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

Lecture - 42
Scanning Electron Microscopes - Analysis of Cementitious systems 1 - Part 1

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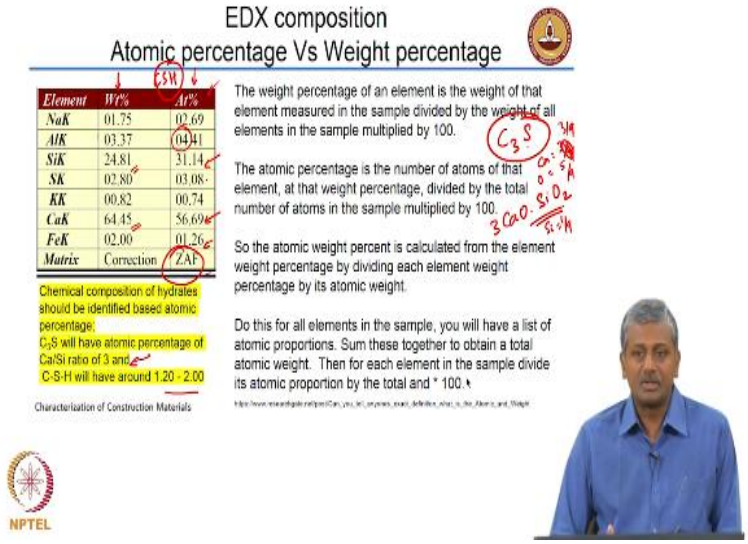

Hello everybody. So in the last class we were talking about the composition measurements that you can actually do by collecting the X-rays that are emanating from the sample after the electron beams strike the sample. So this composition that you get is typically in the percentage by weight of the component that is present in your sample. You can also then convert it to the atomic percentages based on the molecular masses of the different elements that are actually present and the atomic percentages are what determine the actual phase composition. So we saw an example of how C_3S or C_2S could be detected by X-ray analysis and you can get an estimate of the actual chemical composition of C_3S or C_2S.

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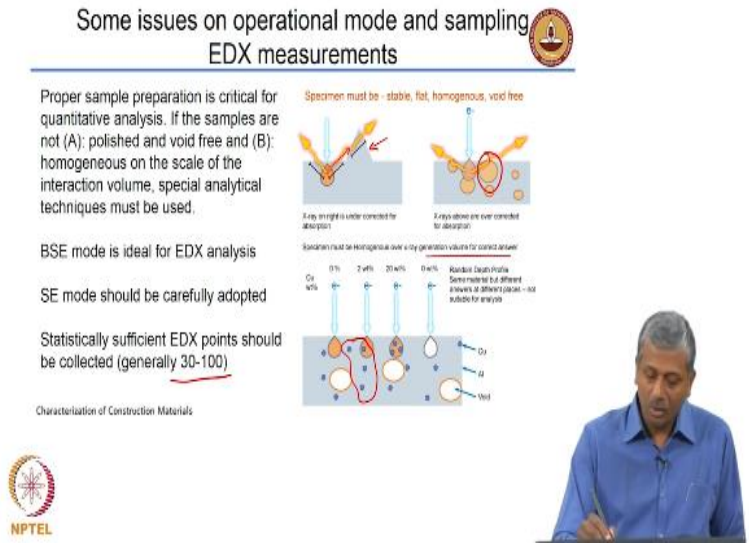

Now there are certain rules to be followed when you are actually doing measurements with EDX. It is not very simple to get X-ray counts when you actually do the analysis or when you do the microscopy itself. First of all proper specimen preparation is important. So, for example, if the samples are not polished or not void free and they are not homogeneous in the scale of the interaction volume, you can get a lot of errors from this.

For example, if you have a sample in which the polishing level is not good enough and you have a relief on the surface like this the X- rays that are trying to escape can get blocked from those locations. So you cannot really have that X-ray travelling right through to be detected by your detector. If you have voids again, there will be a lot of additional scattering that will happen and your X-rays will not actually reach the intended detector. And because of that you need to ensure that your sample is properly impregnated with epoxy that fills up the voids and you do not really get any chances of internal scattering happening for the X-rays that are coming out from the sample.

