**Admixtures And Special Concretes**

**Prof. Manu Santhanam**

**Indian Institute of Technology Madras**

**Department of Civil Engineering**

**Lecture -44**

**Mineral Admixtures : LC3 - Part 2 : ComparisonLimestone with other SCMs**

**LC3- Effects of calcined clay types:**

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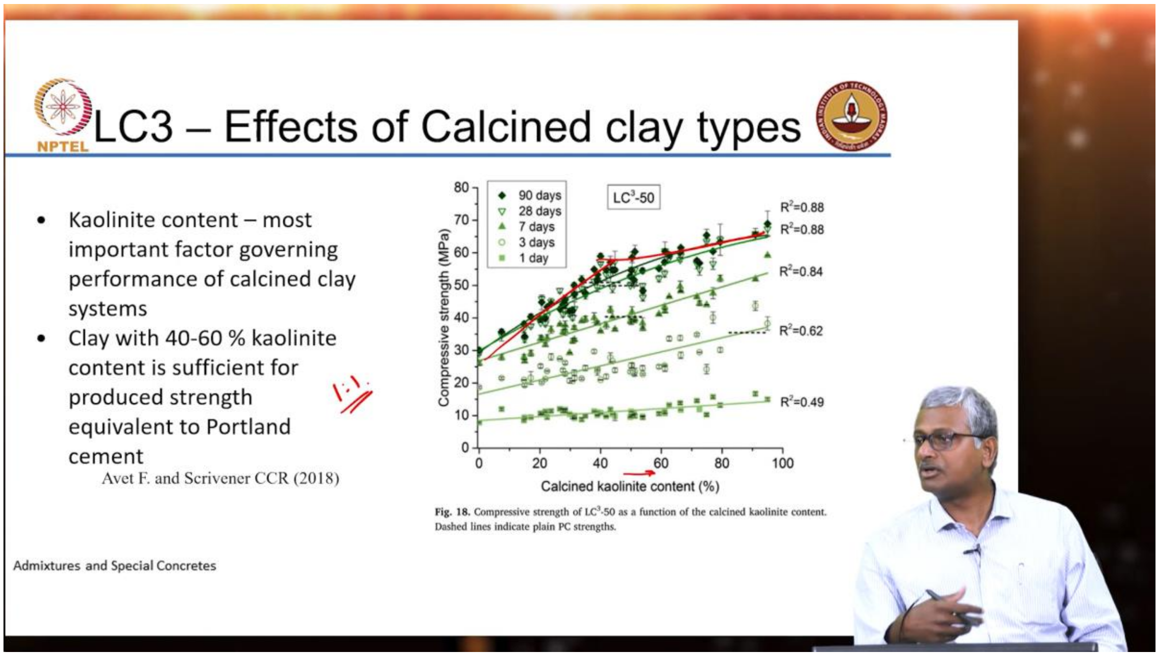


So, again as I was saying earlier when you are going much beyond 60% in calcium kaolinite content the strength increase that you get is only marginal. See that the graph starts straightening out like that more or less. So, your between 40 and 60% is sufficient for a strength equivalent to Portland cement and that is where the strength of this material lies in because not always you get fresh or pure china clay. You have to make do with impure varieties of china clay which has impurities. Sometimes the clays look red why? Iron content. Iron content and other oxides that are present sometimes even quartz may be present in your system. So sometimes even calcite may be calcium carbonate may be present in your clay which makes it more yellowish when you burn such clays to make bricks you get yellowish-coloured bricks when you have the iron oxide-rich clays they give you the reddish bricks. So all of these go to show that there is lot of material that can technically be utilized in the form of calcium clay because so much of it is actually dumped and not utilized.

The only problem is when we start going from kaolinite to illite or montmorillonite our reactivity is not as good. Kaolinite is basically a 1:1 clay. What is 1 :1 that means the plates are arranged in terms of silica and alumina one plate of silica and one plate of alumina like that the arrangement is. In the case of montmorillonite or illite you have a 2:1 system the reactivity gets hampered because of the kind of structure that some clays have.

**LC3- Effects of limestone:**

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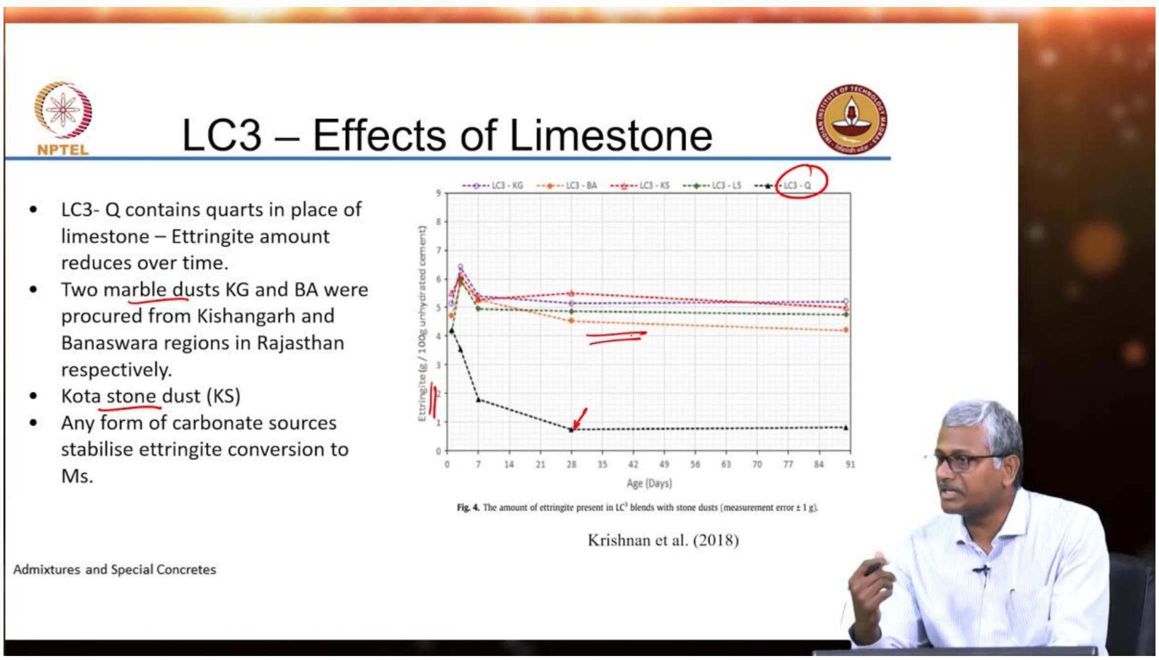


Anyway that is more involved discussion we will not go there but what I wanted to also tell you is that it is not just pure limestone that is required to make such systems you can start working with impure limestone also.

