Advanced Concrete Technology
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Lecture - 23
Mineral admixtures - Part 6

Let us resume our discussion on limestone calcined clay cement. We were talking about the fact that limestone is increasingly being used as a cement substitute in different proportions, sometimes as an additive as a performance improver to regular Portland cement or sometimes as a replacement for cement in larger proportion that leads to the development of Portland limestone cement.

But what we also discussed was when limestone is used in combination with reactive alumina, it gives an entirely different perspective to the early hydration chemistry that actually takes place in such systems. So these are ternary blended systems where we not only make use of pozzolanic reaction of the silicoaluminate mineral admixtures, we also make use of the carbonate aluminate reaction that happens because of the limestone and the reactive aluminate that is contributed by your mineral admixtures.

So that way, you get a system that fills up pore spaces very early in the process and we saw that the best kind of materials that are suited for this purpose were the ones which had a high amount of reactive alumina. So calcined clay is probably the best SCM purpose and we saw that with this kind of a system, you do not necessarily have to have a very pure kaolinite. When you have a very high content of kaolinite like 90% and above, you are talking about products like metakaolin, which could be quite expensive.

What we would like to do is, utilize the waste clay, clay reject material that is available at the quarries or mines where they are getting kaolinite out for other industries like ceramics and paints. So in those cases, the clay which has a kaolinite content of 40-60% as small as that is suitable enough to be used as ingredient in the ternary blended limestone calcined clay cement.

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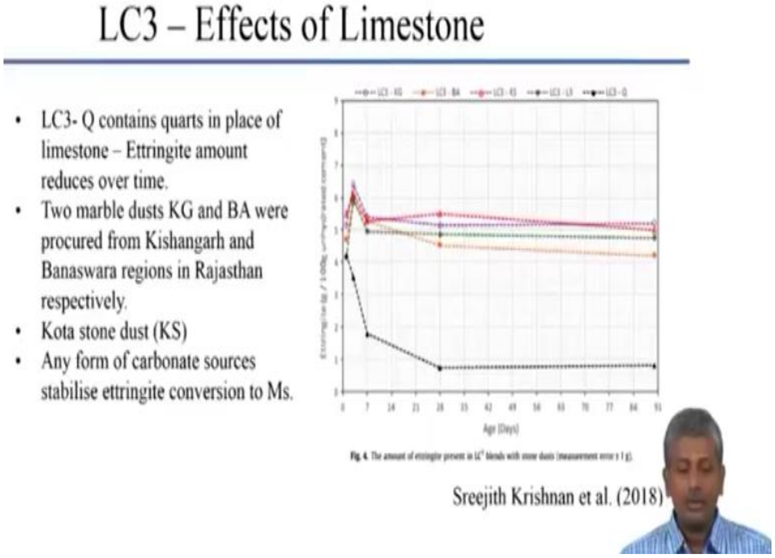

LC3 – Effects of Limestone

- LC3- Q contains quarts in place of limestone – Ettringite amount reduces over time.
- Two marble dusts KG and BA were procured from Kishangarh and Banaswara regions in Rajasthan respectively.
- Kota stone dust (KS)
- Any form of carbonate sources stabilise ettringite conversion to Ms.

Fig. 4. The amount of ettringite present in LC³ blends with stone dusts (measurement error ± 1 g).

Sreejith Krishnan et al. (2018)

Effects of limestone obviously are towards the physical packing effect that you get as a filler as well as the chemical effect that you get when it reacts with the aluminate. Interestingly, there are several limestones, which are considered to be unusable by the cement industry. When you have limestone, which is lying as a reject in the cement industry, much of that is simply getting dumped, not really being utilized for cement manufacture.

Even if it has to be utilized, what the cement industry has to do is, get very pure grades of calcium carbonate to add along with this impure grade of calcium carbonate, so that they get an overall formulation that is suitable for cement manufacture. However, if you can find alternative uses for this limestone, it can really make a lot of sense. So people have explored the use of this waste limestone from cement industry.

As well as there are other like marble dust, which can also contribute to calcium carbonate or Kota stone dust. Again, you know that the stone processing industry in several parts of the country produces lots of wastage. Even if you look at the granite quarries, which are doing granite slabs or the Cuddapah slate slabs, the amount of wastage generated could be as high as 80-85% in many cases. That means they are only utilizing about 20% of the material properly.

So this wastage is often available as dust and when you are talking about limestone based materials, the dust could be quite useful from a perspective of limestone calcined clay cement. So there is evidence to show that any form of carbonate source can stabilize the ettringite formation at the early stages and prevent its long term conversion to the monosulfate phase. So again, this figure is showing the amount of ettringite present in LC3 blends with stone dust.

Here, is with the specific type of LC3 and again with other types of stone dust, you are again stabilizing the amount of ettringite that is actually forming. So ettringite is not really reconverting to monosulfate in this case. This diagram here is with quartz. So that is what is marked LC3 quartz. That means instead of limestone, they have used another inert filler like quartz.

So you are not really getting that reaction that you expect with limestone and aluminate from the SCM in that case. So you only have unreactive crystalline silica and quartz, which is not really doing anything like that. It is only probably doing the filler effect to some extent, but not really the chemical effect that you expect with limestone.

With all the grades of limestone, whether it is Kota stone dust or regular limestone, all these are actually leading to stabilization of the ettringite that is forming at the early stages. That means it is not converting back to monosulfate.

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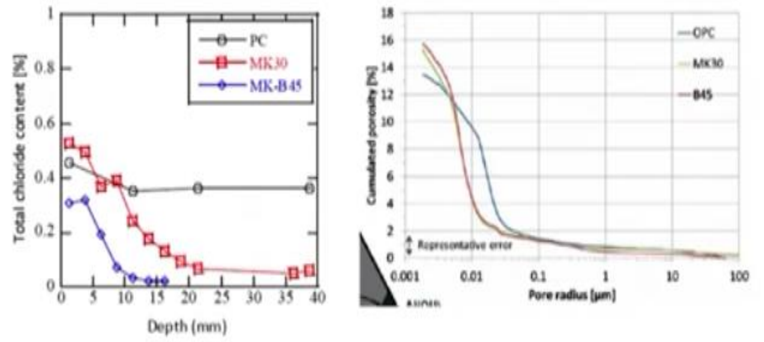
LC3 – Durability performance



Research results from EPFL Switzerland and UCLV Cuba

Now in terms of durability performance, LC3 has been shown to have excellent durability particularly with respect to chloride binding capacity. As a result, you should look at the chloride diffusion results that are presented on the left side of this graph. If you look at the data for Portland cement, it shows that a fairly high content of chloride exists way into the depth of the concrete member.

Whereas when you do the same with concrete that is having 30% metakaolin substitution of the Portland cement, you substantially bring down the extent of chloride ingress into the concrete and further when you are using limestone and calcined clay as combination, you are actually getting this down further to a much lower chloride diffusion characteristic for your concrete. That means you are improving by several orders of magnitude the chloride binding characteristics that leads to an increase in the chloride resistance of the concrete.

Once again, this is the porosity expressed in terms of the pore radius. So this is basically the graph that you get when you do the mercury intrusion porosimetry study that we talked about earlier. So here as you put more and more pressure in the mercury, it keeps intruding smaller and smaller pores. So the pore radius is decreasing in that direction, that means you are increasing the pressure in that direction. As you increase the pressure, more of the pore start getting filled up.

Because with higher pressure, the mercury will be able to intrude into smaller pores. So what you see here is that as compared to ordinary Portland cement, the pores sizes that you see with the metakaolin substituted blends as well as the LC3 are much smaller. That means you need to actually exert more pressure on the mercury to intrude those pores.

That simply tells you that your system with limestone calcined clay cement will end up having a much lower porosity and lower pore size distribution. So overall you get a much more positive influence on durability.