Again one aspect you need to remember is that the specimen should be homogenous over the X-ray generation volume for the correct answer. For example, if you have a lot of heterogeneities present in the sample at the point that you are trying to analyze, you will get a mixed response, you would not really get the best answer. For example if you are looking at an image where you have a large grain of unhydrated cement, that is let us say C_3S, and you choose

a spot for the X-ray analysis that is just near the C3S grain. That will be a zone or a boundary zone, where C3S is in contact with the other products of hydration like C-S-H which are just outside. So, at that point your overall interaction volume that is there, if you remember the X-rays have an interaction volume which corresponds to a depth of penetration into the specimen of nearly 5 μm. So you are actually collecting the X-rays from a bulb of the sample, which is about 5 μm in diameter. So if you are very close to a different phase, then you are likely to get some signals emanating from that phase and not just the only phase that you are pointing at. So, you need to be careful about selecting your points carefully for EDX.

The other aspect is if you want to get an overall range of compositions or to get an approximate idea about the exact composition of the phase, you need to have sufficient number of points collected over that phase. Now the idea is that, you need to be statistically accurate with respect to the kind of phase compositions that you are working out. So typically we want a sufficient number of EDX points, typically 30 to 100 is what we need to collect to ensure that we get the right compositional analysis of the phase that you are looking at. Just by 1 or 2 points detecting the chemical composition is not accurate, i.e., as engineers we should know that anything needs to be statistically proven and for that we need to ensure that we have sufficient number of data that is collected. All the more, this makes it important that you point your X-rays at the right location which offers a good degree of homogeneity within the space that you are trying to assess.

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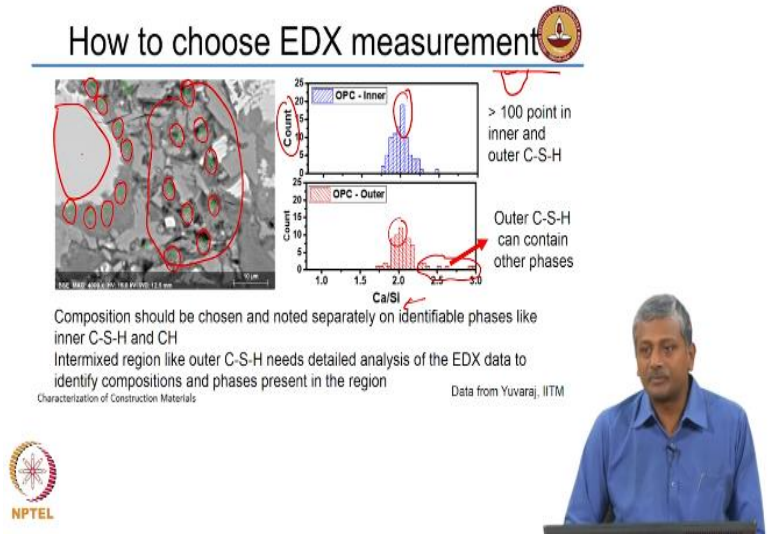

Now, again just to give you an example of how to choose EDX measurement over a given sample. So here again, there is a scanning electron micrograph of a cement paste which is hydrating. So here you have an unhydrated cement grain and around it you have this boundary which is formed by a dark gray phase or some level of gray phase and that is basically what is known as your inner C-S-H, calcium silicate hydrate.

Now slightly away from the cement you have these whiter phases, you see the whiter deposits that are there. Those whiter deposits could be calcium hydroxide phases, and then there is a different level of gray in between these white deposits. That is basically your outer C-S-H. So, this is calcium hydroxide, which is slightly white as compared to the C-S-H, but not as bright as the unhydrated cement grain.