I already told you that only a part of the limestone actually dissolves to take part in the reaction remaining simply serves as a filler. So why not we start using other limestone-bearing materials for instance here in this paper done at IIT Delhi they had used marble dust. Marble dust also is calcium carbonate if you grind it fine enough there is significant bit of carbonate dissolution you can get to produce the required effects. Kota stone dust see if you go to all these stone processing units the amount of polishing and grinding they do on the stone tons and tons of it gets wasted. Of course, with marble dust they start utilizing it for other products like showpieces and things like that they make but the quantity that is generated is significantly higher than what can be usefully utilized. So there is lot of material available here and such material could be useful as a component in this ternary combination as you can see here when simply quartz is used in the LC3 in combination with your calcite clay you are not really getting the stabilization of ettringite.

Whereas when you use any other type of limestone whether it is calcite from marble dust, calcite from Kota stone dust or calcite from limestone you are not really seeing a major difference in performance. Again this is another point of strength with respect to LC3 that you are able to actually produce now concretes with basically waste materials which may not be utilized usefully otherwise. That is the most important objective here.

**Refinement of pore structure in LC3:**

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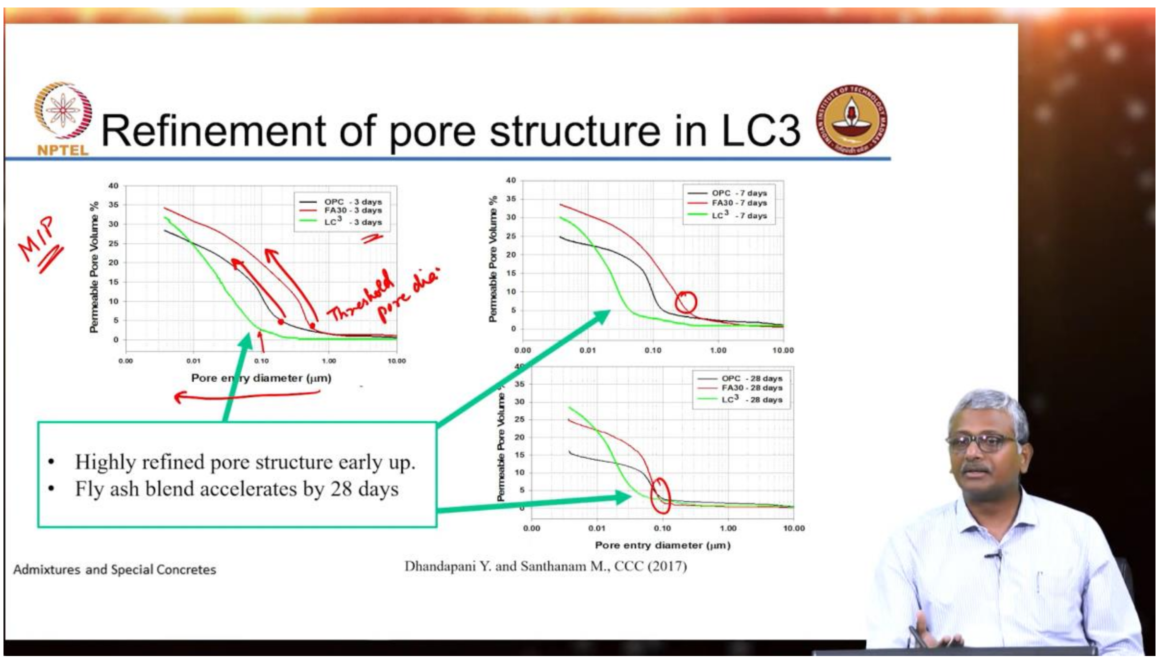


And all this happens primarily because we refine the pore structure we already saw the reasons why refinement of pore structure happens you fill up more hydration product early itself. So here the comparison is between OPC 30% fly ash and LC3 and what you see here is that at at 3 days your LC3 system is already much finer as compared to the OPC. As I said this is the result from mercury intrusion porosimetry experiment.

So here we are pressurizing your cement paste or cement concrete with mercury and mercury starts intruding the porosity the greater the pressure the smaller the pores that the mercury intrudes. So, as we are going this direction pore entry diameter is reducing that means the pressure is increasing I put more and more pressure. What you are seeing is there is a sudden point where your mercury starts filling up your system so that may be some sort of a threshold pore size. Like a threshold pore diameter you are overcoming that small pore to push a lot of mercury into your system and what you are clearly saying is that by 3 days your LC3 system is even finer than the Portland cement system. By 7 days the fly ash is catching up and by 28 days your fly ash and cement are nearly at the same level.

So if you do continuous curing the fly ash is able to produce that performance but LC3 does not need that level of curing to reach the extent of performance. So very important to understand your problems of prolonged curing may not persist with LC3 but there is a caveat there if you are trying to get a better carbonation performance from concretes which have high replacement of cement increase in curing always helps. If you do more curing there will be less carbon dioxide penetration. So, you can obviously design your system to attain strength in the case of LC3 that is not a problem you can attain strength early because of this refinement of pore structure but if you have to decide upon curing that is from the perspective of providing a more durable system against carbonation.

**Comparative pore size distribution by MIP- OPC, FA30 and LC3:**

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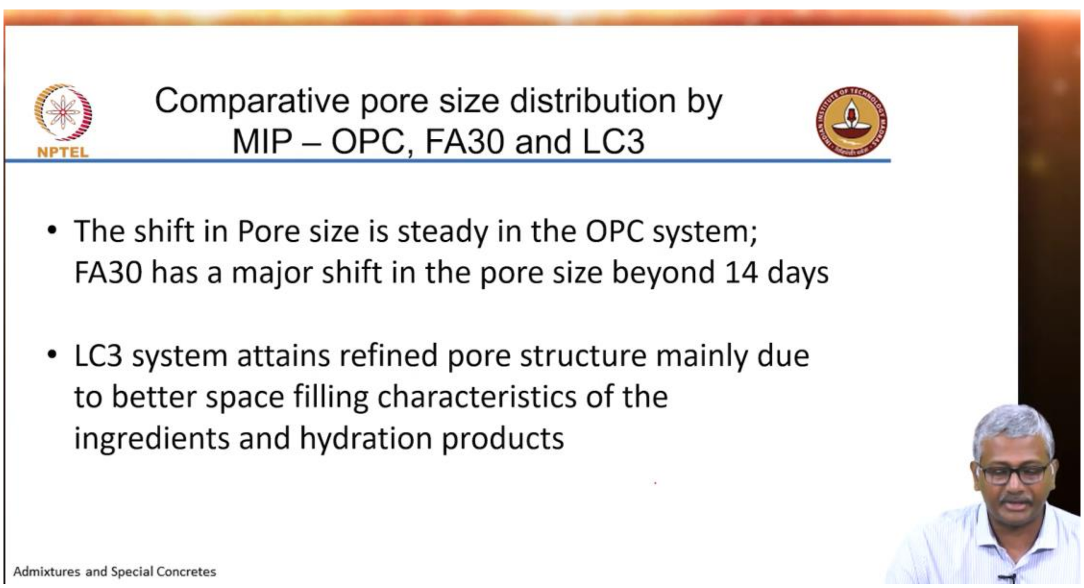


So as I said shift in pore size is quite steady in the OPC system whereas the fly ash system only starts moving beyond 14 days where it gets sufficient pozzolanic activity from the fly ash.