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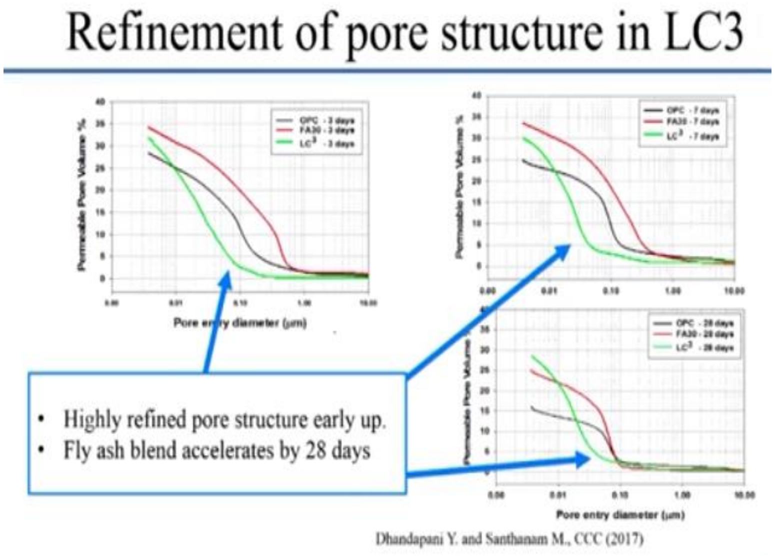

Refinement of pore structure in LC3

- Highly refined pore structure early up.
- Fly ash blend accelerates by 28 days

Dhandapani Y. and Santhanam M., CCC (2017)

Now again, this is result that is produced at our lab and again it shows the same kind of trend or same kind of scenario and here the comparison is made not just with OPC, but also with 30% flyash replace mix. So you know that flyash does not really perform very well at the early ages. It requires some time before which it can actually show the true pozzolanic potential. So at 3 days, you can see very clearly that OPC itself is finer than the flyash system.

LC3 is much finer, so you get a highly refined pore structure as early as 3 days. If you compare 7 days, the flyash is coming closer and closer to the OPC and by 28 days, the flyash is almost better than that of the OPC, but LC3 continues to be, the green curve is representing LC3, showing a very fine pore structure.

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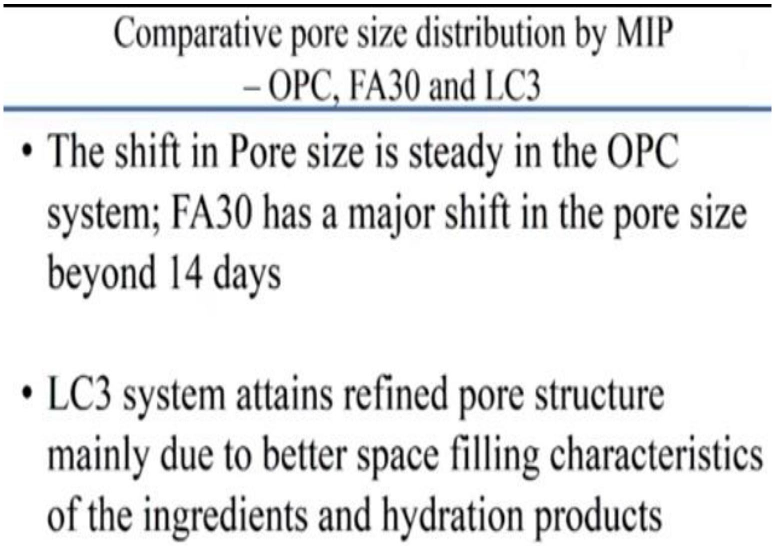

Comparative pore size distribution by MIP – OPC, FA30 and LC3

- The shift in Pore size is steady in the OPC system; FA30 has a major shift in the pore size beyond 14 days
- LC3 system attains refined pore structure mainly due to better space filling characteristics of the ingredients and hydration products

Now the shift in pore size is steady in the OPC system. You expect that as the rate of hydration slows down after 7 days, your pore sizes are not going to change that much after 7 days. From 7-28 days, again going back to the previous slide, the OPC system still had the same sort of critical porosity that it had at 7 days. The pores were not really reducing in size. Overall porosity may have been coming down with extra hydration.

But the critical size, which has to be intruded by the mercury to completely penetrate the system, that critical size is getting reduced as the age of hydration increases. With LC3, you see that at 3 days itself, you have a fairly fine size of pores, 0.1 micron is the critical pore entry diameter. That is about 100 nanometers. When you come to 7 days, this comes down to about 0.09 or 0.08 or something like that.

But then, between 7 and 28 days, again with LC3, there is not much of a change. You do not see much of a refinement in porosity. That means most of your reactions are nearing their physical completion, practical completion at 7 days itself. Now again, please remember your Portland cement paste system is a system which can continue to grow or can continue to hydrate as long as there is space available for more hydrate products to fill up.

Once the space is restricted, you cannot really form and nucleate these hydration products, which will further keep on refining the pores. On the other hand with flyash concrete, you know very well that the pozzolanic reaction is much slower, because of which there is substantial reduction in the pore sizes from 7 days to 28 days in the case of flyash and possibly when you extend the curing to 90 days, you may even see that effect quite strongly with respect to flyash based mixes.

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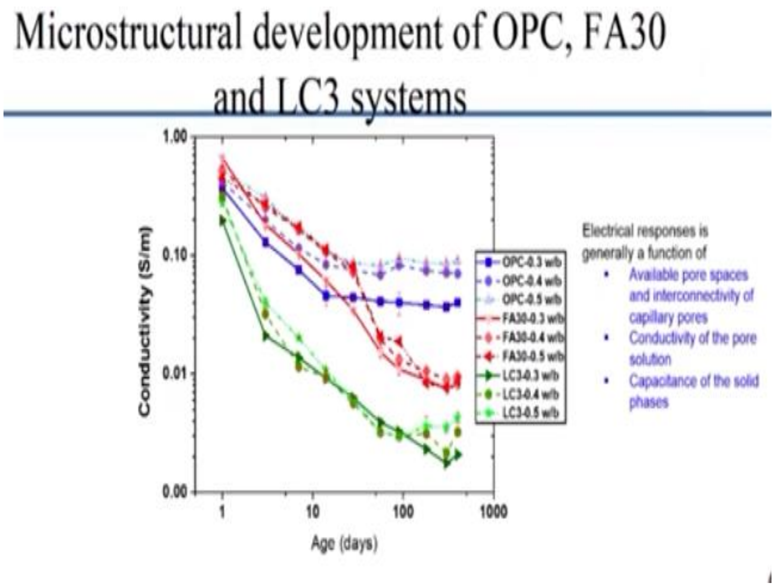

Microstructural development of OPC, FA30 and LC3 systems

Electrical responses is generally a function of

- Available pore spaces and interconnectivity of capillary pores
- Conductivity of the pore solution
- Capacitance of the solid phases

Again what we have seen is the microstructural development in terms of mercury intrusion porosimetry. This diagram is actually showing you the system in terms of the measurement of conductivity. Once again, conductivity is because of what, because of interconnected porosity ones and then the second is the ionic concentration of the pore solution. So once again when you have LC3 or any mineral admixture-based systems, you end up reducing the interconnectivity of the pores.

So you expect the conductivity to come down any way and further with systems like LC3 or silica fume for instance, you are also going to trap the alkali ions, thus reducing the pore solution concentration, and because of that, we expect that the conductivity drop is going to be quite drastic at very early ages itself. So all these green curves basically are limestone calcined clay systems. The flyash system, just because it hydrates much slower, tends to start dropping its conductivity significantly only beyond about 28 days of hydration.

Whereas the OPC system has stabilized even after about 10-14 days of hydration. Again this is showing the same effect with flyash, with OPC and with LC3. So this is an interesting cartoon that you can show. So you have your LC3, which is making up the hare in the tortoise and hare story, but of course in the story the ending is a little bit different. The tortoise wins and the hare loses, here the tortoise is losing because it is slow.

Because LC3 is faster getting to the cash, that is what at the end. There is more cash available.

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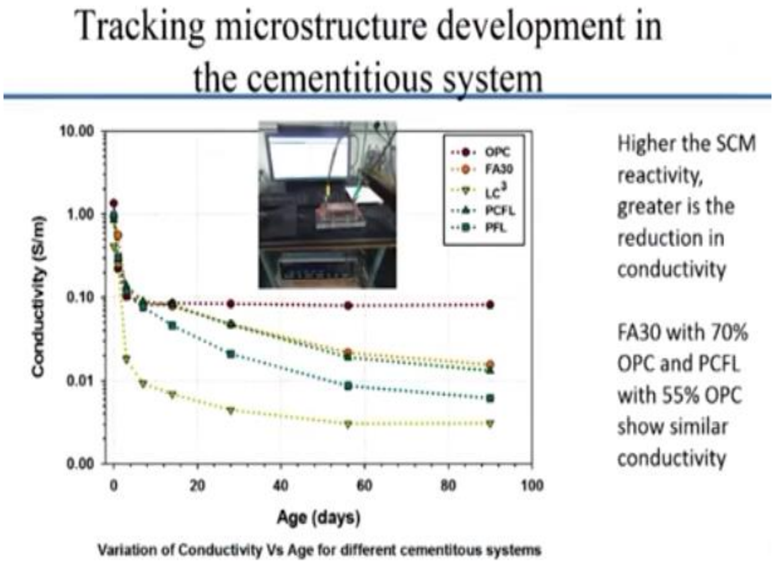

Tracking microstructure development in the cementitious system

Variation of Conductivity Vs Age for different cementitous systems

Higher the SCM reactivity, greater is the reduction in conductivity

FA30 with 70% OPC and PCFL with 55% OPC show similar conductivity

Again this is similar result, so I am not going to talk about this in more detail.