This is a backscattered electron image. Now, why do the unhydrated cement grains appear the brightest? So unhydrated cement grains have a high density because they do not have any voids or pores within their structure. You are seeing the grain as a whole, and it does not really have a pore inside. Whereas C-S-H, we know that the process of formation is such that, there is an internal porosity that gets created with C-S-H because of which you look at C-S-H as a less dense phase as compared to an unhydrated cement grain. So you see unhydrated grains appear the brightest. Among the cementitious phases which phase will appear the brightest? You have C_3S, C_2S and C_3A and C_4AF. C_4AF will look the brightest - why? Because it has got iron in

it and that causes it to have a higher density. So the reflectivity will be maximum from iron-bearing phases.

So if you see these almost perfectly white spots in-between that could be from your unhydrated iron-bearing compounds like C_4AF. So there are different shades of grey that you observe in this backscattered image. What you need to do now is to select carefully the locations from which you want to do the analysis for. Let us say, in this case inner and outer C-S-H.

So now you see the green spots that have been marked, those are basically the numbers which are being given to the spots that have been analyzed. If you look closer the spots are actually marked in yellow. So the yellow spots, if you see for inner C-S-H are in these locations. So, right in the middle of the rim that is being created by the hydrating C_3S particles, which represents the inner C-S-H, several points are being chosen along that rim and what you are showing here is the count of X-rays vs. the Ca/Si ratio, atomic ratio that has been determined from the spot analysis of the X-rays collected from those particular spots. So you see here, that the average Ca/Si ratio in the inner C-S-H happens to be around 2.1. You get a lot of spots with an X-ray analysis that suggests the Ca/Si ratio of about 2.1.

On the other hand, the outer C-S-H that is collected in this case, does not show much difference as compared to inner C-S-H, except that you have a wide range of C-S-H compositions here and not just centered perfectly around this 2.1. You have a more boarder distribution of the Ca/Si ratio in the points here. But look at where the outer C-S-H points are being taken, you have them in these locations. The problem is twofold: One is the inner C-S-H does not appear in a fairly wide distribution or wide rim until about 7 days of hydration. So, if you are looking at very early stages of hydration, looking at inner C-S-H may be a difficult task. So at least 7 days of hydration is required before you can start observing the inner C-S-H. Outer C-S-H on the other hand, please see that it is mixed so much with so many other products. There are so many other points or rather so many other phases that are present, right in the vicinity of the outer C-S-H. So when you are actually collecting the signal for the outer C-S-H, it is quite likely that you will also get the intensities contributed by the other phases that may be likely in

that bulb of the sample (5 μm diameter bulb) that forms underneath the electron beam. That is basically your specimen interaction volume.

Please remember in backscatter we are only taking a slice. When you take a slice you see this grain here. Now, you do not know if this grain goes down gradually or ends abruptly. So, what I am talking about is you take a slice, when you see the cement grain, which is represented by this unhydrated C_3S. We do not know if the grain is like this that we are only having a small amount of that grain penetrating the sample or a larger volume that is penetrating. So because of that, you do not know where exactly you are getting the information from, if you are not directly in the phase. So what we need to be careful about is how likely are we to get an intensity count from the other phases that are in the vicinity of the object that we are trying to look at.

So here, in outer C-S-H there is always a chance of getting signals from the additional phases that are present around the outer C-S-H. So intermixed regions like outer C-S-H need detailed analysis. So the indications of the higher Ca/Si ratios, that you are seeing in the outer C-S-H is the contribution from the other phases that you see intermixed with the C-S-H.

So, what are the other phases that are there - you have calcium hydroxide obviously, but apart from this there are other aluminate, sulphate phases also like ettringite and monosulphate, that could also be contributing to the higher calcium contents of the system. Because you know that ettringite and monosulphate phases do not have any silicon in there. So it is mostly calcium and aluminium. So here, if you are looking at Ca/Si ratio you get actually points which could contribute or which could be contributed from those other phases that do not really contain silicon.