**Microstructural development of OPC, FA30 and LC3 systems:**

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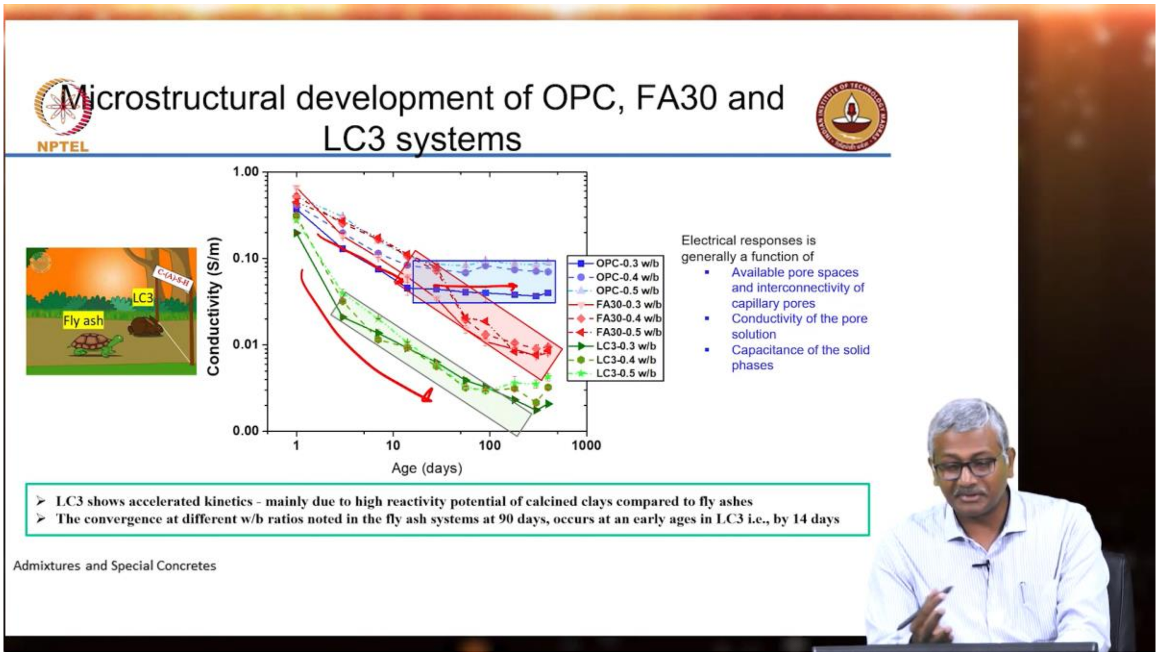


Now you can study the pore structure also with the help of conductivity we discussed this earlier that the more interconnected the porosity the greater will be the conductivity. So you can actually see what happens to conductivity as age increases you can clearly see that the LC3 systems are dropping off in conductivity much faster. Your OPC systems drop off fast but then not much happens beyond about 14 days you are not seeing much of a change. In the fly ash system there is a gradual drop right? But then you start overtaking Portland cement at later ages beyond 56 days. So, it is important to understand that as long as you continue curing the fly ash system will definitely reach a stage when it is having a better durability as compared to your plain Portland cement system but if you do not do adequate curing you may not get there.

Now again please always remember whenever I am talking about electrical properties there is always that aspect of ionic strength of the pore solution that always comes in. So the result cannot be just looked at as a beneficial reduction in permeability it could also be contributed from the reduction in ionic conductivity. What is LC3 doing? It is capturing more of calcium hydroxide. All the alkalis that are in the system are getting bound in the amorphous structure. So there is not much alkali available in your system, pore solution conductivity goes down so overall conductivity also goes down.

So you have to look at conductivity as a composite effect of reduction in permeability plus reduction in the ionic strength. What I am just trying to say is do not believe a result in its entirety there is always a reason why the result is being shown up like this. So, actually when you see electrical results on LC3 the performance will be a couple of orders of magnitude better than cement. I will show you some results but that does not mean that concrete will behave exactly in the same way. It may be better definitely it is better but two orders of magnitude does not mean that your concrete and site will perform 100 times better than Portland cement it is not going to happen.

This was just what I was talking about my student Yuvraj made this interesting picture with the tortoise and the hare story but of course here the hare is winning the tortoise is still lagging behind but if the LC3 decides to sleep and not hydrate further maybe the tortoise may overtake it sometime in the future.

**Concrete- comparative mix designs:**

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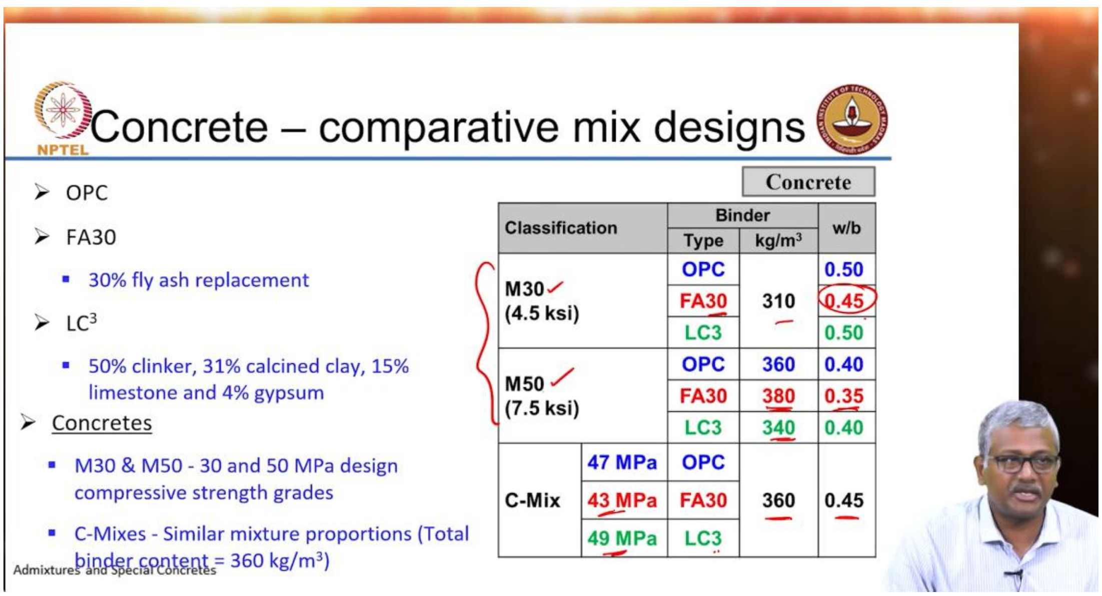


So we can do all kinds of studies on paste and mortar but the real performance obviously has to be tested in concrete and as I said earlier it is always important to compare concrete at equivalent strength grades. So that is how we design this set of concrete mixes. So we designed for M30 concrete and M50 concrete as two different strength grades and we adjusted the binder content and water binder ratio to get that strength at 28 days. So as you can readily imagine with the 30% fly ash replace mix we had to go for a lower water binder ratio to get the same strength at 28 days.

