Admixtures And Special Concretes

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Lecture -49

Mineral Admixtures : Pore solution analysis

Hydration characteristics of concretes with mineral admixtures:

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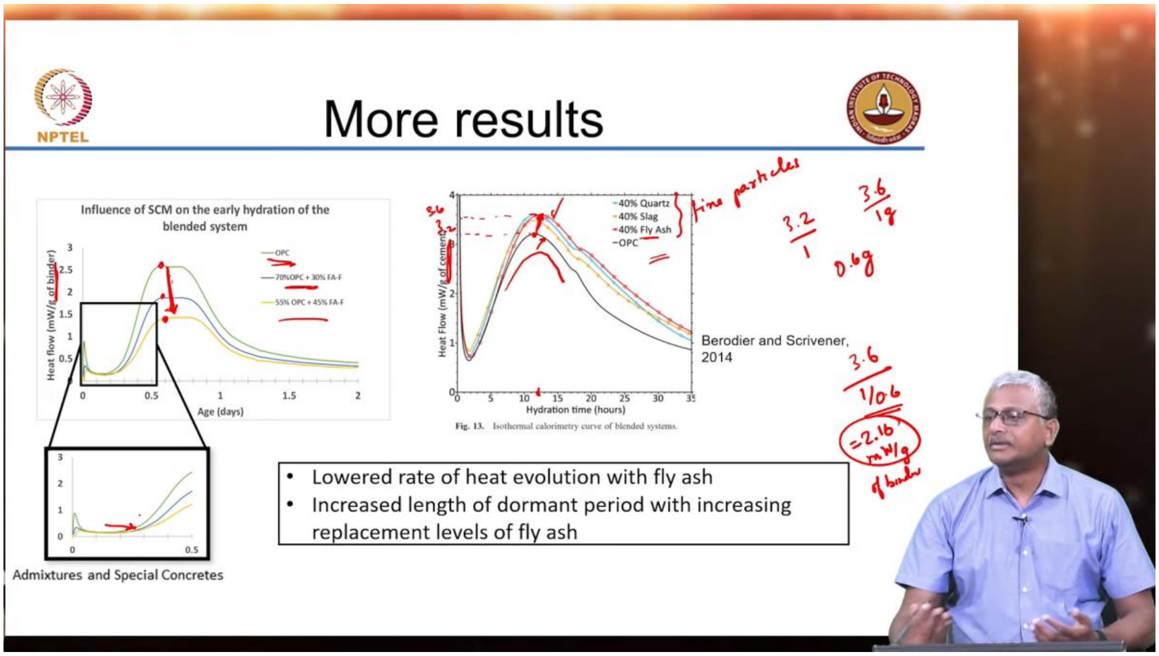

More results

Influence of SCM on the early hydration of the blended system

Fig. 13. Isothermal calorimetry curve of blended systems.

Berodier and Scrivener, 2014

- Lowered rate of heat evolution with fly ash
- Increased length of dormant period with increasing replacement levels of fly ash

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Good morning all, so in the last class we were talking about how we can look at the hydration characteristics of concretes with mineral admixtures with the help of calorimetry and very often you see results presented in papers in two different fashions, one is heat rate per gram of binder, the other way is to present it in terms of heat rate per gram of cement. When you present in terms of heat rate per gram of binder it explains to you what is the collective reactivity of the combination of cement and mineral additive, right. But when we present it in terms of heat rate per gram of cement it gives an indication of how much the cement reaction is getting accelerated because of the presence of the mineral additive. So in the example that we saw in the last class, so what you saw from this picture here is this heat flow is presented in terms of milliwatts per gram of cement and compared to the OPC mix the mixes with the mineral additives even at about 40% replacement are still showing much higher numbers, right. So, the peak heat rate is much higher even with your mixes with 40% replacement OPC with fly ash, quartz, and slag and that is because it is presented in terms of milliwatts per gram of cement. So, as I had mentioned earlier cement is only 60% of the entire system.

So, the heat rate that is being attributed to the cement needs to be normalized to the actual binder that is present if you want to present in terms of the binder heat rate. So if you do the normalization you actually get the binder heat rate of only 2.16 milliwatt per gram. So with 40% replacement of cement your actual heat rate because of the binder being there is only about 2.16 as compared to nearly 3.2 for the case of plain cement, right. So nevertheless there is a clear indication that in the presence of fine mineral additives the cement hydration especially C3S hydration gets accelerated. So that is one thing that you need to always remember. The other aspect is if you look at the early age characteristics of fly ash-based concrete mixes very often you will see this delay in the onset of the main peak which means increase in the length of the dormant period happens when you have higher replacement levels of fly ash.

Now obviously that is related also to the fact that your setting time is also increased when fly ash is used as a cement substitute.

Aluminate-sulphate reactions:

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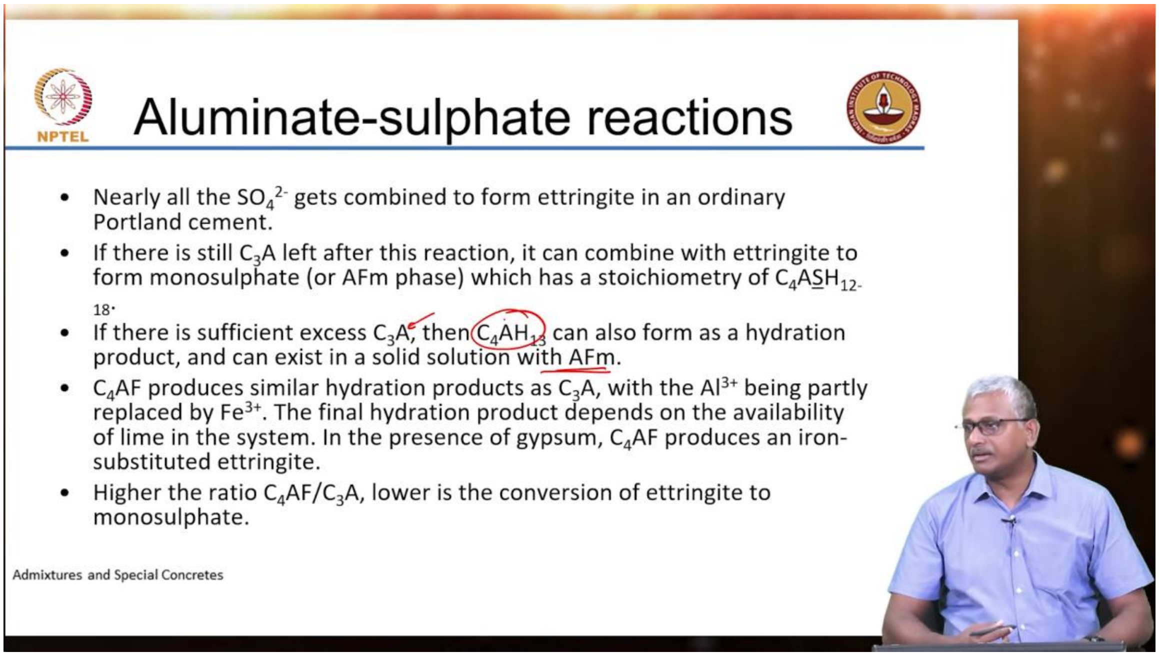

