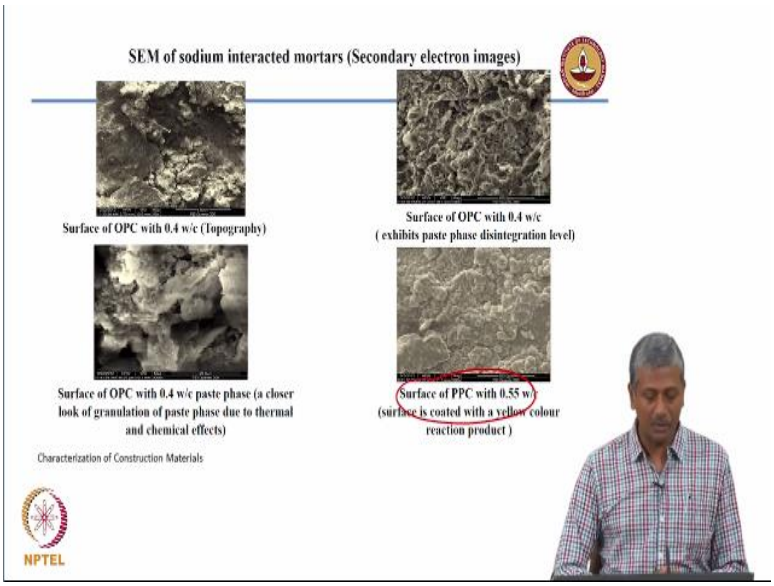

So we try to look at the secondary electron images from these systems, because at the time that this study was performed we had no way of starting off with the very good polishing that you see with the backscatter electron images, but nevertheless we have also attempted that in this case. So here we 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 seem to protect the inside significant level.

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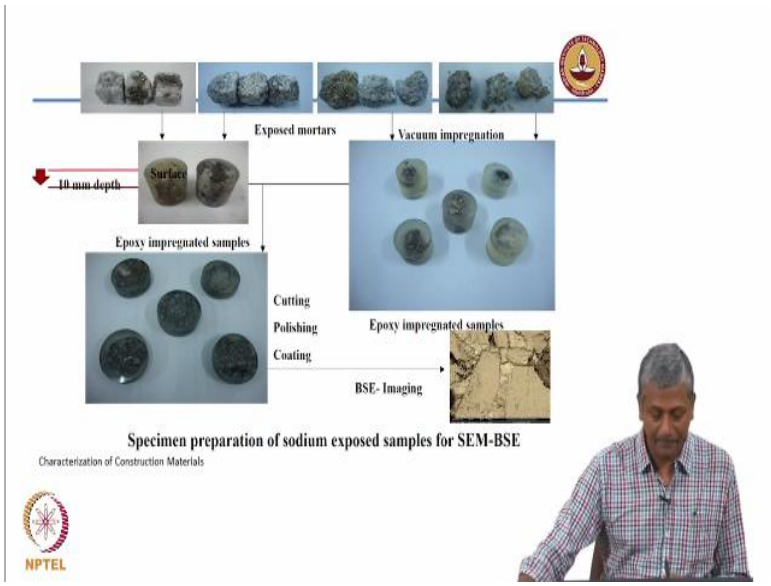

Now, of course to prepare the backscattered specimens, we had to deal with the extremely fragile and ready to break sort of cubes which were taken out from the fire but nevertheless we did vacuum impregnation with low viscous epoxy and the epoxy impregnated samples were then polished and quoted for backscattered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

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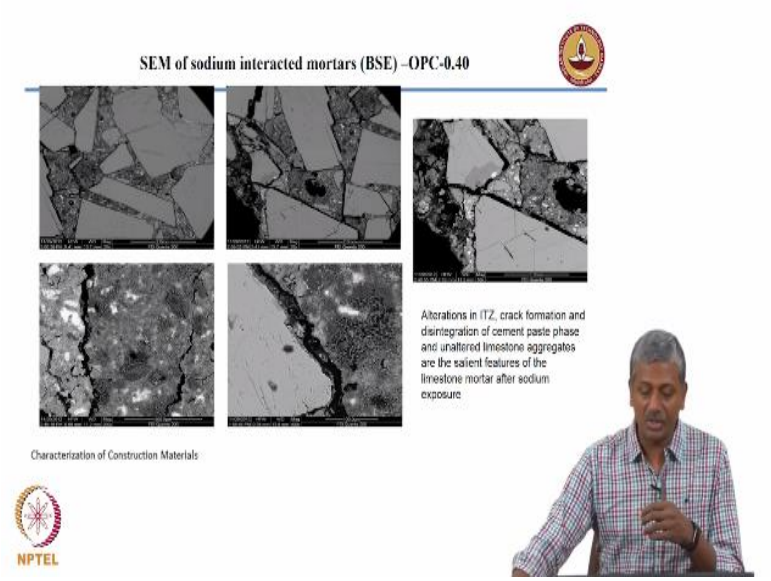