Similarly, for M50 you can see both binder content is increased and water binder ratios decreased for fly ash paste mix. With LC3 more or less the same as OPC in fact here even lesser LC3 is used to get the 28-day strength as compared to the OPC. But we also did a comparison at equal binder content and water binder ratio. So this was the strength-based comparison and this was a comparison based on an equal amount of binder content and water binder ratio. Again as you can readily imagine since LC3 produces higher strength than OPC you have greater 28 days strength fly ash at 28 days is able to get 43 MPa as opposed to 47 for OPC.

Now in reality the difference between 43 and 49 is not really significant you can discard that result as being anything of significance.

**Compressive strength evolution in the concrete mixes:**

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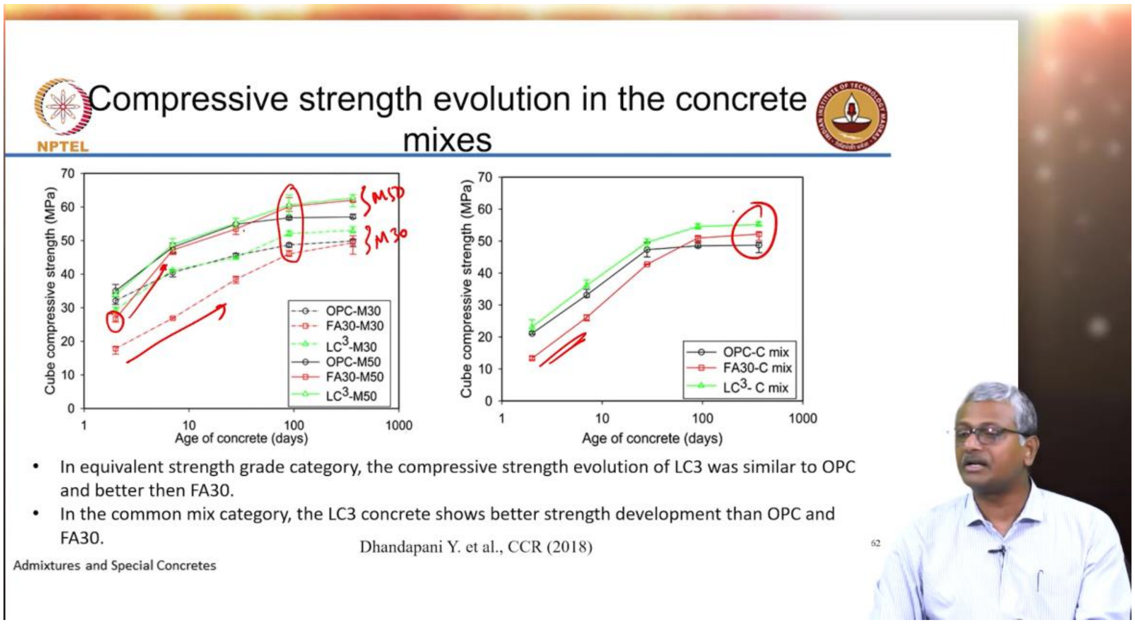


So let us look at the strength evolution you can readily imagine yes fly ash will react slowly so you can see that fly ash only catches up at 7 days or it ages much later. For instance, here there are 2 curves given this is for M30 and this is for M50. For low-grade concretes the fly ash paste mix is even lower in terms of its strength rate but in the high-grade concrete it is able to actually catch up by 7 days itself. But all the mixes are ending up almost in the same location after like this is 1 year data.

All of the mixes are ending up even at let us say even at 90 days more or less they are giving the same sort of a result. When you compare the common mix that means the mix with the same binder content and water binder ratio as I said there is some difference early on as you can imagine fly ash will be slower to react but later all of the concretes are attaining nearby the same strength. So there is definitely an early age strength benefit to LC3 which you do not see with fly ash systems.

**Second set of concretes:**

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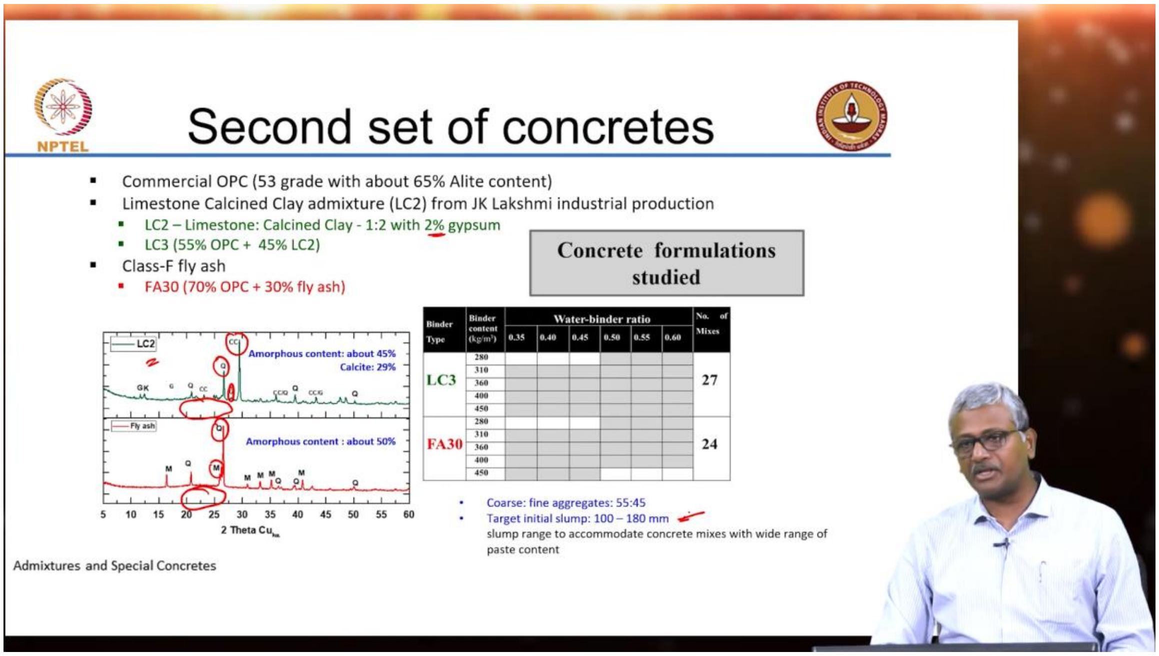


Now in the second set of concretes what we did was not use LC3 the previous example showed LC3 that we did a trial production of in a cement plant. But in the second example we just used a mixture of limestone and calcined clay individually brought in and used it as an admixture replacing the cement and concrete. Okay.