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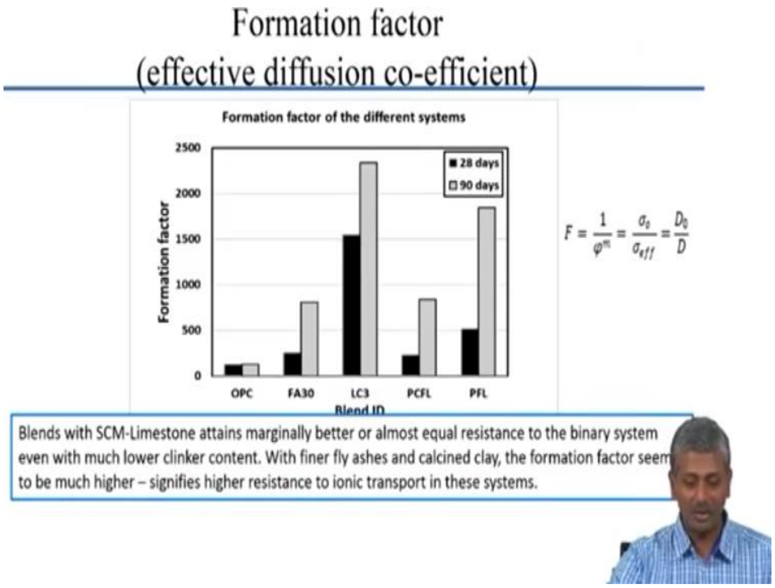

Formation factor (effective diffusion co-efficient)

Formation factor of the different systems

$$F = \frac{1}{\varphi^m} = \frac{\sigma_0}{\sigma_{eff}} = \frac{D_0}{D}$$

Blends with SCM-Limestone attains marginally better or almost equal resistance to the binary system even with much lower clinker content. With finer fly ashes and calcined clay, the formation factor seem to be much higher – signifies higher resistance to ionic transport in these systems.

Now what happens is the interconnectivity of the porosity that determines the conductivity of the system can be converted to something called the formation factor. Now formation factor is also known as the effective diffusion coefficient. Please remember your concrete is basically a mixture of interconnected network of pores and then solids around these pores. When you try to conduct charge through this concrete, the conduction will primarily happen through the interconnected porosity.

Then, your solid phase also can have some influence in that conductivity. So based on the interconnected pores or how straight or how tortuous these pore systems are, you will ultimately get an effective conductivity, which you can use to calculate this formation factor. So formation factor is nothing but the conductivity of the pore solution divided by the effective conductivity of the system.

So the formation factor being low implies that your conductivity of the system is influenced mainly by the conductivity of pore solution. If you are having a very high formation factor, it implies that the conductivity of the system is extremely low irrespective of the conductivity of the pore solution. Did you get my reasoning there. So this formation factor is the ratio of the conductivity of pore solution divided by the conductivity of the overall system.

If the overall system has very low conductivity irrespective of your conductivity of the pore solution, the formation factor will be high. So when the system has very low conductivity, what does that mean, it has got much better resistance to penetration of aggressive fluid. So the higher the formation factor, the better is your concrete with respect to durability.

Please remember that the conductivity experiments were done on cement paste and the formation factor, which was actually taking inputs from the conductivity measurement was again determined on cement paste and this will later be applied to understand what would be the potential durability of these concrete systems. As compared to OPC, your LC3 is at a completely different level of formation factor.

Of course, FA30, the 30% flyash replace mix at 28 days, it is not that much different from OPC, but by 90 days the significant additional hydration that leads to much higher formation factor.

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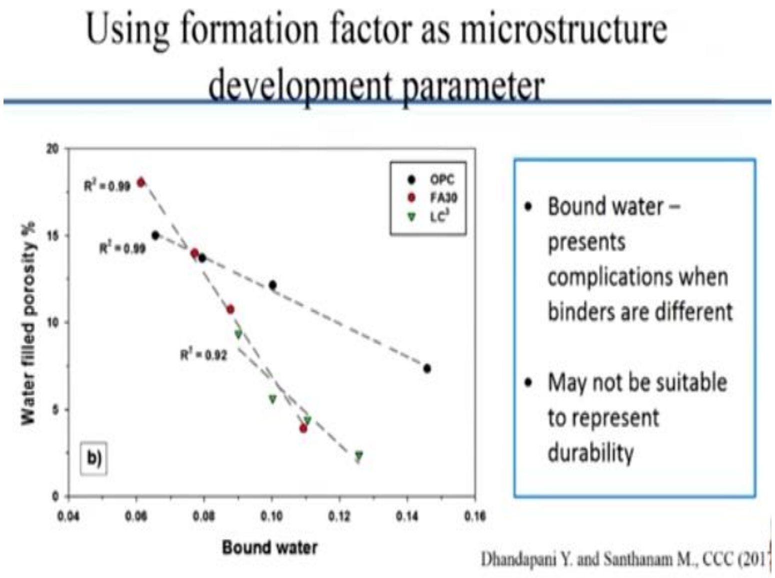

Using formation factor as microstructure development parameter

- Bound water – presents complications when binders are different
- May not be suitable to represent durability

Dhandapani Y. and Santhanam M., CCC (201

So now how does this formation factor work, the formation factor seems to be a much better indicator of your water filled porosity than the bound water content. This is actually plotting the water filled porosity in the system as a function of the bound water content. Please remember bound water, we talked about the fact earlier that this is the water that is bound to the structure of the hydration products, more hydration, more bound water.

As more and more hydration happens, you expect the interconnected porosity to reduce. So with increasing bound water content, you expect that your water filled porosity is going to keep coming down, but unfortunately what happens is when the binders are different, like your OPC binder or your flyash-30 binder, or LC3 binder, your results are quite different. There is no clear dependency. There is no single dependency on this.

But when you use formation factor, you get a much better relationship with respect to all concrete mixes irrespective of the type of binder. You see here porosity is plotted as the function of the formation factor and you see a much better correlation between the results. Of course, this is not a linear correlation, but still you have a very good quadratic or other exponential fit in this case. Now when you use this sort of an equation, what you can effectively end up doing is understand the influence of formation factor on the durability parameters.

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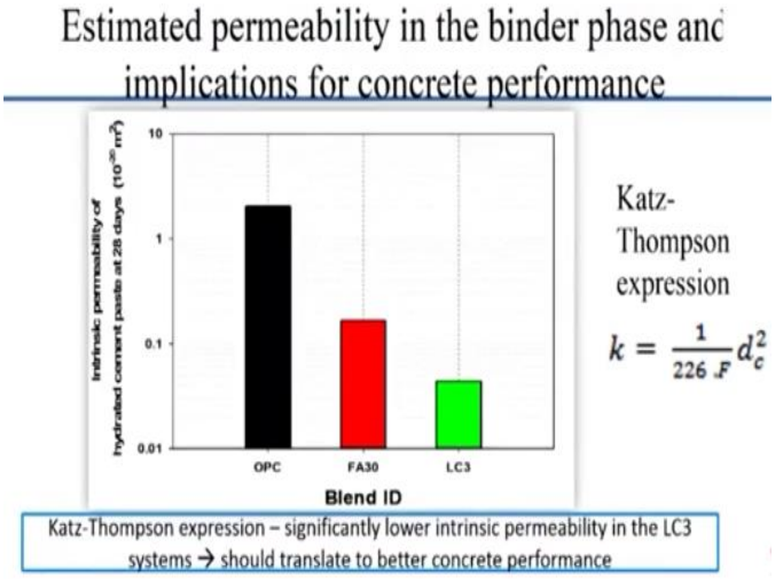

Estimated permeability in the binder phase anc implications for concrete performance

Katz-Thompson expression

$$k = \frac{1}{226 . F} d_c^2$$

Katz-Thompson expression – significantly lower intrinsic permeability in the LC3 systems → should translate to better concrete performance

That can be done further with the help of this expression called the Katz-Thompson expression. Here the permeability coefficient K, which is also called the intrinsic permeability that means, you are expecting this value to be there in the system. Intrinsic permeability of the system is given as:

$$K = \frac{1}{226 * F} * \mathrm{dc} * \mathrm{dc}$$

Where K=intrinsic permeability, F=formation factor and dc=critical diameter. Please remember we talked about mercury intrusion porosimetry, where we pick up this critical diameter.