NPTEL

Aluminate-sulphate reactions

- Nearly all the SO_4^{2-} gets combined to form ettringite in an ordinary Portland cement.
- If there is still C_3A left after this reaction, it can combine with ettringite to form monosulphate (or AFm phase) which has a stoichiometry of $C_4A\underline{S}H_{12-18}$.
- If there is sufficient excess C_3A, then C_4AH_{13} can also form as a hydration product, and can exist in a solid solution with AFm.
- C_4AF produces similar hydration products as C_3A, with the Al^{3+} being partly replaced by Fe^{3+}. The final hydration product depends on the availability of lime in the system. In the presence of gypsum, C_4AF produces an iron-substituted ettringite.
- Higher the ratio C_4AF/C_3A, lower is the conversion of ettringite to monosulphate.

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Now just to come back to this aspect about sulphate optimization if you remember our discussion in the first couple of lectures on cement chemistry we know that there is sulphates available in your system and there are aluminates available the reactive aluminates are basically your C_3A. Initial hydration reactions involve the combination of C_3A with the sulphate in the presence of water to start forming ettringite and in the normal cases where there is an excess of aluminate present this ettringite slowly gets converted to monosulphate. So if there is sufficient excess C_3A then your final product becomes AFM and sometimes you also have other calcium aluminate hydrates that can form as a hydration product and exist in a solid solution form. Now what happens here is that if you have a mineral additive it is bringing in an additional source of alumina like fly ash or slag or calcium clay it is bringing in alumina and in the case of alumina from calcium clay or slag there is a higher reactivity in the system.

Alumina from slag or calcium clay is of a more reactive type so there will definitely be a requirement of this alumina to be compensated by an excess bit of sulphate. So that is why we want to do what is called as sulphate optimization in the case of mineral admixture-based concrete.

Aluminate reactions and optimum sulphate content:

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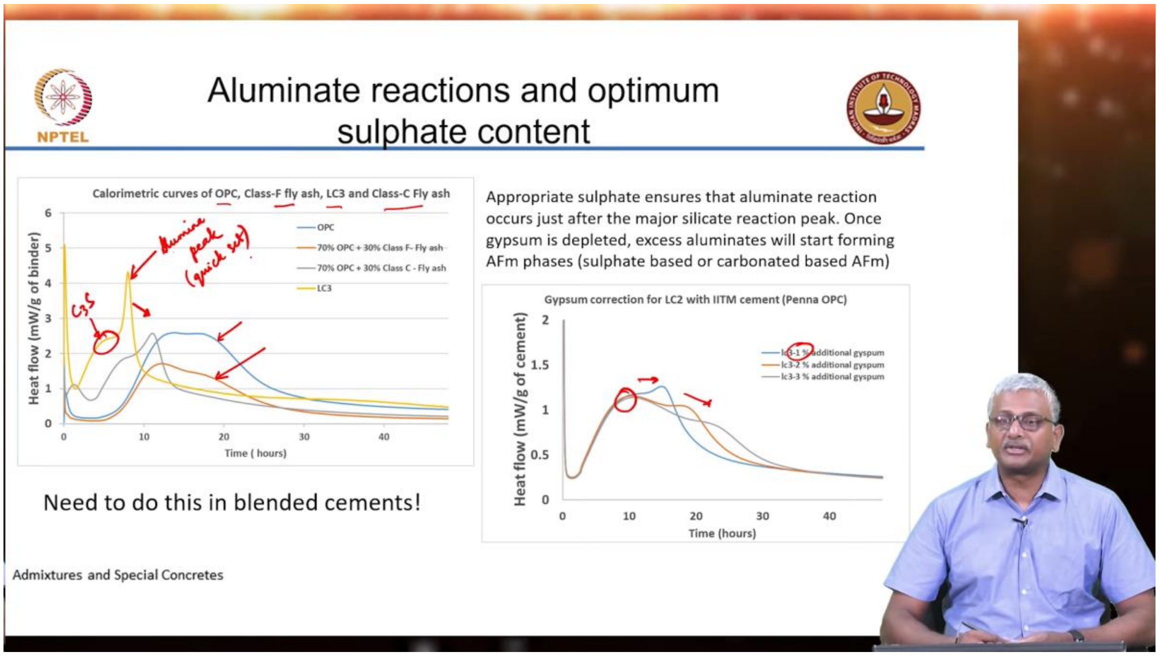

Aluminate reactions and optimum sulphate content

Appropriate sulphate ensures that aluminate reaction occurs just after the major silicate reaction peak. Once gypsum is depleted, excess aluminates will start forming AFm phases (sulphate based or carbonated based AFm)

Need to do this in blended cements!

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So again here what is presented here is calorimetric curves of OPC class F fly ash LC3 and class C fly ash. LC3 is limestone calcium clay cement. So here again you can see these reactions that are attributable to the alumina if your sulphate is not properly optimized.

So your OPC is this blue curve, OPC is the blue curve this 70% OPC plus 30% class F fly ash is here. Now in the class C fly ash and in the LC3 especially in the LC3 the alumina is in a very reactive form and here this peak this is because of the C3S reaction primarily silicate hydration but the peak that comes after is because of the alumina, this is the alumina peak. Now the danger of having less sulphate in your system is that this alumina peak may completely encompass the C3S peak also. You may end up completely encompassing the C3S peak and not allowing your silicate hydration reactions to proceed normally. So you want your silicate hydration to happen in a normal fashion because that is what leads to the strength development in your mixture.

So what you need to do is bring in sufficient excess sulphate so that you can push this alumina peak to a later time period. You put in more sulphate in your system so that this alumina peak gets delayed as you are doing in a case of a normal Portland cement. So that is what is being done in this case in the diagram on this right here. So, you see that LC3 curves are presented here, LC3 with 1%. So this is the same LC3 here which is showing a very high peak at about slightly less than 10 hours.