So, of course, we had to up the gypsum content for ensuring that the overall gypsum levels can be controlled equivalently. So here again we can see the LC2, what kind of a pattern is this? (refer to the test results on left of the slide) What experiment is this? X-ray diffraction.. So the distinct peaks that you see are from crystalline materials that are present. So you see the peaks for calcite or calcium carbonate, you see the peaks for quartz and you see some peaks for gypsum also. Okay. In the case of fly ash you see the peaks for quartz, you see the peaks for malite but you also see this wide amorphous area that is exhibited by the materials that is basically showing their reactivity.

So there are several concrete formulations that we studied here, we ensured that all the concretes were chosen in such a way that we could adjust the superplasticize dosage to get the nearby the same initial slump, not much difference.

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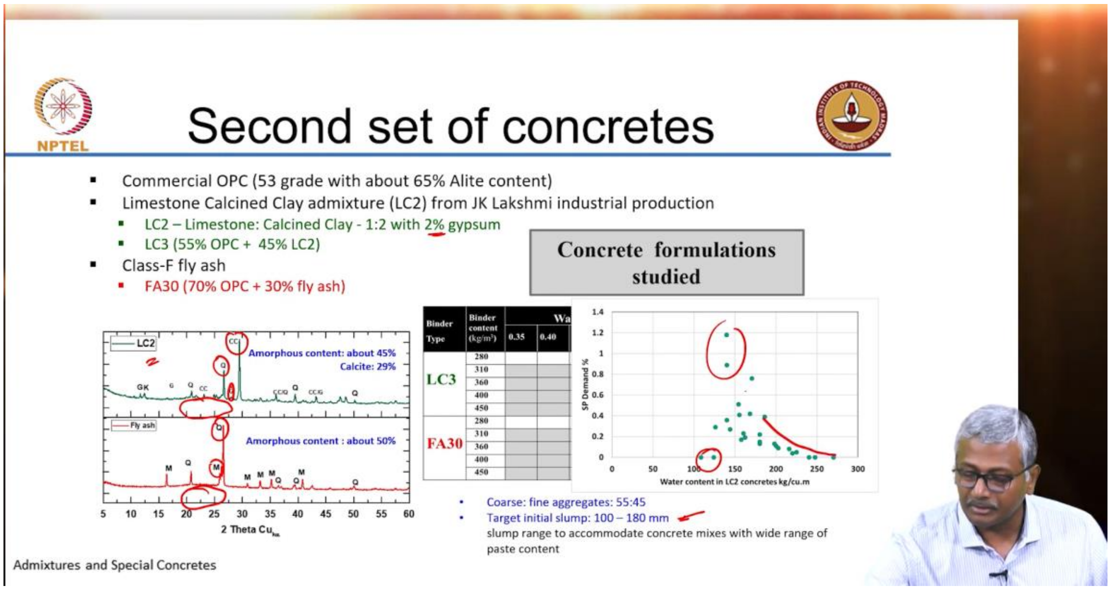


Again you can see the superplasticizer dosage for different water contents of the concrete. So very clearly obviously the lower the water content the higher the dosage. And of course, there are some systems where you have less SP demand, those are basically some outliers where we had a problem with the aggregate, so those are not to be considered. So in general as the water content goes down the SP demand goes up.

**LC2 admixture for range of concrete grades:**

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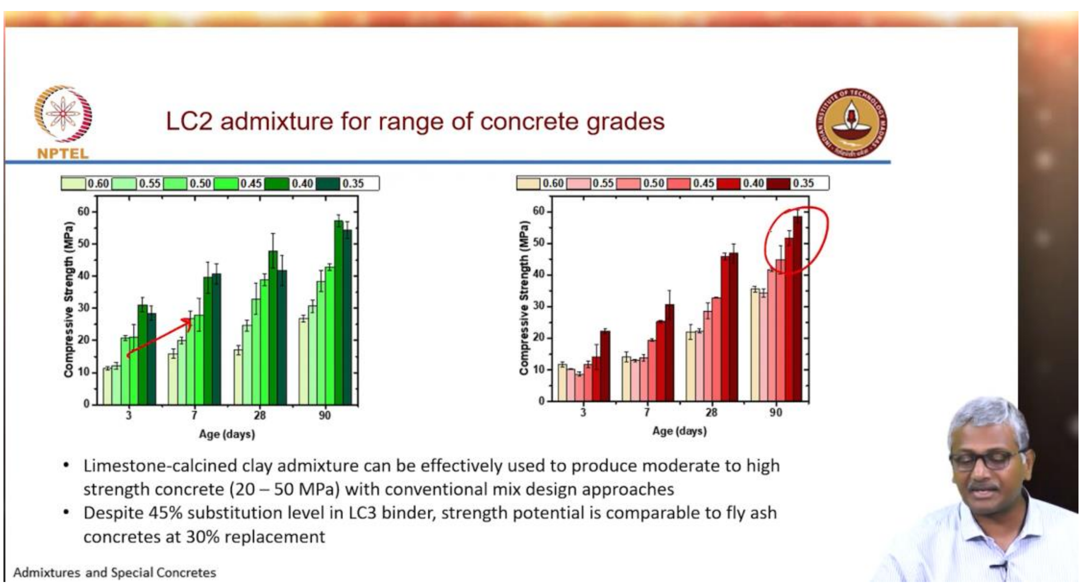

So these are the strengths for a range of concrete grades with LC3 and with fly ash based systems.  Again you can clearly see that you are gaining strength early by 3 and 7 days you have gained sufficient strength but by 28 days your fly ash systems evolve or 28 days and 90 days your fly ash systems have caught up with the LC3 systems, again it shows the same thing.