So here you can see examples of backscattered electron imaging. Now here what you can make out quite clearly is that different system seems to exhibit different levels of cracking at the interface with the aggregates and that could happened because of the relative differences in the thermal expansion coefficients of the cementitious paste and the aggregate. Now it is interesting

to note that while most structures should cracking the extent of cracking around the aggregate was maximum in the system, which had high alumina cement.

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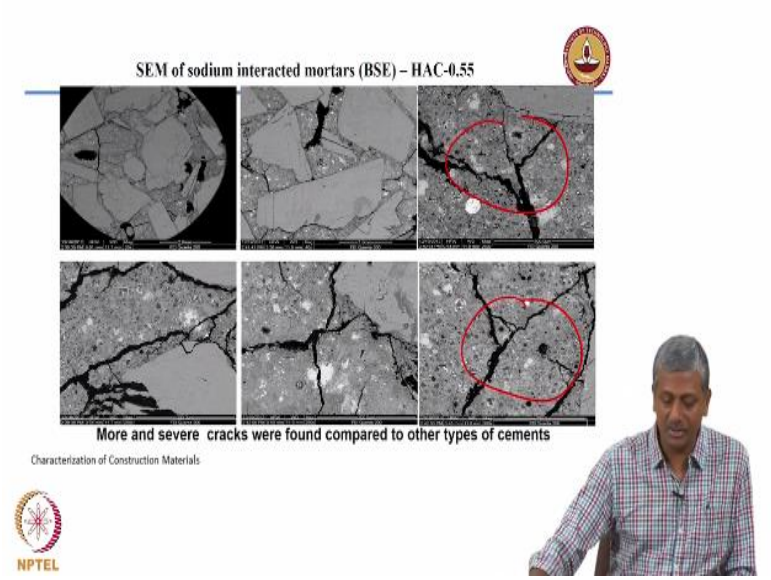

So this OPC, this is your PPC we can see in PPC, the cracks are limited. But in high alumina cement the cracking was extensive. Not just between paste aggregate within the paste itself the cracking was extensive. So there was some level of incompatibility which we did not really go into much more detail because of lack of time and we just let into conclusion that at high temperatures the system between the alumina cement and limestone aggregate seems to have some level of incompatibility.

Which causes more excessive cracking in the system which leads to more disintegration as supposed to other cementitious system.

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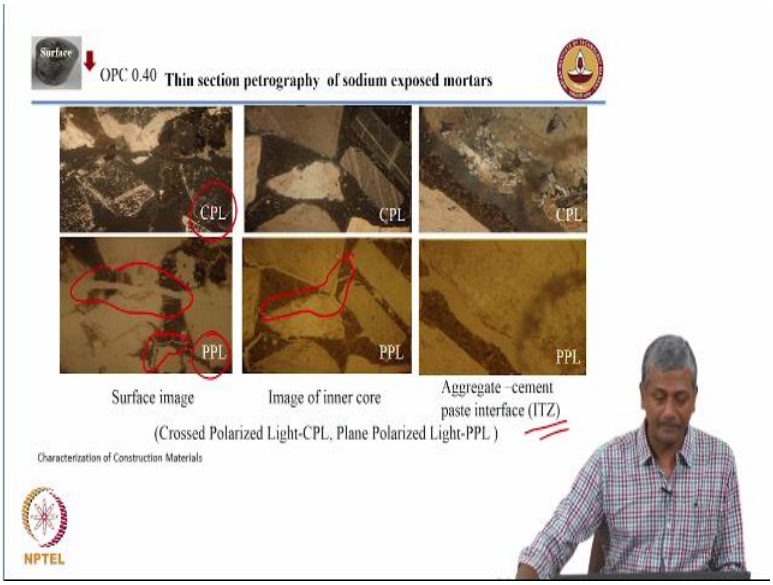

So again I am not going to conclude this more detail, I just want to also show you the comparative studies done with optical microscopy. So here we prepared 10 sections, of these epoxy impregnated samples and try to monitor the extent of cracking that happens inside the system. So now here the image is a presented crossed polarized light as well as plain polarized light.