So you use this equation to get an expression called intrinsic permeability. Now obviously, when the intrinsic permeability is high, your concrete permeability is expected to be high. When the intrinsic permeability is low, your concrete permeability will be expected to be low. Again here, as you see very clearly, as you come from OPC to FA30 to LC3, there is a drop in the intrinsic permeability. The question remains whether this will translate into a better durability performance or not.

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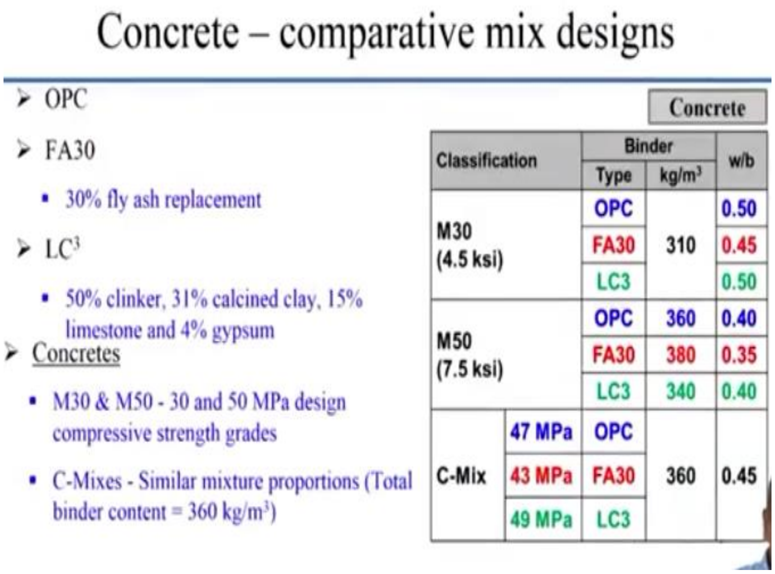

Concrete – comparative mix designs

- OPC
- FA30
  - 30% fly ash replacement
- LC^3
  - 50% clinker, 31% calcined clay, 15% limestone and 4% gypsum
- Concretes
  - M30 & M50 - 30 and 50 MPa design compressive strength grades
  - C-Mixes - Similar mixture proportions (Total binder content = 360 kg/m^3)

Concrete

Classification		Binder		w/b
		Type	kg/m^3	
M30 (4.5 ksi)		OPC	310	0.50
		FA30		0.45
		LC3		0.50
M50 (7.5 ksi)		OPC	360	0.40
		FA30	380	0.35
		LC3	340	0.40
C-Mix	47 MPa	OPC	360	0.45
	43 MPa	FA30		
	49 MPa	LC3		

For that obviously you need to do extensive studies. So we actually have performed studies on different types of concrete. You have M30 concrete, M50 concrete and a concrete, which was designed with the same binder content and water-binder ratio. Please remember, M30 and M50 could mean different water cement ratios based upon the type of binder. For example, compared to OPC, you may need lower water cement ratio to get the same grade of concrete, when you use flyash.

This M30, M50 is basically with OPC, flyash 30% and LC3 mix and with the M50, of course, you can see very clearly there is a significant difference in the binder contents, in the case of M30 you have the same binder content, but some difference with respect to the water-cement ratio that was needed for the flyash paste mix. For LC3, there was no need to change that.

In fact for M50, for the type of LC3 that was produced in this, you could actually use the same water-cement ratio as the OPC mix, but you needed lower binder content, as opposed to the OPC mix to obtain the same grade of concrete. Now the common mix had 360 binder content and 0.45 water-binder ratio. So here we were working with 3 different binders. We designed 3 concrete mixes, 1 based on 30MPA grade, 1 based on 50 MPA grade and 1 based on a common binder and water-binder ratio grade.

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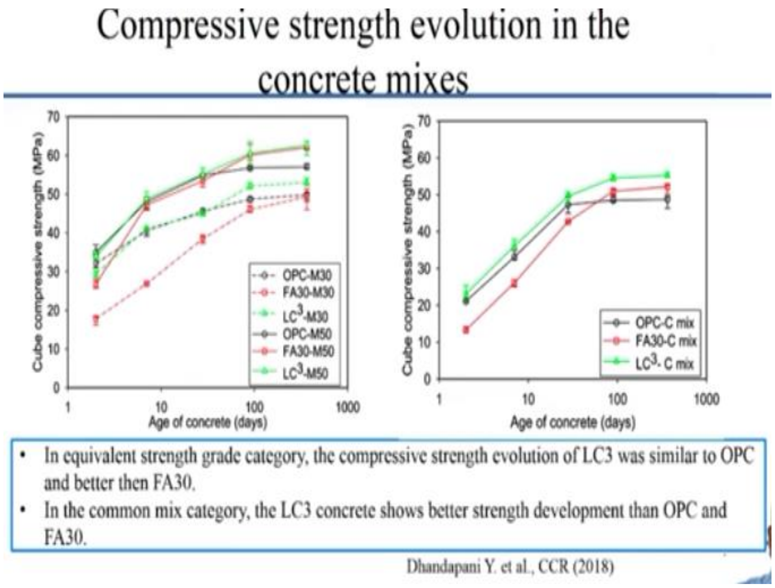

Compressive strength evolution in the concrete mixes

- In equivalent strength grade category, the compressive strength evolution of LC3 was similar to OPC and better then FA30.
- In the common mix category, the LC3 concrete shows better strength development than OPC and FA30.

Dhandapani Y. et al., CCR (2018)

Let us see how this works. The strength evolution is not much different ultimate strength, but what you see as your LC3 and OPC systems are obviously obtaining strengths much faster than your flyash system that is again expected. It is not really something surprising. In terms of the common mix, when you compare the same binder, LC3 appears to be marginally higher than your OPC and flyash based systems.

Marginally higher, I would not say it is very high, because the difference is less than 10 megapascals out of a strength of nearly 60 megapascal. I am not going to really talk about that as being major. So this is actually strength development all the way up to one year. So fairly long term performance have been collected in this case, but more importantly, we have to look at the results of the durability parameters.

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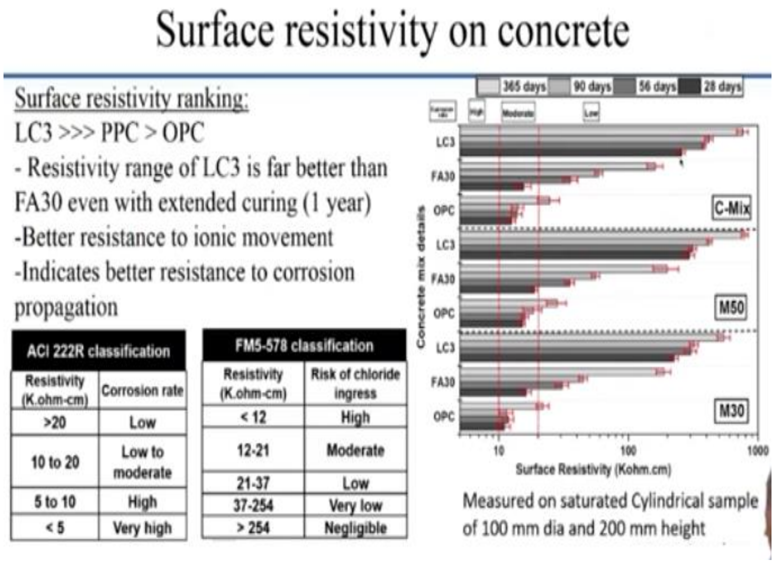

Surface resistivity on concrete

Surface resistivity ranking:

LC3 >>> PPC > OPC

- Resistivity range of LC3 is far better than FA30 even with extended curing (1 year)

-Better resistance to ionic movement

-Indicates better resistance to corrosion propagation

ACI 222R classification

Resistivity (K.ohm-cm)	Corrosion rate
>20	Low
10 to 20	Low to moderate
5 to 10	High
< 5	Very high

FM5-578 classification

Resistivity (K.ohm-cm)	Risk of chloride ingress
< 12	High
12-21	Moderate
21-37	Low
37-254	Very low
> 254	Negligible

Measured on saturated Cylindrical sample of 100 mm dia and 200 mm height

Once again, surface resistivity, which we saw earlier with flyash and slag based mixes as to how they compare it with OPC, we saw that you could actually get the resistivity to be at a very high level, when you replace cement with 30 or 50% slag or flyash. In this case, the comparison is totally different. With OPC, your resistivity is more in the range of 10-20 kilo ohm centimeter. Whereas with LC3 concretes, you are in the range of several 100s kilo ohm centimeter.