**Normalized strength development:**

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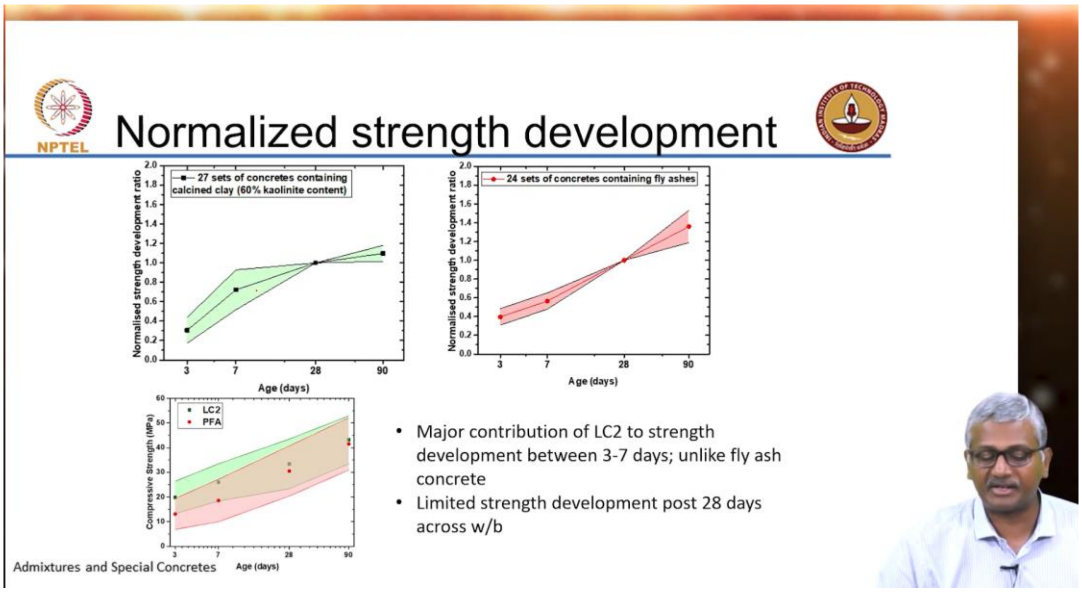


So if you look at the normalized strength development curves you can again see that.  So again here the calcined clay had 60% kaolinite content.  So what this is trying to show you is that the rate of strength development was much faster with LC3 in the beginning but later fly ash concrete started picking up after  28 days.

**Conclusions regarding strength development:**

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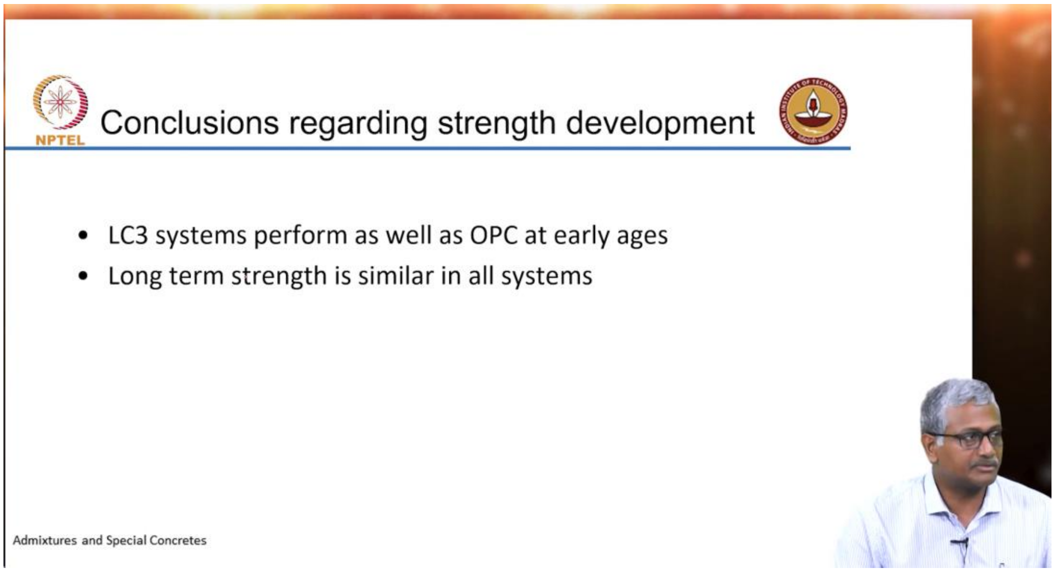


So LC3 systems perform as well as OPC at early ages, so much of the early curing or need for prolonged curing may not be there and long-term strength is similar in all the systems at 28 days and beyond you really do not have much to distinguish.

**Surface resistivity on concrete:**

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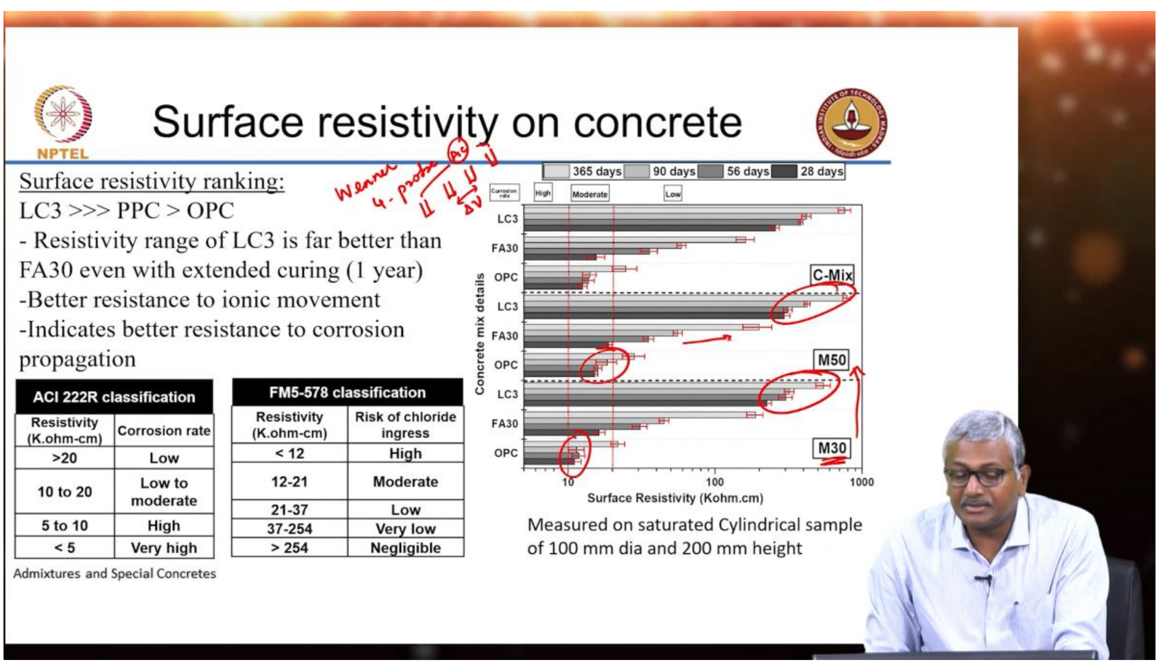

But the real advantage comes when we start measuring durability parameters like surface resistivity. Again it is a technique that is using an instrument called Wener 4-probe. So there are 4 probes as the name indicates. Across the outer probes you apply an alternating current and measure the potential drop across the inner probes and this is directly in contact with the surface of the concrete and we establish the resistivity based on the potential difference that is measured by the inner probes.