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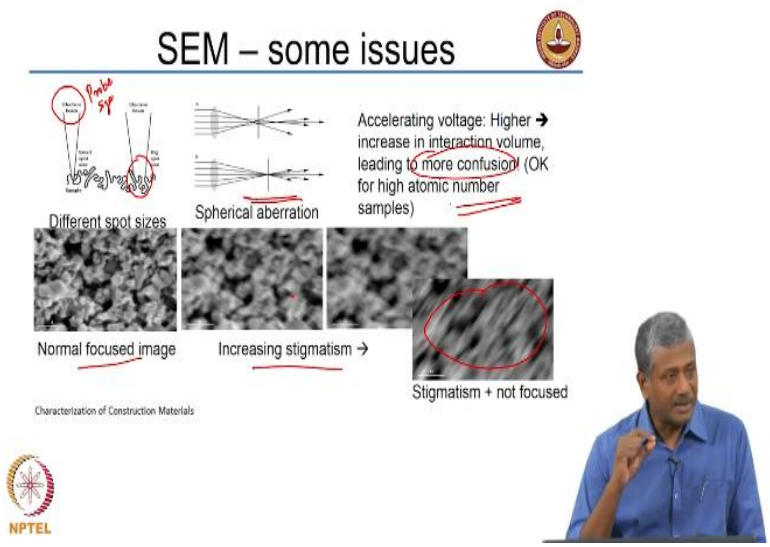

Now just in the case of optical microscopy, you have issues related to SEM also that can spoil the quality of an image. We talked earlier about the fact that because you are trying to control magnetic fields, you can often get issues of astigmatism. So, you see here when you increase the level of astigmatism the image appears to be focused very poorly and you have some sort of a shift of the image along one direction. Let us say X or the Y direction. You see how the image has actually shifted completely and it leads to a completely poor quality focus that you get. So if you control the magnetic fields and equate the focal lengths along X and Y direction, then you will be able to get a much better focused image. You can also get a normally focused image here if you do a good control of the astigmatism which is not seen in these 3 images that are shown on the right side. The image on the left side is the actual focused image, and you can see how that actually changes when you have increased levels of astigmatism in the sample.

The other aspect is the size of the electron beam has to be small enough to actually look at the features on your sample. If your features are extremely minute then you need to choose electron beams which have a very small diameter, which we call it as probe size. So if you want to get a much clearer image with respect to minute details of the surface, then you need to reduce the probe size. That is basically the diameter of the electron beam that is striking the sample. You see here as the electron beam diameter becomes larger, you can miss those minute features on the surface.

Spherical aberration is quite similar to what we have in typical optical lenses. Most of us wear glasses to ensure that we are able to correct deficiencies in our own lens by adding an additional lens on top. So here the problem is not that acute, you can actually control that by simply adjusting your magnetic fields so that the rays converge properly at one point instead of having different locations of convergence.

The other problem is, as we discussed earlier, that we are trying to have higher accelerating voltage to increase the amount of interaction that we have with the sample. Now that is good, but the only problem is it can lead to more confusion. Like we saw in the previous case where, if you want to collect X-rays to look at the compositional analysis of the phases that you are actually observing, the amount of information you get will be from a larger depth if the accelerating voltage is more. So you will get a lot more confusion in the way that the data is actually interpreted. But for higher atomic numbers samples, which are quite dense, we want the penetration to be at least sufficient to get some representative idea about what we are looking at. So because of that it is all right in those cases to have a higher accelerating voltage.

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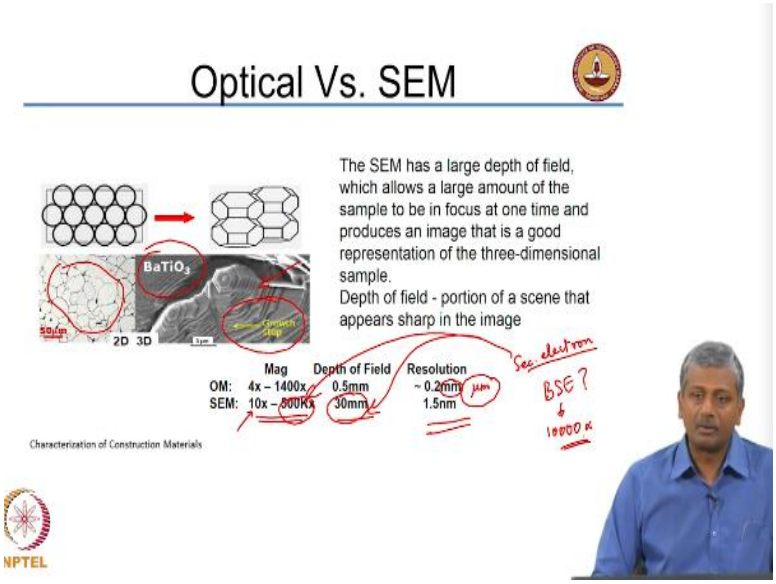

