Characterization of Construction Materials
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Lecture - 43
Scanning Electron microscopes - Analysis of Cementitious Systems 1 - Part 2

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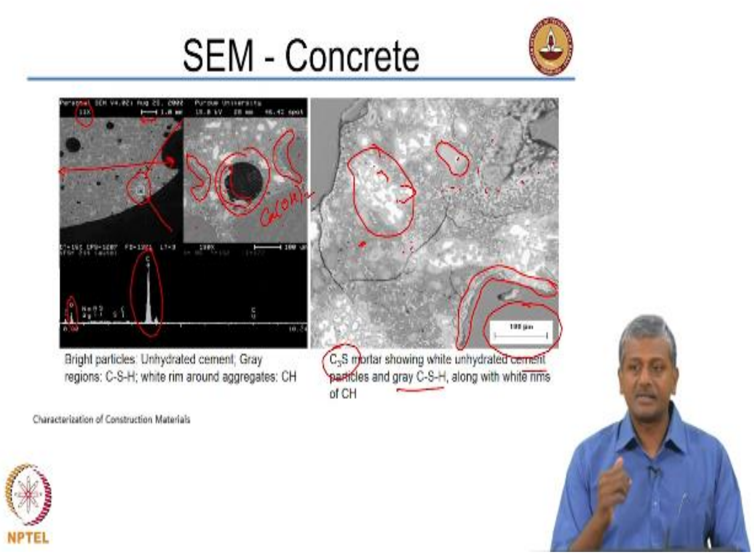

SEM - Concrete

Bright particles: Unhydrated cement; Gray regions: C-S-H; white rim around aggregates: CH

C_3S mortar showing white unhydrated cement particles and gray C-S-H, along with white rims of CH

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Now, again these are backscattered images taken from mortars, not concrete. There is no coarse aggregate in this case. So you have here a system in which again this is a much lower magnification image on the left side, it is an image taken at only 11x; 11 times magnification. That means the field of view you are looking at this width corresponds to 1 millimeter. So this entire field of view is probably about 10 millimeters or so. That is what you are looking at.

When you look at electron microscope images or any other microscopy images, make sure that you always see that there is a scale bar presented. That is absolutely important. Without the scale bar, the picture has no meaning. If there is no scale bar, the picture has no meaning. That is why, when people go for field explorations, you see that when they take the images of various objects, they put some object for reference like a pen next to the object that they are trying to image. The idea is to just provide an idea of the scale or size of the material. So any image which does not have a scale bar on it is a waste. You need to have a scale bar always with an image. And, most microscopes automatically give you the scale bar, but in some cases you may have to actually additionally put in the scale bar to ensure that you are able to show that very clearly on the image.

So here you see an example on the left side, of a cement mortar. And a smaller area in the cement mortar is zoomed and magnified on the right side, you see here you have aggregates that are siliceous aggregates and you have the paste in between the aggregates. There is also an air void and what you see here is a deposit lining the air void. A spot analysis of the deposit shows that you get calcium and oxygen peaks and that is basically calcium hydroxide. So if you look at most literature, as to where calcium hydroxide can be found in cement paste, typically calcium hydroxide is found mixed with the outer C-S-H, but because the interfaces between the aggregate and paste as well as the voids provide a large enough area for this highly crystalline phase to grow and nucleate into a much larger size. That is why you find air voids typically lined with calcium hydroxide. If you notice very closely at the aggregate-paste interface also, you see a whitish layer forming. So there is indeed a large amount of evidence that indicates that calcium hydroxide does grow in the spaces next to the aggregate. Why does it want to grow in that space? Because what happens in the interfacial transition zone? You have much larger porosity available at the ITZ. So, there is more space for a crystalline material like C-S-H to grow.

If you see the image on the right, it is an image taken from a C_3S mortar. That means, there are no aluminate phases in this case. You only have C_3S reacting with water to produce cementitious hydrates. So again, please note this level of light gray, which you see around the aggregate - that is your calcium hydroxide. You can also see calcium hydroxide in several other locations. You see all those whitish specks in between the gray - that is your calcium hydroxide.

But what you also see are these white specks which could represent grains of C_3S. And you see that these grains of C_3S have hydrated in specific locations, these are all the hydrate products; the grey level around the white is the hydrate or inner C-S-H that is actually formed in this case.

So what you see here is a grain of C_3S as that has got almost completely hydrated. You only see a small speck of white inside. So you can see the features very clearly in this case. So, you see the cement particles which are white. You see the gray levels - different grays of the inner C-S-H and the outer C-S-H; you see the outer C-S-H is darker. Why do you think the outer C-S-H appears darker? Because it has got more pores; porosity in outer C-S-H is much greater. Inner C-S-H is denser, because it is forming right on the surface of your C_3S. Outer C-S-H is formed by dissolution of the cementitious particles. So in the process of formation of outer C-S-H, lot of porosity is entrapped within the structure of the outer C-S-H. Whereas inner C-S-H is a lot more denser.