So what has happened is with 1% additional gypsum this peak now has been pushed a little bit to the right. With 2% to 3% it gets shifted further to the right. In other words now you are allowing your silicate reaction to proceed normally without being interfered by the aluminate reaction. So, in cement chemistry, it is very important for us in terms of early age strength to have the silicate reaction proceed normally. So whenever you have a reactive alumina source present you need to compensate the system by adding extra sulphate so that you allow your silicates to react early

And if you do that you get normal strength development and you will obviously not have a very quick set. This may actually lead to a quick setting also. If you have alumina reacting fast you may actually get a quick set. So, you will get a controlled setting and you will get a normal strength development. So, research has actually shown that when you have calcine clay-based systems if you do not do the sulphate optimization, you end up getting lower early strengths.

So that is something that you need to be careful about in order to design concrete mixes with the right level of strength development.

Composition of pore solution:

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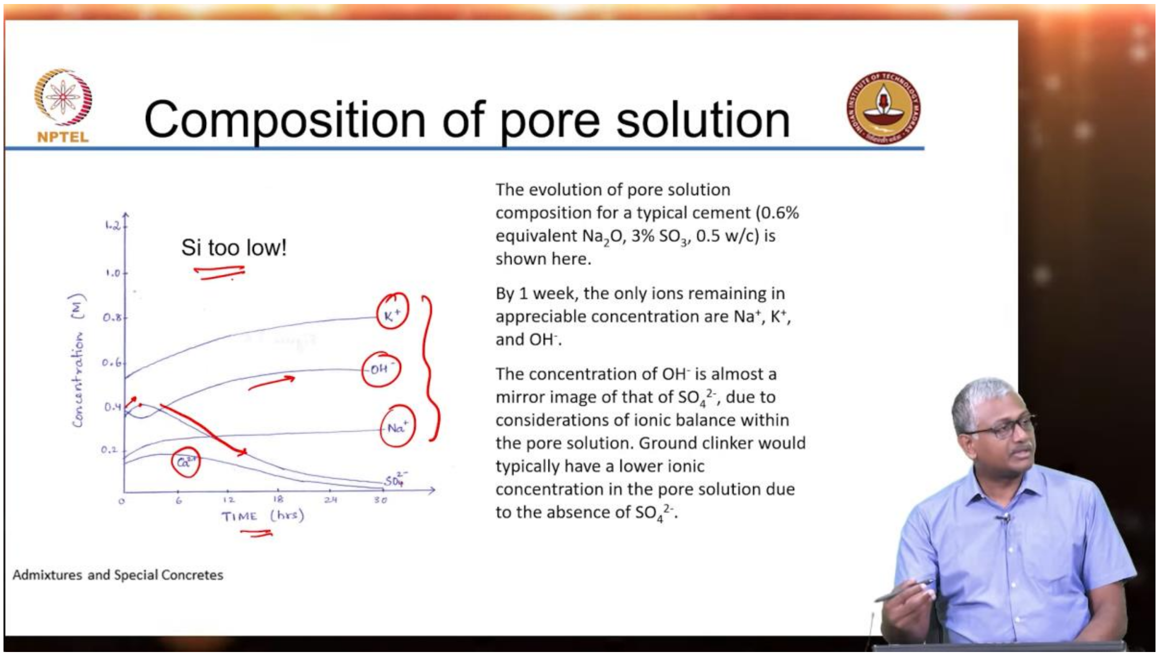

Composition of pore solution

The evolution of pore solution composition for a typical cement (0.6% equivalent Na_2O, 3% SO_3, 0.5 w/c) is shown here.

By 1 week, the only ions remaining in appreciable concentration are Na^+, K^+, and OH^-.

The concentration of OH^- is almost a mirror image of that of SO_4^{2-}, due to considerations of ionic balance within the pore solution. Ground clinker would typically have a lower ionic concentration in the pore solution due to the absence of SO_4^{2-}.

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Now we have been talking of various durability results which are based on electrical studies and we say that the conductivity of the system has a large role to play in the results that we see in the migration based experiments, electrical migration experiments. Now in a normal case when you only have ordinary Portland cement present and you allow the cement to hydrate for some time let the structure get hard and then you simply compress it triaxially you will be able to extract what we call as the pore solution. So if you take hardened cement paste and compress it triaxially at very high pressures close to 400 mega Pascal you will be able to extract out what we call as the pore solution that is the liquid present inside the pores of the system. So, in the pores it is not just water but it is a pore solution because there is dissolved ionic species also present.

If you take normal cement paste after a certain period of time you will see that so this is in plotted in terms of concentration in terms of time and you see here that the sulphate concentration which started off increasing initially because there is a sulphate species in the system that gets dissolved slowly. Gypsum is available other sulphates may be there some sulphates may be released from the alkalis from the alkali sulphates that are already there in the clinker. So, you have a quick buildup of sulphate but then sulphate concentration is going down because of the combination of sulphate in the reactions with the aluminate. Now if you look at OH minus ion concentration generally to ensure that you have a significant negative charge present in the system so as sulphate depletes your OH will increase as sulphate depletes your OH which is necessary to balance the alkali ions in the system that will increase with time. So if you take your system at 28 days this is very early of course but if you take your system at 28 days you will see that the only ionic species that are in significantly large quantities are your potassium, sodium and hydroxyl ions.

So, potassium and sodium positive charge, hydroxyl negative to balance the positive charges. Calcium there may not be much of it available in the pore solution and your siliceous systems are present primarily in the form of C3S and C2S and all that you will probably not have enough silica dissolved in the pore solution at all. So, silicon concentration will be too low in the system. Now what is going to happen is if you start substituting a cement with mineral additives there is amorphous silica available and we saw earlier that amorphous silica has a higher rate of dissolution it will start dissolving much faster than crystalline silica. As a result, if you start doing pore solution analysis from concrete with mineral additives you will start seeing silica also in your pore solution.