What do you mean by plain polarized? When, the polarizer and analyzer are at the same angle. Cross polarizes when polarizer at is at 0 angle and analyzer exactly perpendicular 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 plain polarized can give you 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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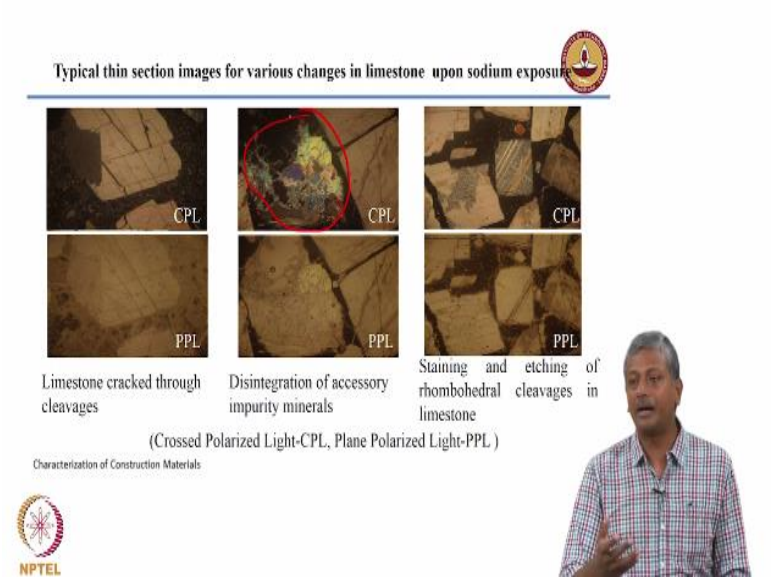

This are thin section images from various changes and limestone upon sodium exposure and what you see are there are these accessories minerals which are present in limestone what we saw is even if limestone is stable at high temperatures 7 to 900 and degree Celsius it may have some impurity minerals with start getting disintegrated at earlier temperatures and that could be the reason why in spite of having limestone as an aggregate of the cementitious water we are still getting a high level of denture ratio.

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So that was just of that study was done actually it was coupled with several other investigations also you to try and understand this problem wholly and suggest a remedy for accidental scenarios to agica. Of course, there is a lot to see as far as concrete microscopy is concerned, there are

couple of interesting websites, which you really benefit from so these two websites are quite good to see the different types of concrete microscopy examples that have been given by this authors on these websites.

Of Course there are whole lot of papers that you can actually go through to appreciate this a lot better. So I want to also show you examples of microscopy from other systems.

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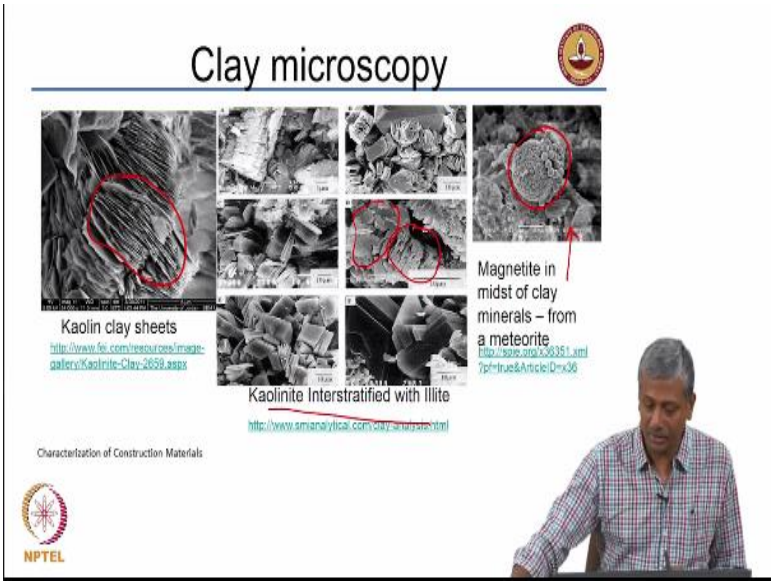