So, just to give a contrast with respect to the type of imaging that is possible with optical microscopy and scanning electron microscopy. We have talked about this earlier that for optical microscopy, you have to prepare a very flat specimen to ensure that you get proper reflectivity or it has to be transparent or translucent to allow light to pass through.

On the other hand in SEM we are now able to distinguish features that are at different locations because we have a much larger depth of field. SEM has a large depth of field and this allows a large portion of the sample to be in focus at the same time.

So for example here, if you look at this barium titanate ($BaTiO_2$) structure, under the optical microscope, all you see is the grain boundaries - the individual grains that are there and the grain boundaries because you have polished the specimen flat. But interestingly when you actually look this under the SEM, you actually see the growth steps as to how the crystallization has occurred of barium titanate. So you actually see the individual crystals of barium titanate here in this case. So the amount of information you get and the details that you can collect from scanning electron microscopy are far greater than what you can do from optical microscopy.

Again, if you look at the comparison, typical magnifications possible with optical microscopy are only up to about 1400x not more than that. But again, please remember, that is a compound lens system, where you have an objective lens magnification you multiply that by the eyepiece's magnification to get the overall magnification. So 1000x does not mean that the objective lens is 1000x. Objective lens most probably will be at the maximum of about 100x. You can change the eyepiece lenses to increase the level magnification. The magnification of scanning electron microscopy can be as much as 500,000x. So we are talking about a completely different range of measurements that are possible with scanning electron microscopy.

Depth of field there is absolutely no comparison, 0.5 millimeter actually, you have to be lucky to actually focus on objects that are 500 µm different in their Z-direction, in the case of optical microscopy. You need much more flatness than that, but you can still somehow image objects that are 500 µm different from each other in terms of their Z-dimension. But in the case of SEM, even 30 millimeters difference in the top and bottom level of the sample can still be imaged all at once. The depth of field is as much as 30 millimeters in the case of SEM.

The resolution, in optics we are limited by the wavelength of visible light. There is an error related to the units that are shown in slide, this is actually not mm, it is µm - 0.2 µm. For

the human eye we discussed earlier that it could be about 0.1millimeter or 0.1millimeter divided by the magnification with which you can observe. So that is the limit of capability of detection of human eye, but when you look at microscopy - optical microscopy can get you to about 0.2 μm at the most, whereas SEM can have a resolution as high as 1.5 nm. So, if you really want to go towards more and more nano level details of your sample, you have to shift to higher order SEM. You need to have a very strong electron beam which can be generated by your field emission type of guns which can increase the level of sharpness that you see in your objects, and in those cases you can actually resolve as much as 1.5 nm.

But if you really want to get to that resolution to a large degree of accuracy, you will have to shift to other techniques like transmission electron microscopy, and that will give you a much better representation at such sizes. It is not very easy to pick these sizes out with scanning electron microscopy.

But what you need to understand is, in terms of your secondary electron imaging, that means when you are trying to look at the morphological or topographical details of the sample, in that case, you have this high depth of field - 30 millimeter, for secondary electron imaging. What about BSE? For backscattered electron imaging, you need to prepare a polished sample. Your sample has to be extremely flat, so that case obviously you do not really get the depth of field. You do not expect that depth of field because your analysis is completely based on the compositional contrast provided by the relative densities of the different phases. Here we are not worried about depth of field in that case, but in secondary electron imaging is where you get the depth of field. Similarly the magnification at the highest levels of 500,000x times is generally provided with secondary electron imaging and not for backscattered imaging. In backscatter, you will be lucky to get good images at around 10,000x and not more than that. It is very difficult to actually polish your sample to such a great extent that you are able to get clear images at magnifications of more than 10000x.