Composition of pore solution:

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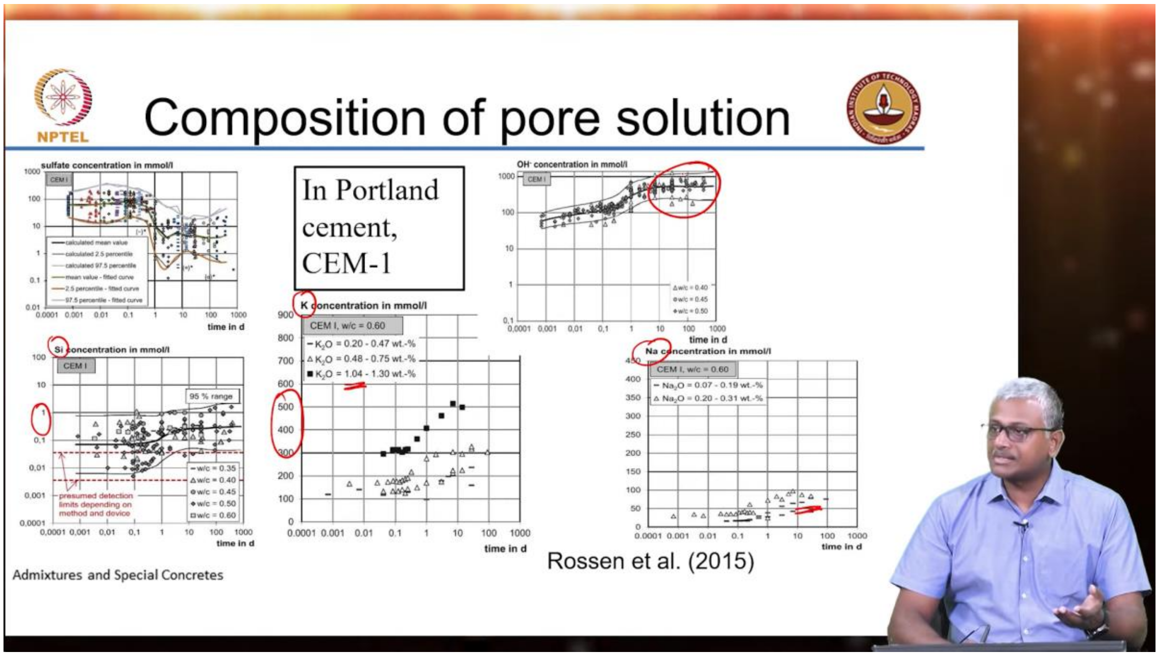

Composition of pore solution

In Portland cement, CEM-1

Rossen et al. (2015)

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So this is an example from a study by Rosen et al of course this example here is of CEM1 that is ordinary Portland cement. So, again sulphate concentration, silicon concentration as you can see silicon concentration is only of the order of 1 millimole per liter that is a very low concentration and that can be expected because in normal Portland cement, you do not really have a very large buildup of silica that can happen. Sodium or potassium concentration you can see the extent here 4 to 500. So, it all depends of course also on the initial chemical composition of the cement. The higher the alkali content the greater will be the extent of sodium and potassium available in the pore solution.

Sodium concentration also is quite high. The OH minus ion concentration is somewhere here nearly 6 to 700 millimole per liter essentially to balance the sodium and potassium concentration. So, this is in Portland cement CEM1. CEM1 is the name given in EN standards for ordinary Portland cement.

Pore solution in blended systems:

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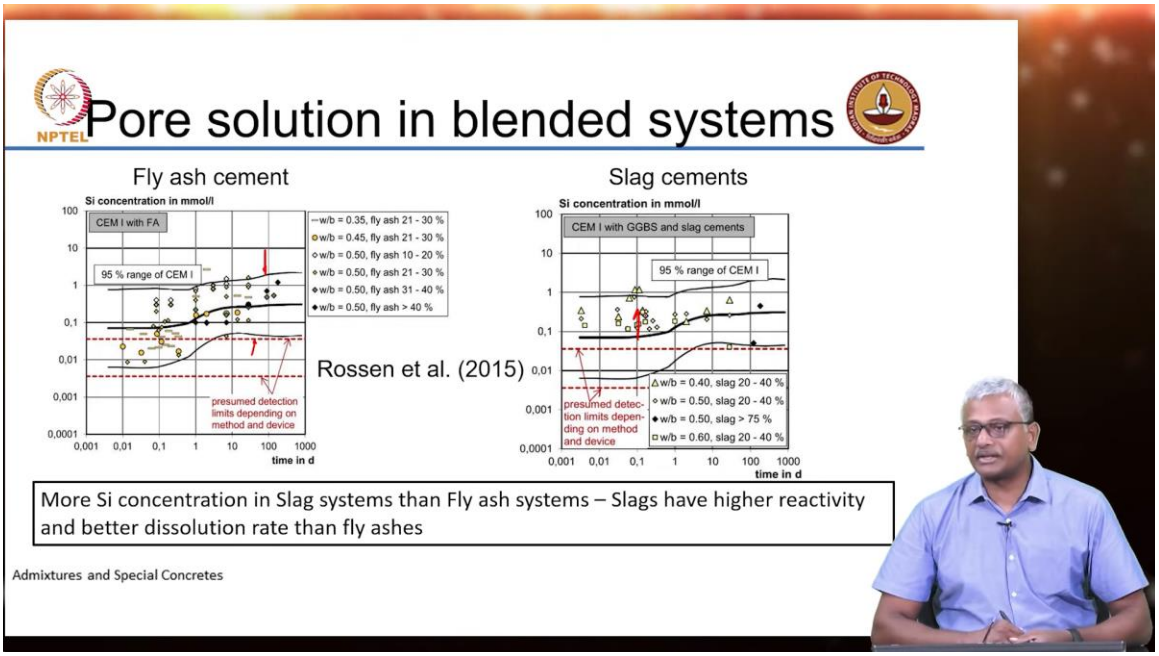

Pore solution in blended systems

Fly ash cement

Rossen et al. (2015)

Slag cements

More Si concentration in Slag systems than Fly ash systems – Slags have higher reactivity and better dissolution rate than fly ashes

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Now when you come to blended systems let us say fly ash cement if you look at the silicon concentration.

Now silicon concentration the first case was quite small in the case of Portland cement. In fly ash it is marginally higher but more or less the data for fly ash seem to indicate that they are falling within the upper and lower bounds of what is found in typical cement. But if you look at slag again some increase in the silicon concentration is found when slag cements are there. So, there is a slightly higher silicon concentration in slag cements. Slags generally have a higher reactivity and better dissolution rate than fly ash.

So one way to check the reactivity of your mineral admixtures is also to find the extent of soluble silica in your system and more soluble silica indicates more amorphous silica present in your system.