Like clay, clay is very exiting structure to be looked at under microscope has these plate like features. You can very clearly see how well you can see the sheets in secondary electron image. Now interesting example here is the presence of magnetite in mix of clay minerals from a meteor, so this is a sample come from space. You see how well we can actually monitor this and here you have an example of kaolinite clay, which is interstratified with Illite 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 very powerful tool to study the structure of clays. Microscopy is very good for studying structure of clays.

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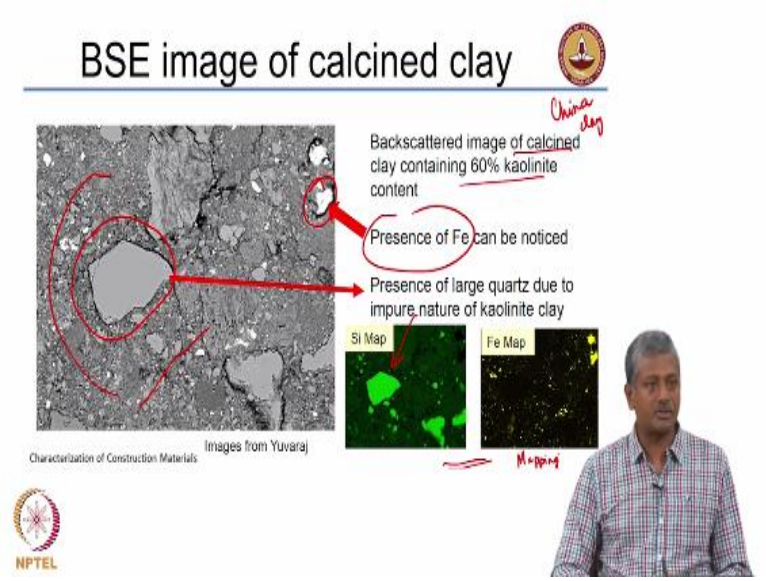

This is an example of calcined clay which we use for our recent studies to make the limestone calcined systems that go as replacement, so here this an example the maxcated image of calcined clay containing 60% kaolinite content. So please remember when we extract clay from earth it will be present with the lot of impurities. The ceramic and paint industry typically take the very high purity clay which they also called as the China clay.

China clay is the extremely white kaolinitic clay almost 95% purity 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 degrees plus because they want inert material that acts like filler a white filler is what they want whereas for cementitious materials, we can burn it at around 750 to 800 degrees Celsius.

Because that actives the clay which is against to the activation of clay that happens in the rotary kiln cement manufacture. So at 750-800 we do not produce the crystalline kaolinite we produce a metaculline, 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 is lot of iron in it when you extract it from the mines that will look like red, 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 cementic Pozzolanic qualities of that clay itself even with 60% kaolinite. So here you can see the presence of iron in this systems, calcined clay systems. And you can also see other impurities that are present now, what is this impurity? We did a energy dispersive spectroscopy mapping to see that these impurities actually just quartz, sillica.

This is obviously crystalline silica which is not going to be of any use as far as reactivity concern. But nevertheless the remaining part of the system which contains your reactive aluminum silicate from the calcined clay will give you high degree of Pozzolanic. So this is the mapping feature associated with energy displaced 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, so you will actually be doing this in the lab when we show you the demonstration.

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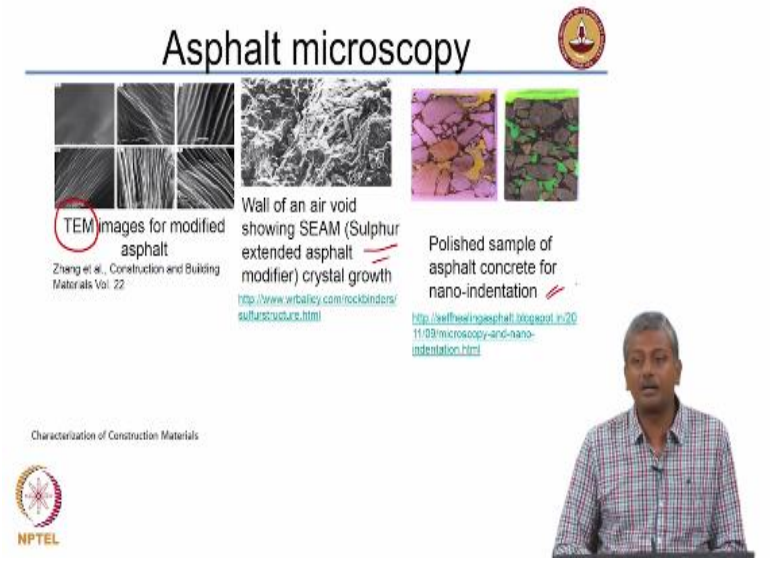