I am not going to go to the specifics here but once again please remember when we are measuring resistivity or inverse of conductivity again 2 components will come into play. One is the conductivity of the pore solution, the other is the actual interconnectedness of the porosity. So you see here this is what I was talking about with OPC you are in this range here around 10 to 20 surface resistivity but with LC3 even for low-grade concrete you are in 200 to 500 range. Completely different range of performance and that is something which is not directly translating into actual service life. But it is a good indicator, rapid indicator of the relative performance. As you can also see from the other as you increase the grade of concrete from M30 to M50 even the OPCs are improving but only up to about 20 kilo ohm centimeter whereas your LC3 concretes are going significantly fly ash-based concretes if you prolong the curing period.

So these were cured all the way to 1 year. So you have results from 28, 56, 90 days and then 365 days. So if you cure for very long period of time fly ash-based concretes are also reaching that level of resistivity.

**Early rise in concrete resistivity with calcines clay systems:**

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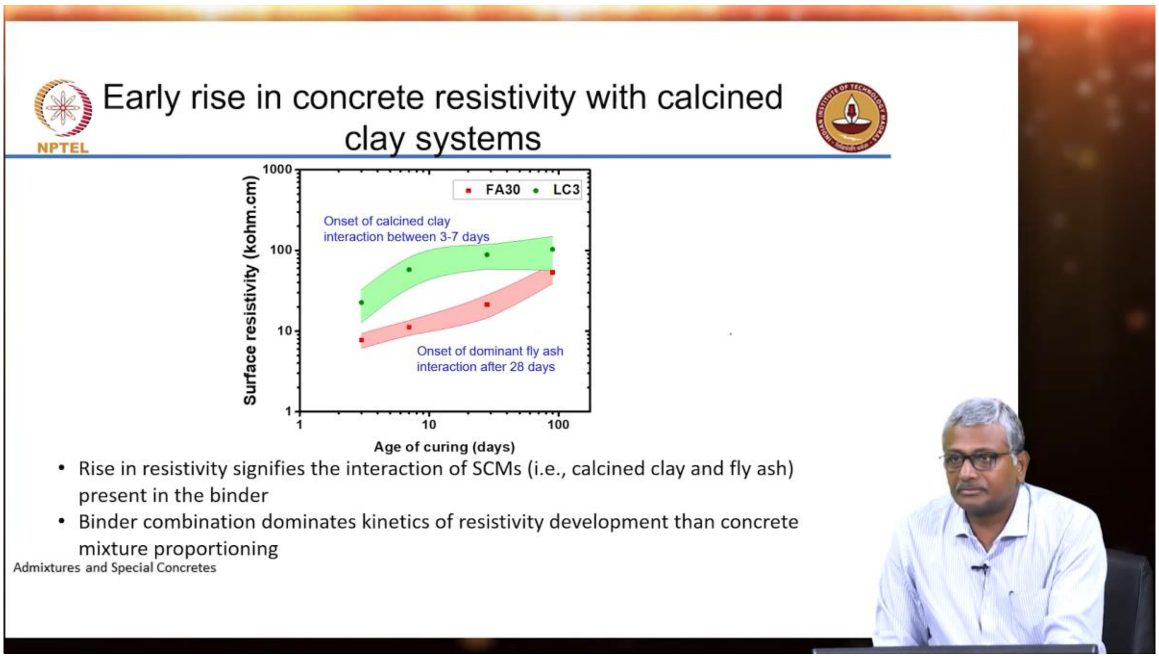

But once again the trend is the same calcined clay resistivity increases rapidly at early ages fly ash-based systems start interacting later beyond 7 or 14 days is when you start really getting the benefits from fly ash significantly.

**Chloride penetrability by RCPT (ASTM C1202) and Migration test (NT 492)**

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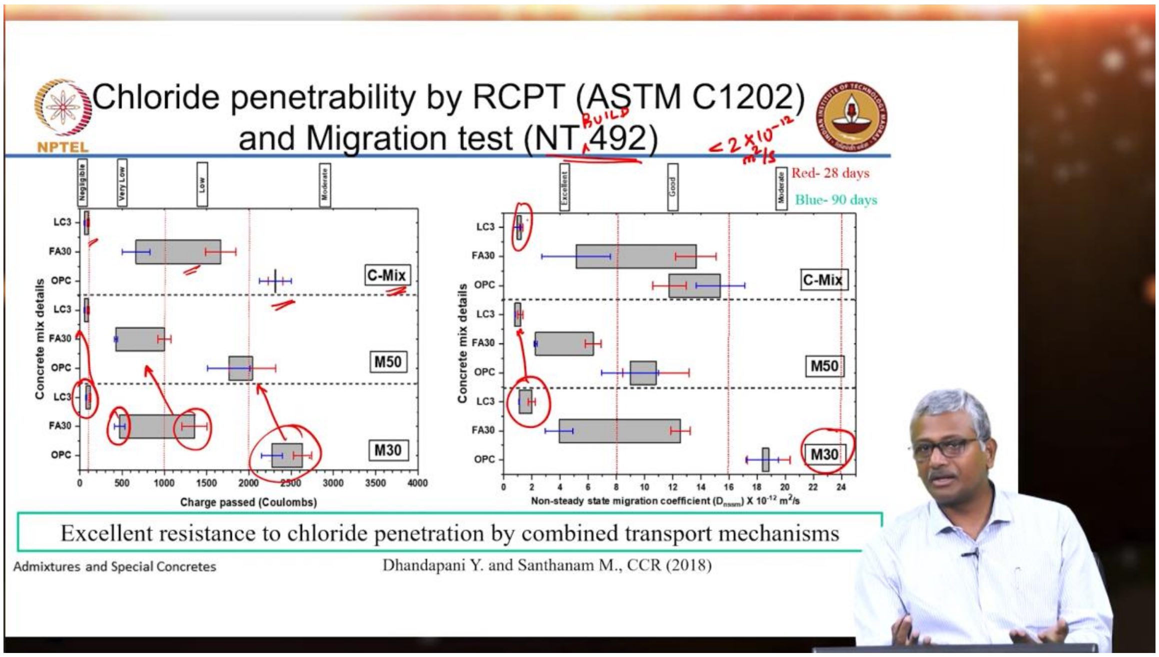


Just take a few more minutes to finish up because most of the results are sort of interconnected.

So, chloride penetrability by rapid chloride penetration test and also there is another test called migration test which actually gives you a clear value of a migration coefficient. Again, my aim is not to get into the test methods but please remember these are also based on electrical methods. So, there will always be that double contribution. So again with chloride penetrability with the M30 concrete we are in this range of 2500 coulombs. The red indicates 28 days the blue is 90 days.