The calcium hydroxide, of course, you cannot directly appreciate the difference between calcium hydroxide and inner C-S-H in terms of gray levels in this image probably. But if you do a proper contrast, you will actually get calcium hydroxide very clearly apart from your inner C-S-H in terms of difference in gray levels.

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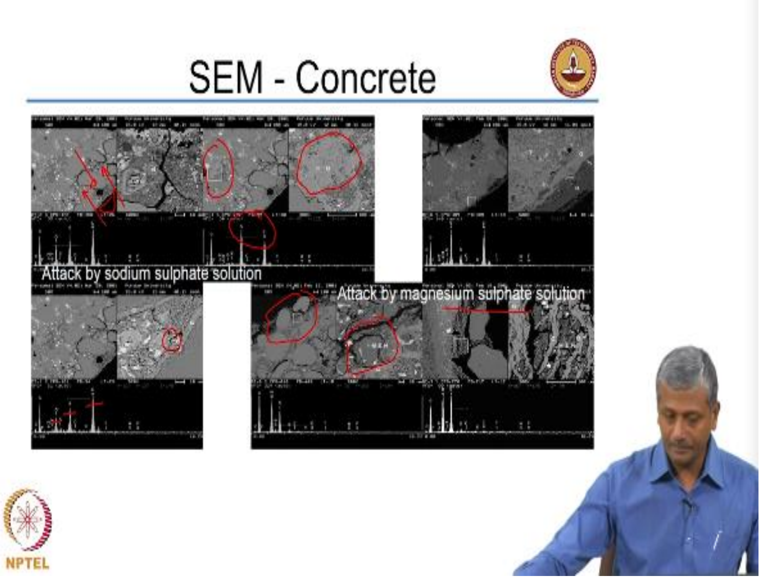

SEM - Concrete

Attack by sodium sulphate solution

Attack by magnesium sulphate solution

Again, other examples of concrete, specimens which have been attacked by sulphate solutions, when external sulphates enter the concrete they interact with the cementitious hydration phases to produce attack products like gypsum and ettringite. So here (top left image in slide), for example, is a cement mortar, which is in contact with this solution of sodium sulphate. The solution is on the side that is black in color. So the sulphate basically penetrates in this direction (as indicated by arrows drawn) into the sample and you see very clearly that there are zones inside the sample where you form very large deposits, in this case, it is been marked as G because it is gypsum (calcium sulphate).

In the case of other zones which are located inside, there is a spot mark as E which is ettringite because they have calcium, sulphur and aluminum. Ettringite is one of the common phases that forms in sulphate attack which causes expansion and cracking of your concrete.

In the case of magnesium sulphate, you often form this non-cementitious phase called magnesium silicate hydrate. That happens because your calcium silicate hydrate progressively decalcifies; the calcium keeps going out and slowly gets replaced by magnesium. So you have a lot of deterioration near the surface and that is where you see that your C-S-H has been completely converted to magnesium silicate hydrate.

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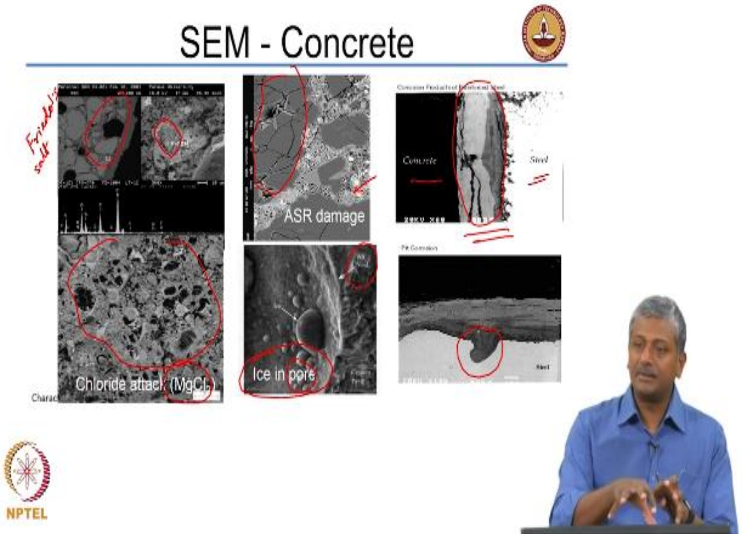

SEM - Concrete

More examples of SEM from concrete are given here. Here (top-left image in slide), you see a phase that has been marked as F-CSH; this is basically a cement mortar, which has been stored in a magnesium chloride solution. Now in magnesium chloride, the chlorides basically will form salts with the aluminates which are called Friedel's salt. The aluminate phases in cement react with chlorides to form phases like Friedel's salt which binds the chlorides and prevents it from getting to the steel to cause corrosion. This binding increases when we replace cement with more aluminous supplementary cementitious materials such as slag. So this is an example of a Friedel's salt phase.