OPC Micrograph:

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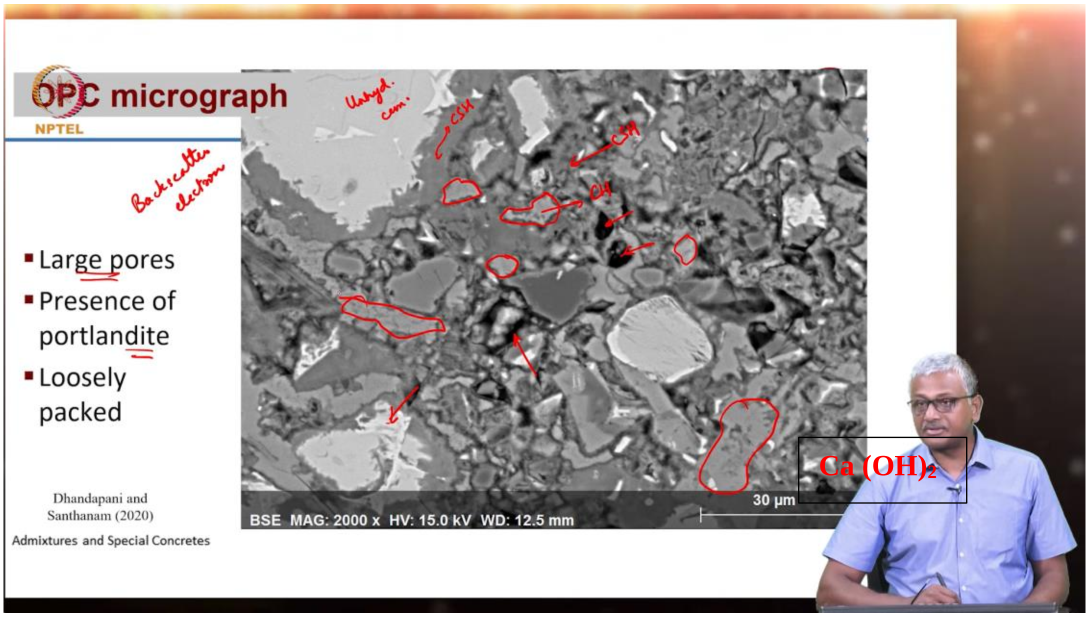

OPC micrograph

NPTEL

- Large pores
- Presence of portlandite
- Loosely packed

Dhandapani and Santhanam (2020)

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Now very often you will see that research studies report results of microscopy and one of the common methods of doing microscopic studies is scanning electron microscopy where they use an electron beam to scan the surface of the concrete and then the interactions that the electron beam generates with the sample can create very different appearances on the surface that can help you distinguish between phases. So, what happens in light microscopy? We usually in school you may have done in biology and stuff like that you have a glass slide and you pass light from underneath and you have a tissue sample that you can actually then look from the top that is called transmitted light microscopy. But you can also have for thicker materials that are opaque that do not let light to pass through you can have a reflected light microscopy. So that means light source and the objective are both on the same side of the specimen.

So that is light microscopy that uses visible light which has a wavelength of 400 to 700 nanometers. But then at that level you will not be able to resolve features very accurately. So that is why we go for much stronger microscopic techniques we can use electrons instead of light because electrons have a much smaller wavelength as compared to light and we can use these to start resolving features and do the scanning electron microscopy which is more or less similar to reflected light microscopy. Here electrons are impinging on the surface of the specimen and they are generating some interactions. The picture that you see here is generated from backscatter electron microscopy.

So backscatter electron as the name implies is the electron that struck the surface and then got reflected. It got scattered back to the top. Scattering can happen in all directions but we are only collecting the electrons that are coming right to the top. Now based on the density of the phases the scattering will be different. If you have a very dense phase let us say something that has iron in it there will be more electrons coming from that location because they are bouncing back from a hard phase.

But on the other hand if you have a pore like that your electrons are meeting a very low density phase or almost zero density phase. So, there is no reflectivity that is why the denser phases appear brighter and the pores and low-density phases will appear darker. So based on this you can actually see several levels of grey that you see here. You have the unhydrated cement here. You have a hydration ring on top so this is CSH right outside the unhydrated cement.

This is CSH which is also present but that is outside the surface of the unhydrated cement. You see some brighter phases these are calcium hydroxide. Those are calcium hydroxide phases. Similarly, you can also make out ettringite sometimes because ettringite is usually present in particle sizes which are too small to be detected as individual phases unless there is a sulphate attack in which case there is a lot of ettringite formed, there is a lot of gypsum formed where you will start seeing those compounds in a large way. So anyway the idea was to show that a microstructure of cement paste when you see under the backscatter electron microscopy system will appear like this which has several levels of grey exhibited by the different phases that are actually present and what you generally get to see is there are large pores so many different pores are there.

Then there is presence of portlandite, lot of portlandite all this is basically calcium hydroxide this whitish phase that is present all this is calcium hydroxide. So, lot of calcium hydroxide actually present in the system. The packing is not dense when you have ordinary Portland cement.

FA30 micrograph:

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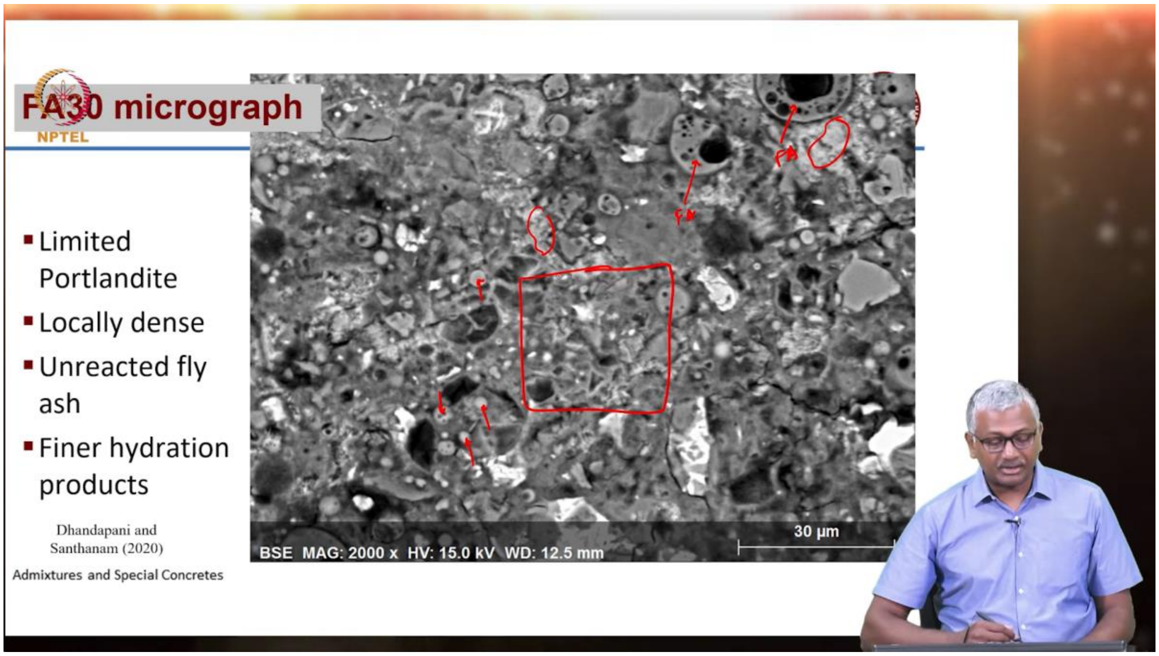