So when you cure for more period of time the permeability is coming down as you can expect concrete is hydrating more, maturing more so permeability is reducing. With fly ash-based system you are reducing already at 28 days to about 1400 but at 90 days you are able to get 500. So that means extended curing definitely helps in fly ash which we all know well. LC3 whether you cure for 28 or 90 days you are in the negligible permeability range, 100 coulombs as compared to 2500 for plain concrete. Same thing with M50 obviously you are improving the performance further because grade is increasing and for the common mix at the same binder content and water binder ratio for Portland cement for the fly ash and then for the LC3.

So very clearly you see these effects. More dramatically today a number of projects for instance the Mumbai Trans Harbor Tunnel project which L&T is doing one of the specifications in the project is the migration coefficient of chlorides in this test called Rapid Migration Test or NT-BUILD 492. So this is the test in which you measure the chloride migration coefficient and the Trans Harbor Tunnel involves the use of a high-performance concrete for which they have specified a value of less than 2 into 10 power minus 12 square meters per second ($2 \times 10^{-12}\, m^2/s$). That is the requirement in the specifications. So there the grade of concrete is some M60, M70 they are using silica fume, complex ternary systems to actually obtain this strength as well as the value of the permeability.

But look what is happening here with M30 concrete your LC3 system is already in that range. With M50 you further improve and of course, your common mix which is more or less like an M50 is at the same range. So less than 2 you are already reaching with LC3 and this is where you are really seeing that benefit. The chloride migration results with such systems with calcined clays in combination with limestone can give you a significant advantage in chloride environments. Carbonation what will happen? Same thing we discussed earlier more cement replaced less carbonation resistance, more CO2 penetration depth.

**Sorptivity Index:**

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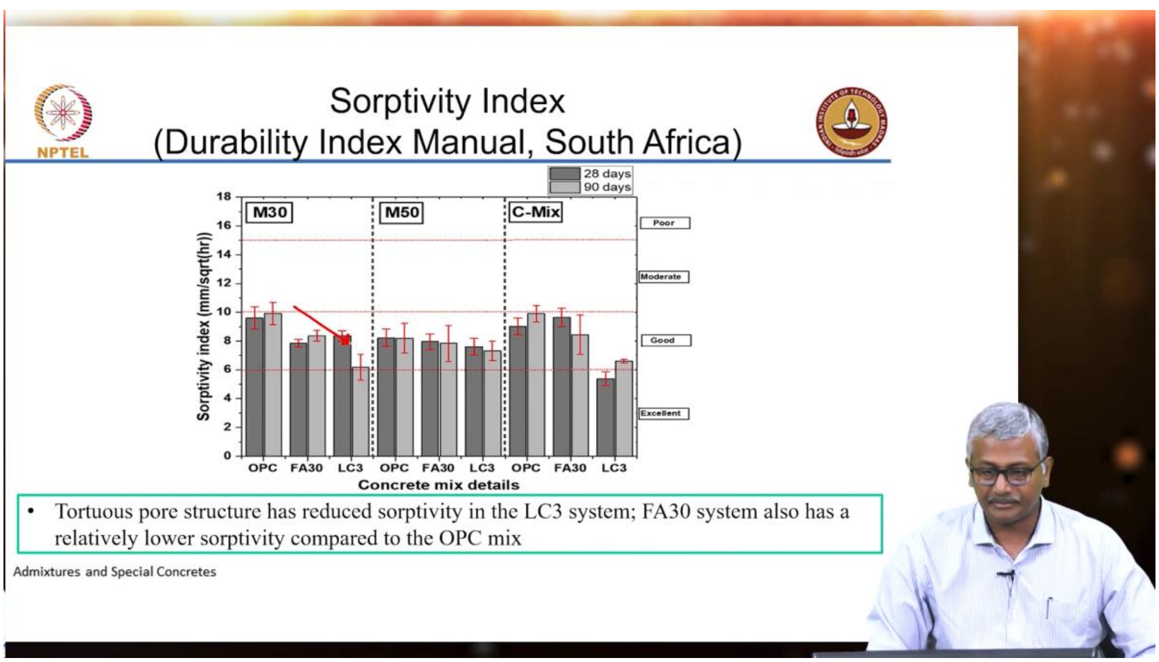

Sorptivity, usually, you do not really see that much of a distinction between different mixes although on an absolute scale yes sorptivity goes down from OPC to flyash to LC3 but again all of the concretes can be qualitatively adjudged as being good concretes.

**Water sorptivity:**

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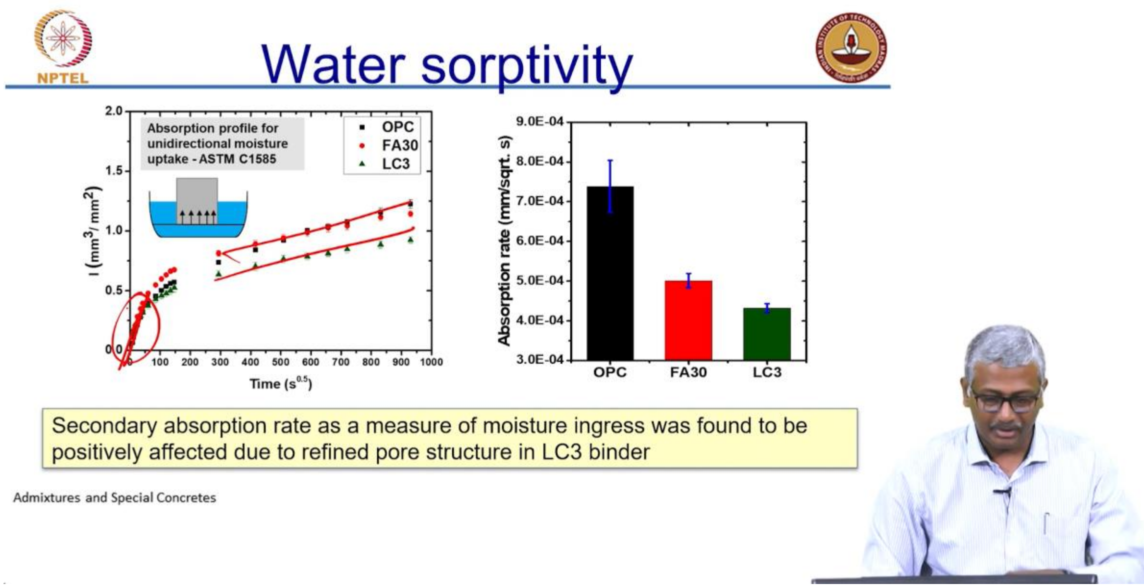


Again water sorptivity also has 2 segments one is this initial slope the rate of uptake of moisture as soon as the dry concrete comes in contact with the wet foundation or wet soil then later in the long term you have this constant rate of water intake and there you can actually see the difference between OPC mixes and LC3 mixes. So important to understand how the test is being done what result is being conveyed. So if you just looked at this initial slope there was not much difference as you can see from this result but when you look at the overall long-term data there is clearly a distinct advantage.