What you also see is, in this magnesium chloride attack, you form a surface zone that is highly porous (bottom-left image in slide). You can see some porosity in this surface zone. But you see here clearly that the internal structure has become completely leached out. So there are a lot of phases that have leached out and you get a very porous appearance on the surface.

This is an example of alkali silica reaction damage (top-middle image in slide). You see the aggregate is completely cracked in this case. Because we know that alkali silica reactivity happens with reactive aggregates in the presence of a strong concentration of alkalis in the surrounding medium. The reaction leads to a complete destruction of the aggregate and this can be imaged obviously as cracks in this case. We saw earlier in optical microscopy also, we could see that the rim forming around the aggregate of the alkali silica reaction gel was the one which was causing the distress in the concrete. So here this is an example of backscattered SEM imaging.

Now this is a very interesting image (bottom-middle image). Again is it a backscattered or secondary electron image? It is a secondary electron image because you can actually see the spherical ice crystals that have lined inside the air void (not a pore). So it’s a large air void, inside of which has been lined by ice crystals. If you remember, we do air-entrainment in concrete to ensure that there is space for the water to transform to ice, so ice should be forming inside the air voids. And this is a very interesting image which shows your ice formation inside air voids.

Another image (top-right image) is of corrosion of steel in reinforced concrete. When you are imaging a backscattered sample of a section taken at the steel-concrete interface, the steel obviously will appear extremely bright because it is much denser than concrete. So here concrete is appearing black. But the rust products which are forming at the interface of the steel and concrete have different levels of gray. And in the bottom-right picture, you can actually see the pit that has formed in the steel. So this basically is an example of pitting corrosion.

So see how nicely these have been imaged as far as the concrete research studies are concerned. So what you are trying to do is understand the nature of the durability problems by the kind of phase alterations that have happened inside the cementitious system, and that is what you’re observing very clearly in these images.

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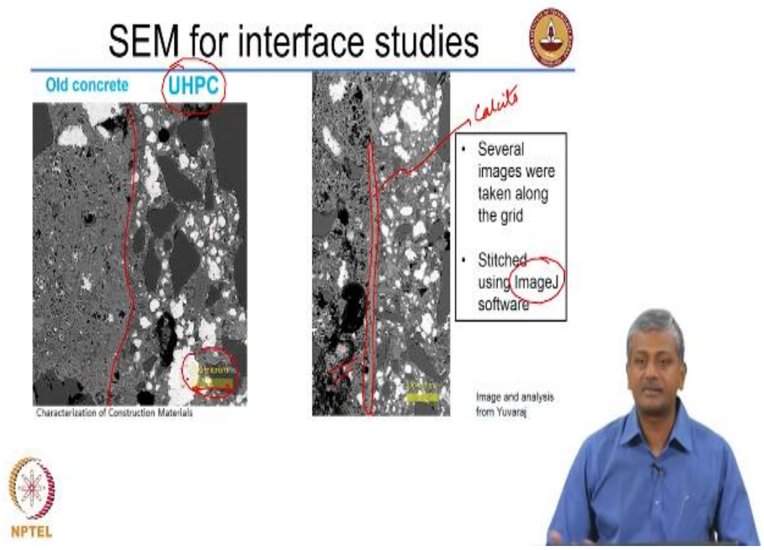

SEM for interface studies

Old concrete

UHPC

Calcite

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

Characterization of Construction Materials

Image and analysis from Yuvaraj

This is an example of some studies that we have done in our lab here, where we looked at ultra-high performance concrete as an overlay for existing cracked old concrete beams that could actually lead to a repair being done on a regular concrete beam. So here you have old concrete and you can clearly see the interface between the old and ultra-high performance concrete layer that is been kept on top.

Now what is the distinguishing feature here is that you have a lot more unhydrated cement in ultra-high performance concrete. Why? You have a very low water-cement ratio, so there is not much chance for most of the cement to hydrate. So ultra-high performance concrete does not lead to a lot of hydration, but it leads to a dense packing because of the kind of particles that you actually select with different particle size distributions to form a compact microstructure. You can see very clearly that the porosity in the UHPC is much lower as compared to the porosity in the old concrete.

Now of course in this case since we had to image a very long interface, you can see that the size (scale length) is about 100 μm. So we are trying to image close to more than 500 μm in this picture. So if you have to take high magnification images, you then each need to stitch them together using some image analysis softwares to try and figure out how the interface actually continues over a certain range.

Again, this is another example of the interface over old concrete. Now interestingly what you see here is this whitish layer formed on the surface of the old concrete to which the UHPC is actually bonded. That whitish layer basically is calcium carbonate or calcite. Why is calcite forming on the surface of old concrete? Because of carbonation - the old concrete is lying outside in the atmosphere and there is atmospheric CO_2 entering concrete and leading to the formation of a layer of calcium hydroxide outside.