FA30 micrograph

NPTEL

- Limited Portlandite
- Locally dense
- Unreacted fly ash
- Finer hydration products

Dhandapani and Santhanam (2020)

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When you replace cement with fly ash you start seeing the remnants of fly ash particles. We discussed the structure of fly ash sometimes they look like spheres and sometimes they may be hollow spheres or partially hollow spheres like you see or sometimes they may be solid spheres like what you see here.

Those are solid silica particles but you see that lot of the fly ash is just remaining there it is not really reacting too much but what you also distinctly see is that there is not so much calcium hydroxide present in the system. There is some amount there is some calcium hydroxide but you do not see a whole lot of it. You mainly see a very diverse grey phase that indicates more C-S-H is actually forming in this case so less portlandite. Locally you can see that there is more density if you look at this area here you have less porosity present in the system more densely packed system has happened. Lot of unreacted fly ash and your hydration products do not have the kind of structure that is exhibited by the plain cementitious system.

LC3 Micrograph:

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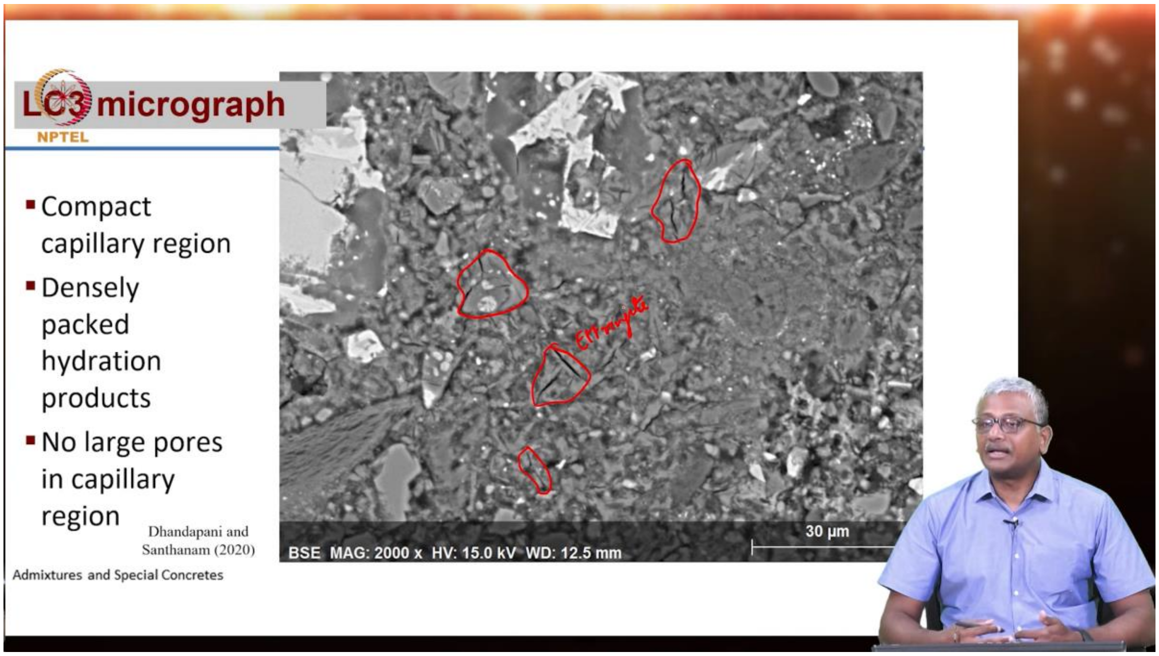

LC3 micrograph

NPTEL

- Compact capillary region
- Densely packed hydration products
- No large pores in capillary region

Dhandapani and Santhanam (2020)

Admixtures and Special Concretes

When you come to systems like LC3, now here you approach a very high level of packing and density. You get a very compact capillary region. Now do not be confused with these cracks they are actually desiccation cracks. We have to actually prepare these samples for backscatter microscopy are prepared by heating in an oven to remove any water that is present in the system because if there is any water molecules it will interfere with the high vacuum that is there in this electron microscope. So, we ensure that we extract all the water in the system and because of that you have some phases that start desiccating or drying that leads to these cracks being formed and these desiccated phases are often if you go closely and look at it is mostly ettringite.

Ettringite phases can be seen in LC3 as we discussed ettringite is stabilized in the LC3 system it is not converted to monosulphate and you can see that the hydration products are densely packed you have lesser porosity even compared to the fly ash system. You do not really see major large porosity available anywhere. So all of these can be an indicator of how your system is going to be in the long term. Again you can actually do the study instead of cement paste you can do it on concrete and look at the region close to the aggregate to see the clear dense packing exhibited by concretes with mineral admixtures and that clearly indicates the benefit of using mineral additive synthesis.

Composition of C-A-S-H:

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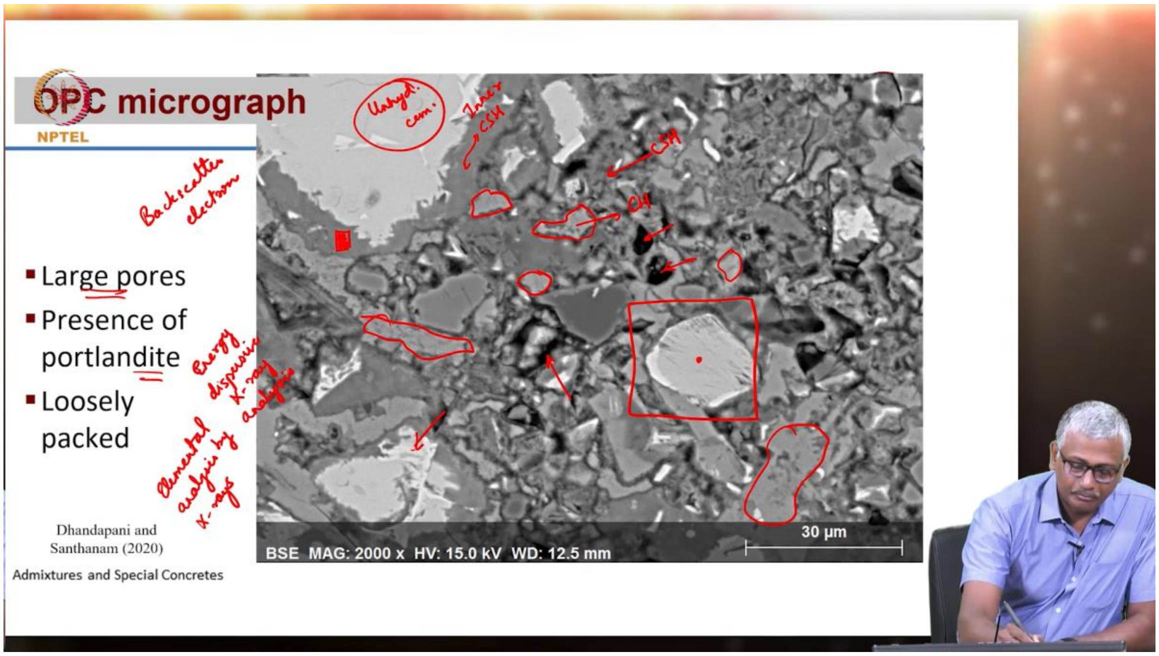

OPC micrograph

NPTEL

Backscatter electron

- Large pores
- Presence of portlandite
- Loosely packed

Energy dispersive X-ray analysis

Elemental analysis by X-rays

Dhandapani and Santhanam (2020)

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Now the other thing you can do with such backscatter micrographs is apart from getting the image you can also collect the x-rays that come out of the system.

So please remember these electrons are travelling at very high speeds, high enough to induce atomic transitions. So for instance you remember the atomic structure the K shell, L shell, M shell and so on. These electrons have sufficiently high energy to knock off an electron from the atom present on the sample. Let us say there is a calcium atom present in the calcium bearing phases there is calcium present. So you can knock off the K shell electron from the calcium.

So, what will happen? The calcium atom is becoming unstable now. To achieve stability what should happen? Some other electron has to come and fill up the space left behind by the K shell electron. So, there is an electron from the L shell that can come in and occupy that space. But is the electron in the L shell at a higher energy or lower energy as compared to K shell? Higher energy. So there is an extra energy available which is getting released now because of this transfer of electron from the L shell to the K shell and much of it is getting released in terms of heat but some can also escape in terms of x-rays.

The energy levels may be high enough that these can be coming out in terms of x-rays. So, if there is calcium atom present in your system you will get calcium x-rays, silicon will show silicon x-rays, aluminium will show aluminium x-rays and so on. So, you can actually collect the x-rays also that are coming out of the object. For instance, you can actually shine the electron beam right on this and collect the x-rays right from that spot or you can shine the electron beam across an area and collect the x-rays from an area. So if you want to get the composition of this CSH which we also know as inner CSH, I will choose an area like this and put my electron beam right on that location and then collect an average composition in terms of extent of calcium, extent of silicon and so on.

So that is called elemental analysis, elemental analysis by x-rays. We are collecting x-rays from the impinging electron that is generating high enough energy transitions to happen in the sample atoms and these x-rays that you are collecting out of the system can then be analyzed for the chemical composition of the phases you are looking at. Now I told you that this is unhydrated cement, how do I know it is unhydrated cement? I know that it is a dense phase. Unhydrated cement is denser than your cement paste CSH. We talked about density of unhydrated cement is about 3.15, CSH density is about 2 or 2.2. I know it is denser, it will appear whiter but what is the composition? I do not know. Am I looking at C_3S? Am I looking at C_2S? I do not know. So to find that out we need to do this x-ray analysis. We also call this system analysis as energy dispersive x-ray analysis.

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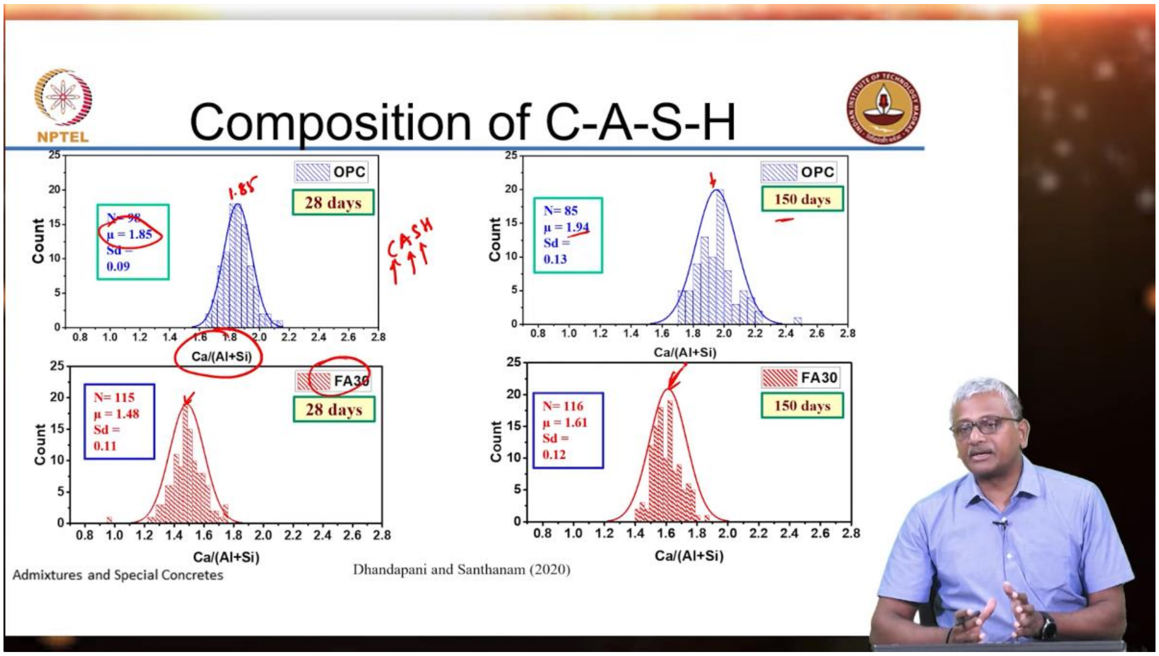

Composition of C-A-S-H

Admixtures and Special Concretes

Dhandapani and Santhanam (2020)

So when you do that you can then start understanding the composition of calcium aluminum silicate hydrate.