This has a major significance with respect to corrosion propagation. If your concrete is highly resistive, that means inverse of conductive, then the flow of ions through your concrete medium is going to be highly restricted. That means your corrosion propagation will be affected severely. In other words, LC3 system is expected to have a very positive influence on corrosion propagation.

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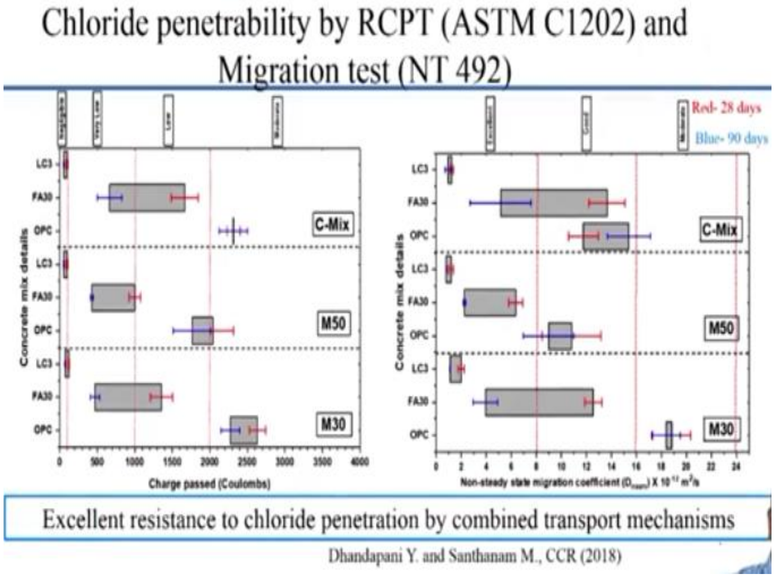

Chloride penetrability by RCPT (ASTM C1202) and Migration test (NT 492)

Excellent resistance to chloride penetration by combined transport mechanisms

Dhandapani Y. and Santhanam M., CCR (2018)

When you look at RCPT, rapid chloride charge passed, your Portland cement concrete is in this range, always around 2000-2500 coulombs. Whereas your LC3 systems are in a range, which was previously thought to be achievable only with silica fume. Remember I talked about the fact that silica fume gives a very positive result with respect to RCPT. LC3 can give you even a better result with respect to RCPT.

You see here that you are obtaining extremely almost negligible permeability as per the scale suggested by the AST test method, which actually looks at the RCPT test. Similarly the chloride migration test another electrical potential applied test where you are measuring the depth of chloride penetration and converting that to an effective diffusion coefficient, you see again the LC3 system seems to have a much better performance as opposed to the OPC or even flyash based systems.

Again the results across the board show that the chloride resistance characteristics of LC3 based concrete are far superior to that of OPC concrete and definitely better than even the flyash concrete. Now again sorptivity is again the unidirectional absorption by capillary action of water through the system, so once again with LC3, you see the softivity values are generally lower as compared to ordinary Portland cement, irrespective of the type of mix that has been tested.

Once again, it is not just with respect to the conductivity, we are also looking at direct water absorption and that also shows a positive result with respect to LC3. Oxygen permeability is presented here in terms of an index. So the permeability coefficient is typically of the order of 10 to the power minus something. So when you take negative log of that, you get a positive number. The lower the permeability, the higher will be the permeability index, because you are taking a negative logarithm of that number.

Again with flyash and LC3 systems, there is a distinct advantage over the OPC system with respect to gas permeability also. So what does this mean that your resistance to carbonation or carbon dioxide diffusion may be higher because of the pore structure, but what does the result of the carbonation show. That is more important for us to understand.

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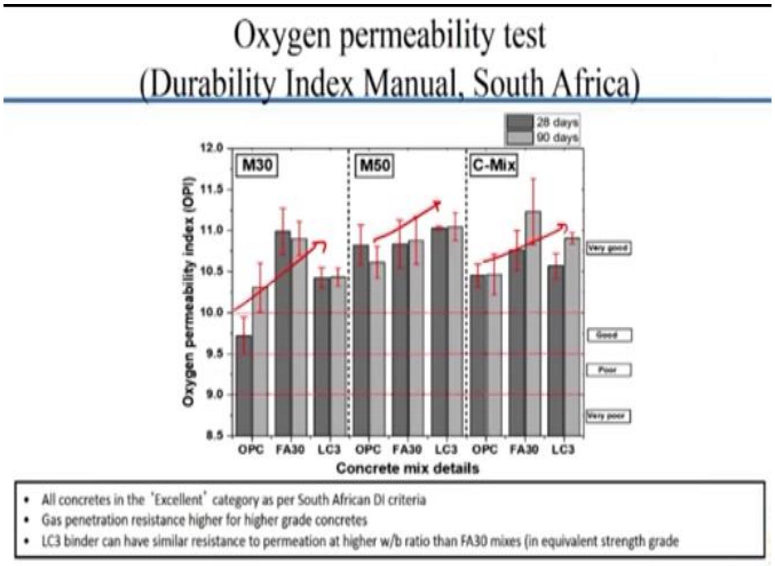

Oxygen permeability test
(Durability Index Manual, South Africa)

- All concretes in the 'Excellent' category as per South African DI criteria
- Gas penetration resistance higher for higher grade concretes
- LC3 binder can have similar resistance to permeation at higher w/b ratio than FA30 mixes (in equivalent strength grade

Again pore structure, once again for concrete it is reflecting the same kind of result that you get for cement paste. So I am not going to talk in detail about this. Bulk diffusion again is a chloride diffusion, which we talked about previously and I already explained to you the results that are obtained in the first few trials with LC3 again here also, compared to OPC, your system with LC3 and flyash.

Because here the concretes were actually hydrated for one year, cured for one year and then tested for chloride resistance, that means at one year, potentially all flyash that has to react would have been reacted. There is no question of more flyash reaction after that. So potentially the structure has been developed completely and there is generally no difference between your flyash concrete and LC3 concrete.

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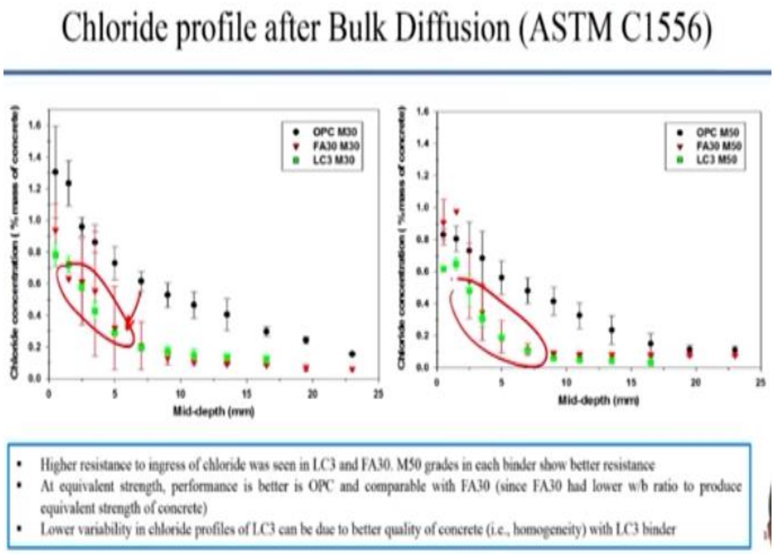

Chloride profile after Bulk Diffusion (ASTM C1556)

- Higher resistance to ingress of chloride was seen in LC3 and FA30. M50 grades in each binder show better resistance
- At equivalent strength, performance is better is OPC and comparable with FA30 (since FA30 had lower w/b ratio to produce equivalent strength of concrete)
- Lower variability in chloride profiles of LC3 can be due to better quality of concrete (i.e., homogeneity) with LC3 binder

Again this is showing you the bulk diffusion for the concrete mix which had similar binder content and water-binder ratio. So at that level, you see that the LC3 is actually able to give you better performance than your flyash based systems and needless to say, anytime you substitute OPC with mineral additives, your chloride diffusion will definitely be better, but the extent of difference is much better with LC3 systems.