But for most of our applications as far as cement and concrete science is concerned, backscattered electron imaging with magnifications of up to 5000x are more than sufficient. We really do not get too much more information beyond that. In metals, of course you can polish to a very large degree. You do not have a problem, polishing metals is easy. You can easily polish

metals because more or less they are homogenous. The problem with polishing concrete is that it is composed of heterogeneous phases and if you try to polish that together, one phase would obviously get polished more than the other and you would not really get a good level surface in the case of concrete. All right, so let us look now at some examples of microscopy study.

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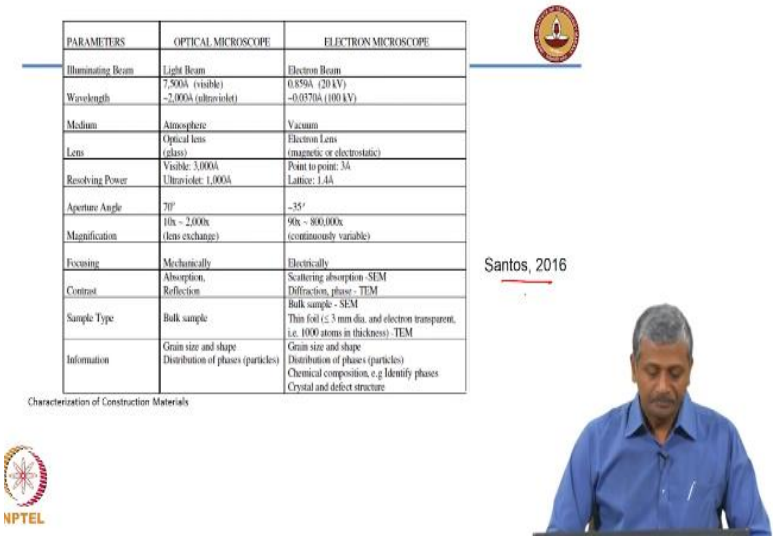

Of course, this is just a table comparing your optical microscope and electron microscope for your information, there is a lot of issues that are presented here. Of course you must realize that such tables are presented in papers which are based on research carried out by individuals. So they may or may not be 100% accurate, information in textbooks are more or less 100% accurate, but when you read research papers you need to take the information with a pinch of salt that everything will not be perfectly accurate. But to the best of the author's representation they provided these numbers for you to compare. So we won't look at this in more detail, we have already talked about this in various phases of our discussion in this chapter.

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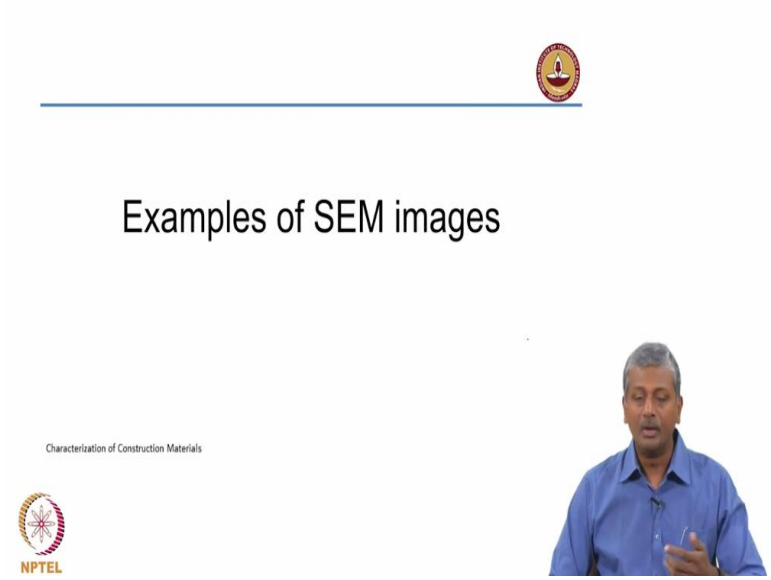

So, we will move on to some examples of SEM images.