So you collect enough number of points on CSH and then analyze the elemental composition and get the estimate of the composition of calcium aluminosilicate hydrate. So what is generally done is the elemental analysis that you obtain is presented in terms of the calcium to aluminum plus silicon ratio because it's C-A-S-H you have calcium, you have aluminum, you have silicon. So, it is presented in terms of calcium to aluminum plus silicon ratio. For OPC if you do a histogram on several points that you collect from the data that you get on several points you will see that the average is around 1.85.

I mean in this study of course it is not always 1.85, it generally varies between 1.8 and 2 in that region. But when you are substituting fly ash at 30% this is coming down to about 1.48. So the histogram indicates that your mean is at 1.48 that means your calcium to silicon plus aluminum ratio has shifted to the left. What does this mean? It is a system that is deficient in calcium or more silicon and aluminum have been introduced into the CSH structure. So it also means that the CSH you have with OPC is different from the CSH that you get with a pozzolanic reaction. Of course that is the subject of a completely different study but nevertheless what you have to understand is there is different degrees of incorporation of silicon and alumina in your system. If you have more silicon and alumina that is in the soluble form because of amorphous mineral additives that are used as cement replacement you will start seeing a much greater influence of that in the C by S plus A ratio.

Now at 150 days again you see that the peak has shifted a little bit to 1.94 and here it is about 1.6. Nevertheless what you clearly observe is that the calcium to silicon plus alumina ratio is coming down when you replace cement with fly ash-based systems.

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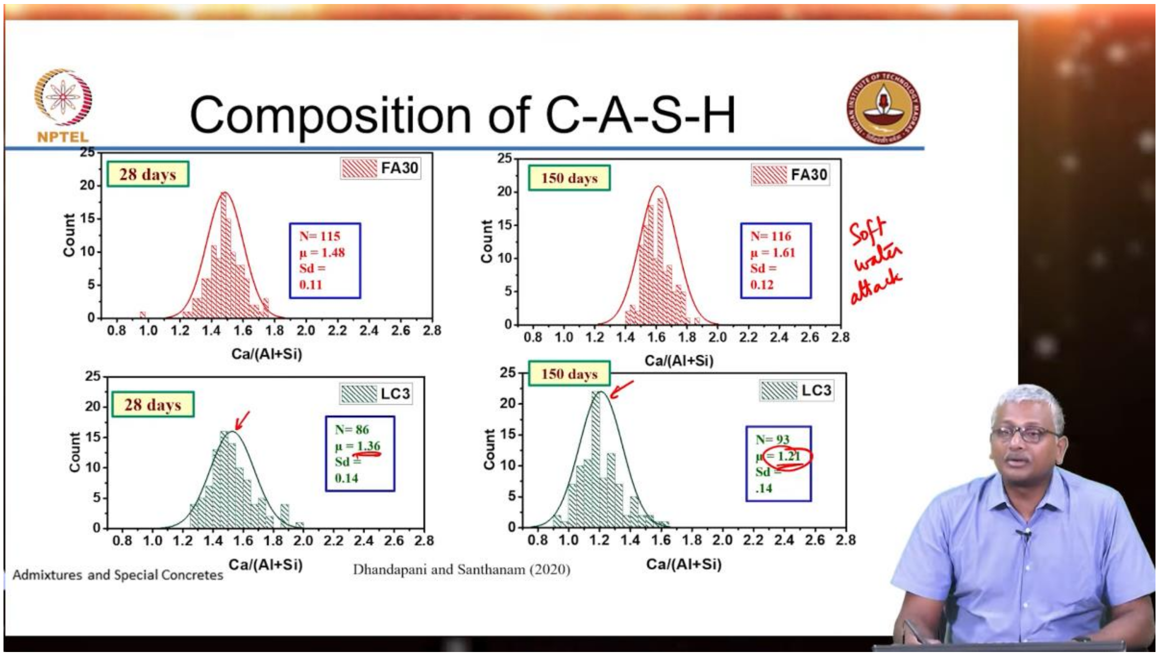

Composition of C-A-S-H

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Now when you go towards LC3 this is going to be even more. The decrease in C by S will be even more in the case of LC3 as you see here at 28 days we are actually seeing about

1.36 as the mean and here 1.21 at 150 days. So, there is a clear shift of the calcium-to-silicon ratio to lower calcium levels.

Now this has many different connotations. So, what happens in the case of carbonation? Carbon dioxide penetrates the concrete and reacts with calcium hydroxide. If there is no calcium hydroxide available it will react with other calcium-bearing species. What are the other calcium-bearing species? CSH, you have ettringite. What will happen is when it starts interacting with CSH that has a low calcium-to-silicon ratio the depletion of calcium will be faster. That is going to create more porosity in your system and increase the rate of penetration of CO2.

That is the reason why your concretes with mineral additives carbonate a lot more with, because of the lowering of calcium to silicon ratio and absence of calcium hydroxide in your system. The other thing is imagine that you put this concrete in water what is going to happen? You will get a process known as leaching. Slowly ionic species will dissolve from the concrete and leach out to the surrounding water. Now if you put concrete in a tub of water there will be only a limited amount of leaching because when the concrete or the pH of the surrounding water becomes equilibrated with the concrete pH you will probably not have further leaching. But if you have flowing water, what is going to happen? That water is continuously getting replenished.

So, the rate of leaching keeps on building up. So, extent of leaching keeps on building up. So, in structures such as foundations that are in contact with groundwater where the groundwater is completely in a flowable state for instance there will be continuous leaching. So, leaching tends to start removing the calcium-bearing compounds first. So if you have a situation where you have only ordinary Portland cement you will generally get a much higher rate of leaching as compared to when you start using blended cement. Especially when you start using things like LC3 your rate of leaching will be lower because you do not have that much of calcium present in your system.

So, the phases that can be dissolved early will be leaching out first. So, compared to CSH your calcium hydroxide leaches out faster much quicker removal of calcium hydroxide can happen in the system. So even in the conditions of simple soft water which is devoid of minerals, this can actually damage your concrete in the long run. So, people have reported soft water attack. May be hard to imagine but soft water can also attack concrete. But this is not something that produces dramatic effects in a short period of time.

This is something that happens over a longer period where you are slowly leaching out the soluble species from the concrete. So, generally in such situations the use of blended cements will be beneficial because it will tie up your structure in a silica and alumina-rich product which will be less soluble as compared to your calcium-rich products.