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Tests on slabs – cured in field-like conditions

- ➤ RC slabs prepared using the M30 grade concrete, subjected to moist curing using Hessian cloth for 14 days after which slab was exposed to environment → Cores extracted for durability tests at 28 days
- ➤ Companion specimens, subjected to continuous moist curing for 28 days

Now the important part is how does this actually perform in the real field. So we were not just testing specimen that we are cast and cured in the lab, we also cast slabs, which were then used to remove cores from the slabs and these cores were actually examined for their durability potential. So again, this is the slab, which is being cast and these are cores that have been removed from the slab at different ages.

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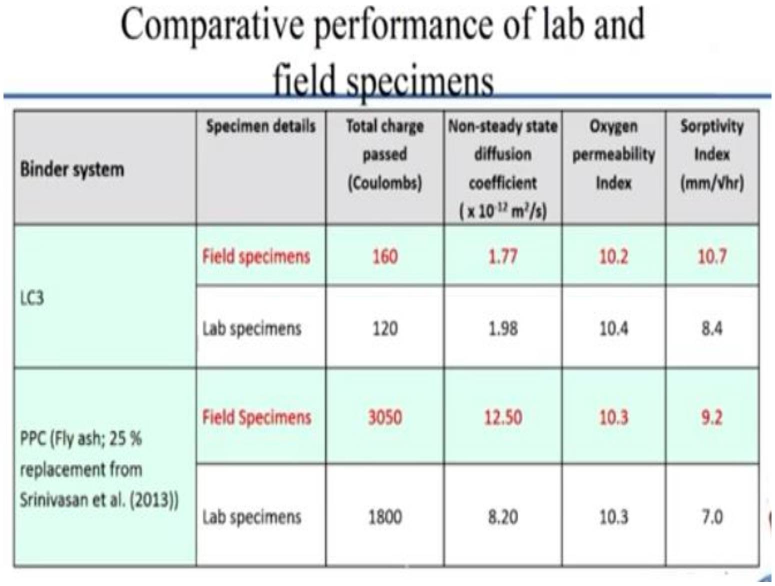

Comparative performance of lab and field specimens

Binder system	Specimen details	Total charge passed (Coulombs)	Non-steady state diffusion coefficient ($x\ 10^{-12}\ m^2/s$)	Oxygen permeability Index	Sorptivity Index (mm/√hr)
LC3	Field specimens	160	1.77	10.2	10.7
	Lab specimens	120	1.98	10.4	8.4
PPC (Fly ash; 25 % replacement from Srinivasan et al. (2013))	Field Specimens	3050	12.50	10.3	9.2
	Lab specimens	1800	8.20	10.3	7.0

So what I am presenting here is a snapshot of the result that was obtained. With LC3, compared to the lab specimen, which showed a charge passed 120 coulombs, the field specimen were still able to show a charge passed to 160 coulombs. That means there is not much difference between the lab cured and field cured specimen. Even your non-steady state diffusion coefficient is not really different by much.

Your oxygen permeability is almost the same. Only the sorptivity index is a little bit different. The capillary absorption of moisture is a little bit higher for the field specimen, but for all the other conditions, your system is performing nearly the same as the lab cured concrete. Lab cured means 28 days lab cured. Field cured means 7 days moist cured and then exposed to the atmosphere. You get nearly the same performance.

But with PPC, here it is a 25% flyash replaced concrete mix. Look at the difference between the lab and field specimen. Major difference is there. Except for oxygen permeability, which is not really capturing that difference very well, but especially with respect to the charge passed and the non-steady state diffusion coefficient your gap is very large. This means that concrete with LC3 may not be very sensitive to the differences in curing that occur in the field.

For example, if you are curing OPC concretes for 7 days, you can continue to cure your LC3 concrete also for 7 days. You do not need to do extended curing like you need for PPC or flyash based systems.

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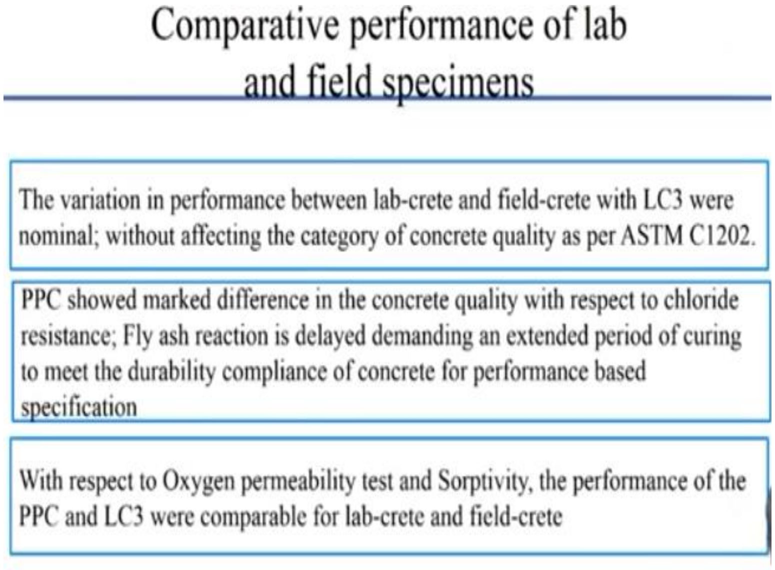

Comparative performance of lab and field specimens

The variation in performance between lab-crete and field-crete with LC3 were nominal; without affecting the category of concrete quality as per ASTM C1202.

PPC showed marked difference in the concrete quality with respect to chloride resistance; Fly ash reaction is delayed demanding an extended period of curing to meet the durability compliance of concrete for performance based specification

With respect to Oxygen permeability test and Sorptivity, the performance of the PPC and LC3 were comparable for lab-crete and field-crete

This is just explaining the result in words, so I leave that to you to understand.

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Sugarcane Bagasse Ash

Sugarcane bagasse ash (SCBA) - by-product from boilers of sugar industries. Reactive silica component – useful as pozzolanic material

Unfortunately, I do not have the result for carbonation in this presentation, but I would like to tell you that in general with respect to carbonation, the performance of LC3 is poorer as compared to OPC or even flyash concrete. Now when you compare the same binder content and water-binder ratio, the carbonation rate of flyash concrete and LC3 concrete is not much different. But nevertheless, both these concretes are poorer as opposed to ordinary Portland cement concrete.

We already discussed why that should be the case, because you have less lime availability in the system. In LC3, you have much greater chance of most of the lime getting depleted. That is because all your reactions, pozzolanic reaction, the carbonate reaction, everything involves lime. So lot more lime consumption is happening in the LC3 system as compared to your flyash based or slag based systems.

You can expect that there is definitely going to be a reduced resistance to carbon dioxide penetration. Now the question is whether that actually leads to carbonation induced corrosion and we discussed that, that will depend a lot on the availability of moisture. If moisture is restricted, as we expect to be the case with LC3, you may not really have a condition of corrosion, even though carbonation depth is greater.

That is enough to discuss about LC3. Now we will look at some more interesting admixtures that can be used more from the local perspective. So we saw LC3, limestone is available wherever cement is available. Clay is mostly available in all parts of the world, so you can actually make LC3 globally, so it is one of the global means of looking at reducing the cement clinker impact in concrete.

Coming from that, we can actually try and adopt more local means of reducing the cement clinker usage in concrete also and one of the local means is the use of sugarcane bagasse ash. So bagasse is basically the fiber that is left behind after you crush the sugarcane and extract the sugar. So bagasse, the fibers have very good calorific value, so they can be burnt quite nicely in boilers and lot of heat can be obtained by burning, which can be used for other purposes, like conversion of: processing the sugar further or it can be used to generate electricity.

So today, it has been mandated by the government that all sugar producing plants, which are using sugarcane to produce sugar, have to have a cogeneration plant. That means they also need to produce power to satisfy their own requirements. So because of that, there is an increase now in the extent of burning of bagasse that takes place and then bagasse burns, it makes this black coloured product called bagasse ash.

For the most part, people are not really concerned with the environment, so that they simply do is mix this ash with a little bit of water and dump it. Water is added so that the ash does not fly around and create a nuisance. So mostly if you go in the vicinity of sugar plants, most of this ash would be dumped, but what you need to look at is this ash has a very good source of silica, just like rice husk ash there is quite a bit of silica that is present in bagasse ash.

Nearly about 70% silica content can be available in your bagasse ash. So that could be a useful resource as a pozzolanic material.