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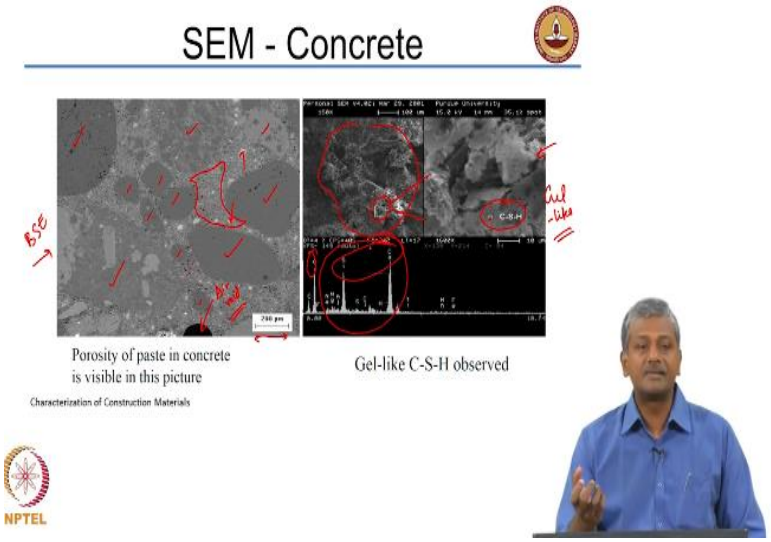

So, let us look first at an image taken from concrete. On the left is a backscattered electron image, how do you know this is a backscattered image? It is very flat. You do not really see any relief or difference in heights between the different phases. So this is a flat surface which has been polished to a large degree and you can see various phases, you can see the aggregates, those are all your aggregates. You can see the paste that is between the aggregate and within the cement paste you also can make out different levels of grain. The unhydrated grains are the brightest and then the porosity - The black spots are the pores, the porosity of the paste is clearly visible in this picture and you can see that the pores are looking darkest or black.

What do you see at the bottom? The black area is a large air void. So you can easily distinguish here what is an air void and what is a pore? You see the pore inside the cement paste and you see the air voids that are much larger in size. So the air void is about 200 μm in diameter whereas, the pores are much smaller than that. Pores can vary over at large size range, starting from a few nanometers all the way to tens of micrometers. So you do not really see those in clear resolution in this magnification of the image, but if you go much larger in magnification, you will be able to resolve the pores also.

What about on the image on the right - is it a backscattered or secondary electron image? That is a secondary electron image. You see what we have tried to do is image a fractured sample of the concrete and a small zone in this fractured sample is magnified to give you the details of what is being observed for the phase that is marked here as C-S-H. And how do we know this is a C-S-H phase? A spot analysis has been taken there and you get the calcium, silicon and oxygen peaks in this location. So, C-S-H obviously is calcium silicate hydrate. The fact that the crystalline morphology does not indicate any specific clear cut definition of a structure shows that this is a gel-like phase. This gel-like appearance is very characteristic of calcium silicate hydrate. So you get X-ray intensities contributed by calcium, silicon and oxygen in this case which leads you to characterize that it is a calcium silicate phase.

Now how do you know it is not a C_3S phase? Because C_3S or C_2S are also calcium silicates, so you should get the same peaks from there. Oxygen should also be there - calcium silicate has oxygen in it. So any unhydrated cement will also show the same peaks but the relative intensities of the calcium, silicon peaks may be quite different in those cases and the fact that the morphology that you are observing here is gel-like indicates that you are looking at C-S-H. If you are looking at pure grains of C_3S and C_2S, you will see much different morphologies being exhibited corresponding to the crystalline structure of those materials.