This is images from Asphalt you have transmission electron images, so modified Asphalt. Now of course much of the recent developments as for as Asphalt is concerned with the use additives in the binder like crumb rubber or you have other polymers which are the modifying the Asphalt characteristics to much better performance across the region of temperatures. So here sulphur extended Asphalt modifier is being shown and you can see crystal growth happening 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 pieces.

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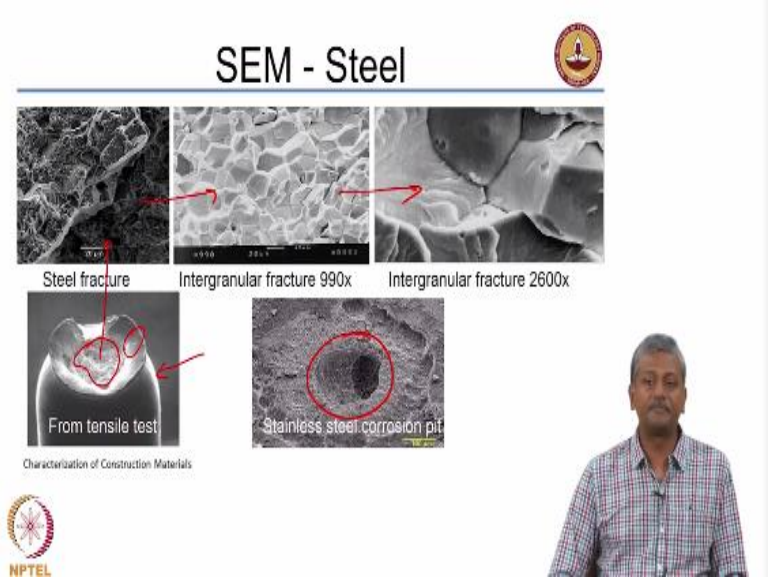

Now with steel you can produce excellent images of steel fracture for instance here, you have a steel specimen that has been pulled in tension and you can clearly see the cup formation in this case. You see the lip here and you see the grain boundary where the fractures actually happened and this steel fracture if you expand you can see features much clearer. So as you increase the magnification you can see the features of the broken grains or separated grains much clearer.

And this is actually a pitting corrosion example from steel, which has been very clearly monitored using scanning electron microscopy.

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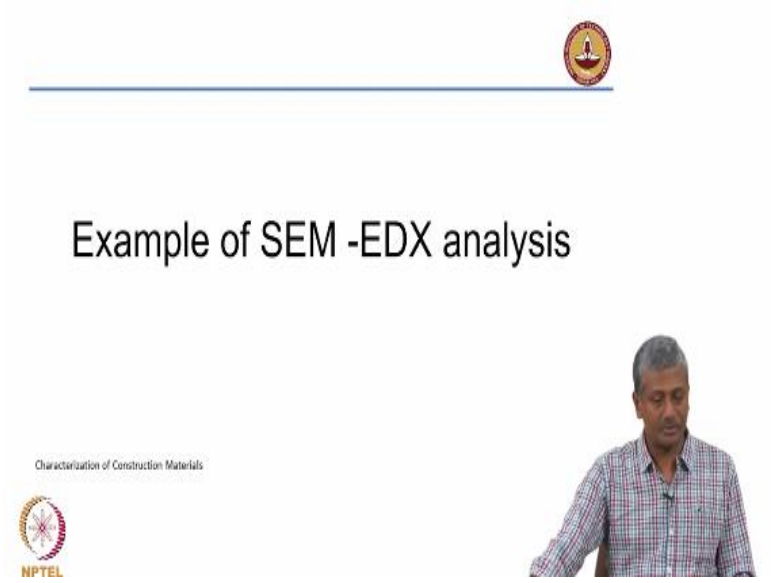

I will also show you a couple of examples of SEM-EDX analysis so you can appreciate how the information from extreme can be actually use to supplement the information again from the images.