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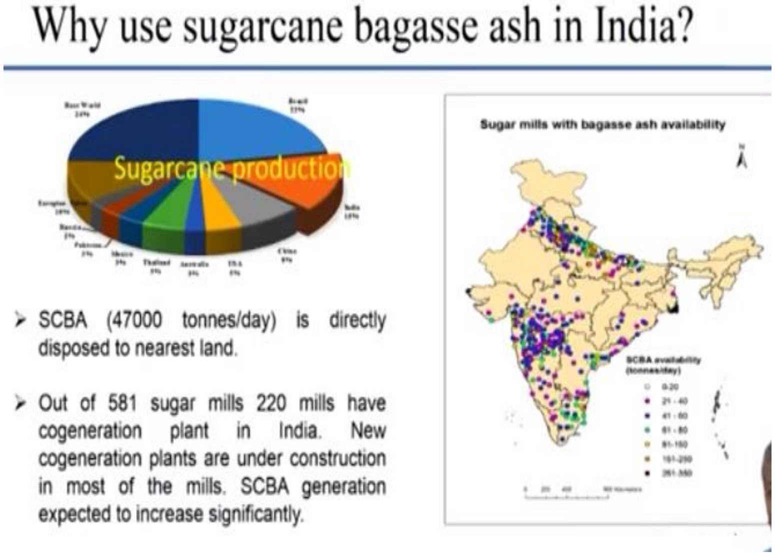

Why use sugarcane bagasse ash in India?

- SCBA (47000 tonnes/day) is directly disposed to nearest land.
- Out of 581 sugar mills 220 mills have cogeneration plant in India. New cogeneration plants are under construction in most of the mills. SCBA generation expected to increase significantly.

In India, it makes a lot of sense because India ranks second in the world in terms of sugarcane production after Brazil. If you look at literature on bagasse ash, you will see a lot of literature coming out of Brazil, obviously because it is available there in plenty. Then India, Thailand, so these are the countries that produce a lot of bagasse. In India, 47,000 tonnes per day of bagasse ash is produced and it is available for usage, but it is mostly getting disposed.

Now if you convert that to a yearly figure, what you get 47,000 tonnes in terms of an year, if you convert that multiply it by 365, what do you get. Let us say multiply it by 300. Let us say 50,000*3 is 150,000 tonnes*100, so we are talking about 1.5 million tonnes/year. How much flyash is generated per year, 250-300 million tonnes of flyash. How much cement is manufactured in India per year, about 300 million tonnes.

So flyash availability is nearly the same as the extent of cement manufacture in India. Bagasse is only showing up to 1.5 million tonnes, but it may make sense to have bagasse or bagasse ash in the areas where the cement production relies heavily on flyash for production of PPC. So when flyash is not available, a useful alternative source for that ash content could be bagasse ash, but then we need to be convinced that whether this material can perform as well as flyash or not.

That is why we undertook a very large research study, but before that, of course, you can see here, that the concentration of sugar plants is in some states. Here you have basically in the Indo-Gangetic plain, you have in Maharashtra, in Tamil Nadu and Karnataka. That is where you have most of the sugar plants located and you can see here the bagasse availability in tonnes per day has been plotted and there was an extensive research program that was conducted here by one of my previous Ph.D. students.

He continues to work on this and what he has done now is produced a GIS enable map, which can actually explore, which can actually tell the cement plant what is the nearest availability of the ash, whether it is flyash or bagasse ash, based on the GIS based network. So that way the cement companies can actually utilize it to determine what could be a useful substitute for them to make the PPC.

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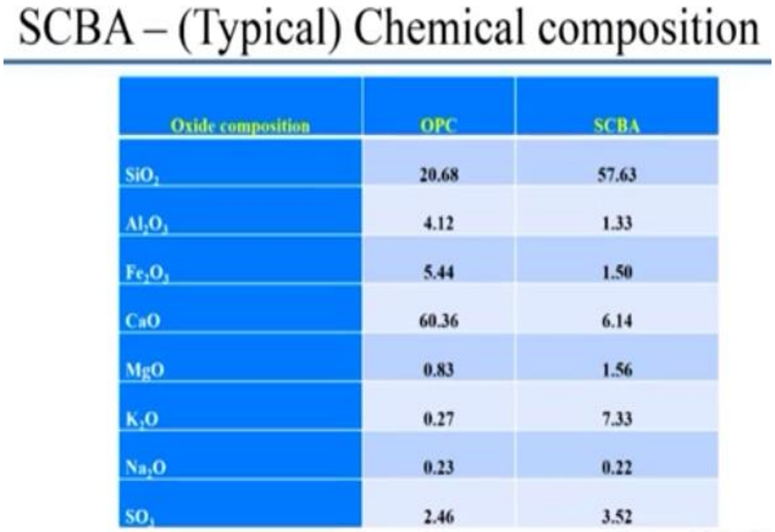

SCBA – (Typical) Chemical composition

Oxide composition	OPC	SCBA
SiO_2	20.68	57.63
Al_2O_3	4.12	1.33
Fe_2O_3	5.44	1.50
CaO	60.36	6.14
MgO	0.83	1.56
K_2O	0.27	7.33
Na_2O	0.23	0.22
SO_3	2.46	3.52

Once again, the proof of the pudding as I said always is in the eating, so is the bagasse ash suitable for use in concrete? For that, you need to test its properties through a systematic characterization and understanding how it actually affects the contributing properties. With respect to OPC, the primary difference with bagasse ash is that, it has got very high silica content, which is quite similar to that of flyash.

Overall on an average, people have reported 60-70% silica in the bagasse ash. Now I was also talking about the fact that these agro-based ashes could have higher alkali contents also. So you need to be a little bit careful in exploring how these system will affect the alkali-silica reactivity in case you have a silicious reactive aggregate that you are using in your system. So you may also have some sulfate that is coming from the bagasse ashes.

So again, you need to be careful about how this will overall affect the performance of your system.

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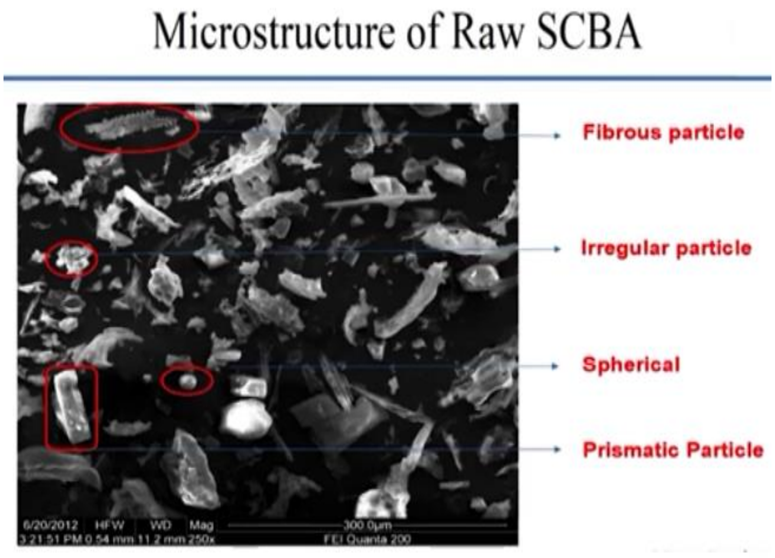

Microstructure of Raw SCBA

Now what we try to do next was to look at, when we collect this bagasse ash directly from the sugar plant, of course it is in a wet state. So it needs to be dried first. So you have to spend some energy to get rid of the water or if you can improve the collection procedures, you can collect it directly from the boiler without really wetting it. So here it is collected in a wet state and then dried and then we try to explore the particle characteristics of the bagasse ash particles.

Under the microscope, bagasse ash seems to be a mixture of different types of particles. You have fibrous particles, which are similar to what you have with rice husk ash. So what is the fibrous particle, unburnt carbon, organic particles. These are the organic particles, which are remnants of the sugarcane, which are still remaining in the system. You have these irregular particles, like this, which are the most important ones from the reactive silica perspective.

Because these irregular particles are the ones, which give you the reactive silica. You also have spherical particles, which seems to indicate there is some condensation from the gaseous state. These sphere may be hollow or maybe solid, but mostly they chose at some level of order has been obtained in the formation of these spherical particles and then you have very finely ordered prismatic particles, which seems to indicate that there is some crystalinity also in the system.

In the boiler, the temperature is typically maintained around 500-600 degree Celsius. Now, you need a very strict control on the temperature to be able to ensure that you have exactly that range of temperatures. Very often, in certain parts of the boiler, you may end up having temperatures, which are in excess of 900.

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Particles in Sugarcane Bagasse Ash

So what happens to silica when you increase the temperature? When you increase the temperature beyond 900, what will happen, recrystalization may happen. To produce the amorphous material, we need some distinct range of temperatures. If you raise the temperature too high, you may end up getting more crystalinity back in the system, which results in the loss of your reactivity in the system.

When you go to above 900 degree Celsius, you start forming these sort of prismatic materials, which are representing highly crystalline systems. What we then try to do was, look at the characteristics of these individual particles in the bagasse ash. So we tried to eliminate the coarse and fine fibrous fractions that were there in the bagasse ash. You can see here that the length of these coarse fibrous fractions is more than 10 mm.

Finer fibrous fractions are probably 3-5 mm in size. The real particles that are useful for us are obviously the fine burnt silica particles, which are much smaller than that.

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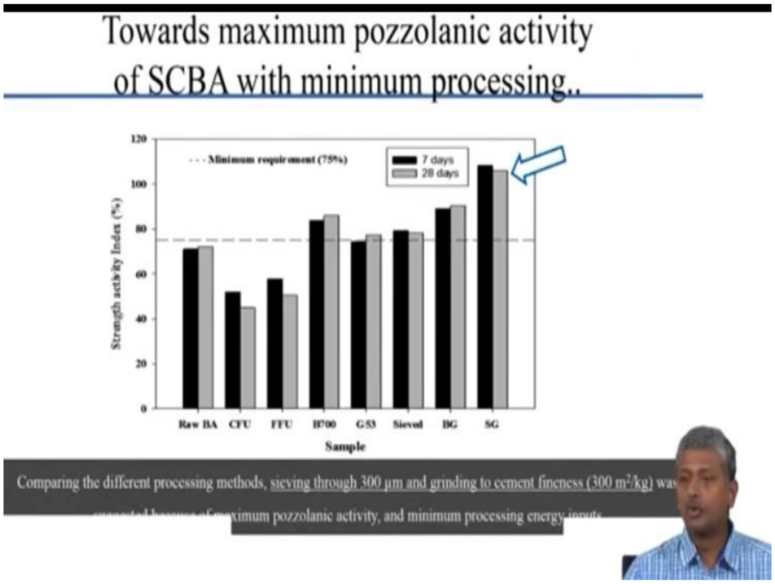

Towards maximum pozzolanic activity of SCBA with minimum processing..

Comparing the different processing methods, sieving through 300 μm and grinding to cement fineness (300 m^2/kg) was [illegible]ximum pozzolanic activity, and minimum processing energy inputs.

What we wanted to do was, explore how best we can utilize the potential of this material without really having the need to process it extensively. Because any processing in terms of heating or grinding and all that requires the use of energy, so any additional energy that you put already starts cutting down the utility of the product. Because if you put in more energy, the utility of the product will reduce.

Because you want to use systems that are waste or by-products from other industries like flyash for instance. For it to compare with something like flyash, you need to produce a system, where you input very less energy. So in this case, we tried several different methods. All these are expressed in terms of the strength activity index. We discussed earlier, strength activity index is simply the strength of the pozzolanic system divided by the strength of the plain Portland cement system expressed as a percentage.

For flyash deemed to be a pozzolan, this minimum strength activity index should be 75%. Your flyash should be at least having a strength activity index of 75% for it to be deemed a pozzolan. So here we applied the same to bagasse ash and prepared blends with 20% substitution of the cement with bagasse ash. Just like you do for flyash, if you look at ASTM C311, that describes the strength activity index test for flyash and we applied the same test here for bagasse ash.

You can see here that the as collected bagasse ash, the raw bagasse ash at 7 and 28 days was falling marginally short of the requirement. Obviously, it needs some processing, otherwise you are not really going to get substantial benefits out of it. When we extracted only the coarse and fine fibrous fractions, our performance is really going down tremendously. That means there is something wrong. We do not want to use those in the concrete at all.

There has to be some way of getting rid of the carbon. There are different ways, 1 is obviously burning at a higher temperature. Instead of 500-600, we took the material. We did an extensive burning study. We found that at 700, we could maximize the potential. Beyond 700 because of the reconversion to crystalline forms, the reactivity came down and we lost the performance. At 700, when you burn it, you are increasing the pozzolanic activity to more than 80% that is good.

Then you are giving substantial extra energy input after the material has already undergone a burning process. So that may not be a viable option at all. We tried a grinding study also. We took this bagasse ash that is collected and kept on grinding it to different sizes. Now interestingly what happened was when we started grinding it in different sizes, it was a carbon particle that were getting ground. The silica, which were harder than the carbon, did not get ground at all.

So until we ground to a fineness of less than 53 microns, we were not able to make this 75% deadline at all. Again too much energy is being input and you are not really getting any benefit out of it, because you are simply grinding the carbon, which is of no use. Now this is interesting, simply sieving it through a 300 micrometer sieve was able to actually extend your pozzolanic activity index to above 75%.

Now that is an interesting thing, because most of the carbon seems to go out. Originally, this loss on ignition of this as collected bagasse ash was of the order of about 20-21%. After the sieving, it came down to less than 6%. That is a major change in magnitude of unburnt carbon that you have in the system. So what we did further was after sieving, we said that anyway when you produce Portland pozzolan cement, the ash is interground with the cement linker.

Let us try intergrinding with the cement or rather when you intergrind with the cement, you get particle sizes that are similar to the cement. So let us try grinding it to a fineness, which is similar to cement 300 square meters/kilogram. When you sieve it and grind it, you obtain a pozzolanic performance that is more than 100%. That means you are actually able to get even better strength than the plain Portland cement mix.

That shows that you have very good potential pozzolanic performance in this material. Now, you also get that from burning and grinding, so 700 degrees burnt material was further ground to 300 square meters/kilogram and that also produced an excellent performance, but why would you do burning when you can actually do sieving. So sieved and ground material, we saw is the best performing of all of these and we use this to produce SCBA based Portland pozzolan cement, which was 5, 10, 15, 20, 25% replacement.

Again 5% replacement is important from the point of view of the performance improver in OPC. There you need to understand what happens when up to 5% material is used. Now 5-20% could be useful from the perspective of blends that you can actually do with other mineral admixtures. At 25%, you want to explore whether it is actually going to produce a significantly good quality PPC or not as opposed to flyash-based PPC, which also contains about 25% of flyash.

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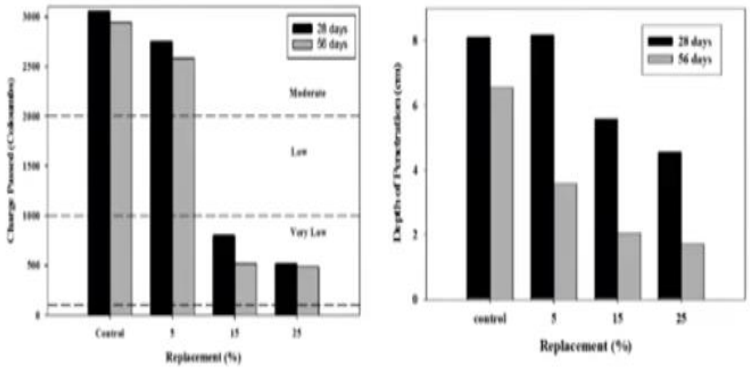
Durability performance of SCBA concretes



Again I am showing you some performance characteristics. Strength, we saw no difference in strengths as opposed to ordinary Portland cement, almost the same level of performance was obtained, irrespective of the replacement level from 5-25%, no drop in the strength at all. The replacement level here is plotted on the x-axis and the charge passed in Coulombs is plotted on the y-axis and you can clearly see as compared to ordinary Portland cement.

Your system is with bagasse ash at least at 15-25% show a very low chloride permeability as opposed to moderate in the case of OPC and when you replace just 5% of bagasse ash, you are able to bring it down marginally and have a positive influence on the performance. Depth of penetration of moisture, this is actually a test where you have a concrete cube, when you apply water pressure and you look at the depth of penetration of water into the system after you apply the same water pressure for 3 days.

This depth of penetration again reduces significantly when increasing levels of bagasse ash were used. Now interestingly what you see is when you cure for a longer period of time, you again get the benefits of the pozzolanic reaction, much better than you get at early ages. That is something that we understand well anyway, because pozzolanic reaction is expected to be slower and in the long term if you continue curing, you are obviously going to get enhanced benefits out of the system. Thank you.