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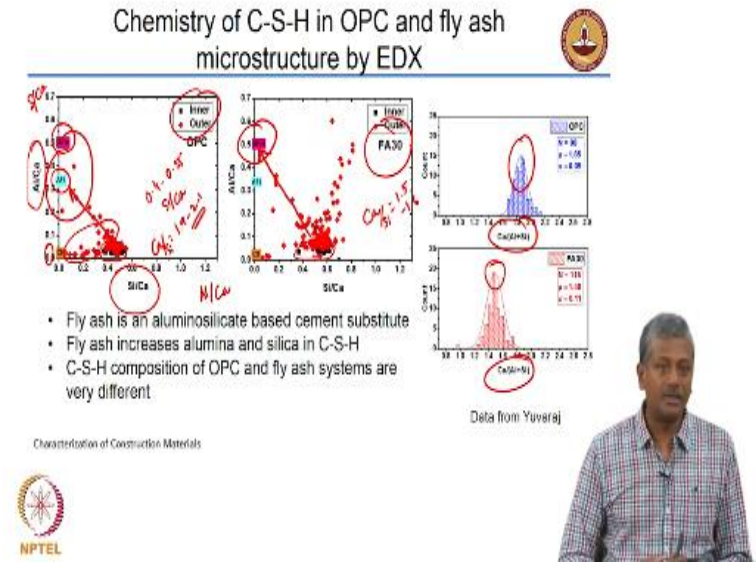

So, this is an example of C-S-H understanding in OPC fly ash microstructure by EDX. So what is typically done is several points are taken as I told you earlier, you would need to take multiple points across the CSH and analyze the atomic ratios of different elements that are coming out in your external analysis. Typical ways of plotting that is to plot either the silicon versus calcium ratio on the x axis versus aluminum to calcium ratio in the y axis.

Or sometimes you can also plot aluminum to calcium on the x axis and sulphured calcium on the y axis is 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 CSH and outer CSH, the black points represents the inner CSH and you can clearly see the black points are all in a very narrow band here.

Narrow band of let us say about 0.4 to 0.55 silicon to calcium ratio. What does that mean in terms of calcium to silicon ratio? We just divide by 1 by these numbers, so you get calcium silicon ratio. So we are talking about 1.9 to 2.1 generally. So, that is the composition of the inner CSH and you can see the amount of aluminium in the inner CSH is limited we are talking about 0 to 0.0 or 0.1 or 0.0 to 0.05 is the amount of aluminum inside the inner CSH.

When you go to the outer CSH, there is a vast range of composition that you see. What is the reason for this vast range of composition? Because the outer CSH is intermixed with several other phases. You can probably hit the calcium hydroxide phases, you can hit entering it or monosulphate phases also in the system and you can see this line is going towards the aluminum calcium axis or aluminum calcium alternate you have AFT and AFM marked there that means AFT is entering it aluminum ferrite dry sulfate AFM is aluminum ferrite mono sulphate.

And you can see that some of those points that you are showing there might be representative of entering ferrite mono sulphate. That is why you can clearly distinguish now the difference that happens with the inner and outer CSH. In the case of fly ash, what is happening at the fly ash system is that again, you get the inner CSH, which is in this range, but you see here that the overall silicate calcium ratio in the inner CHS is also moved to the right.

It is now closer to 0.6 as compared to 0.5. So the calcium desalical ratio which was 1.9 to 2.1 Portland cement systems. In the case of fly ash systems will come down about 1.5 to 1.6. The outer CSH which is a amalgamation of different components seems to point out that your tendency is to form more AFM phases, rather than AFT phases which seems to form in altering potent cement systems.

So, you get the differences compositions analyzed by doing squad analysis on the inner and outer CSH. So here also shown here is a calcium to aluminosilicate ratio in OPC and 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 CSH and the cement reaction produced CSH.

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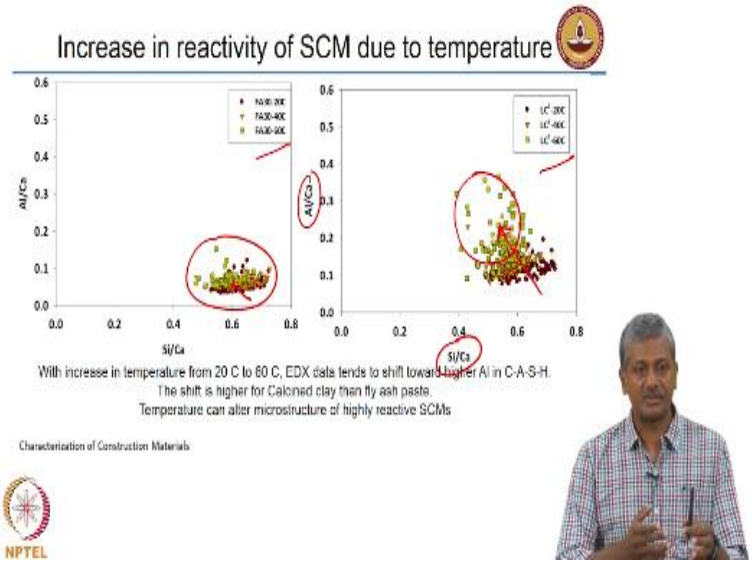

Now we I showed you the scanning electron microscopy images of the Portland cement paste of different temperature in 20, 40 and 60 degree Celsius here this just an example of fly ash in lc3 systems at different temperatures as to what really happens to the composition so what is again plotted here is the elementary ratio versus silicon to calcium 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 when they increase in temperature from 20 to 60 degree Celsius you do not see such a large change, although still the tendency is still move towards the left. In case of LC3 system limestone calcium stone system, the effect is much more significant. So what we are trying to show here is the change in temperature the composition of phases seen to indicate a major change in LC3 system as opposed to fly ash based system.

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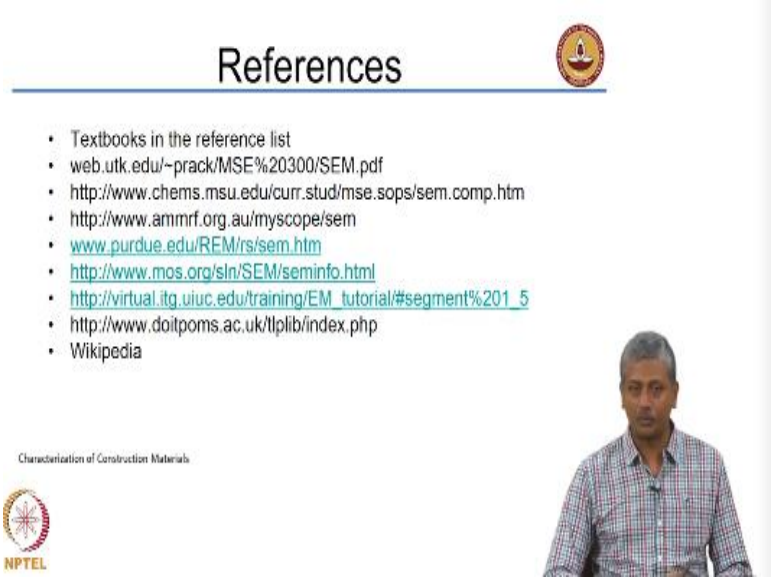

So with that I come to the conclusion of this segment of our course on optical and scanning electron microscopy, whatever also presented here are several other references which can actually add to the information that you can achieve from this lecture there are lot of instances of description of microscopy 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 peer reviewed somebody has actually gone through and certified that the information is indeed reasonable. Nobody can see its accurate, because we are dealing with an experimental science, nothing is accurate here.

What fix in it 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 balance 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 people present only in 0.1% of the our system we need to ensure that we are doing a medical as job of scanning the entire sample. 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 see more confused you can get. You are to be extremely lucky to get this right in the first, right from getting the right level of sample preparation focusing on the area then you really want to focus on because very often you get lost in your specimen because your specimen is a few millimeters in size.

Few area of interest is on 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. Justify why microscopy is needed and what features from microscopy can be actually used to show the reasons to show your microscale theory. Okay I will stop with that. Thank you.