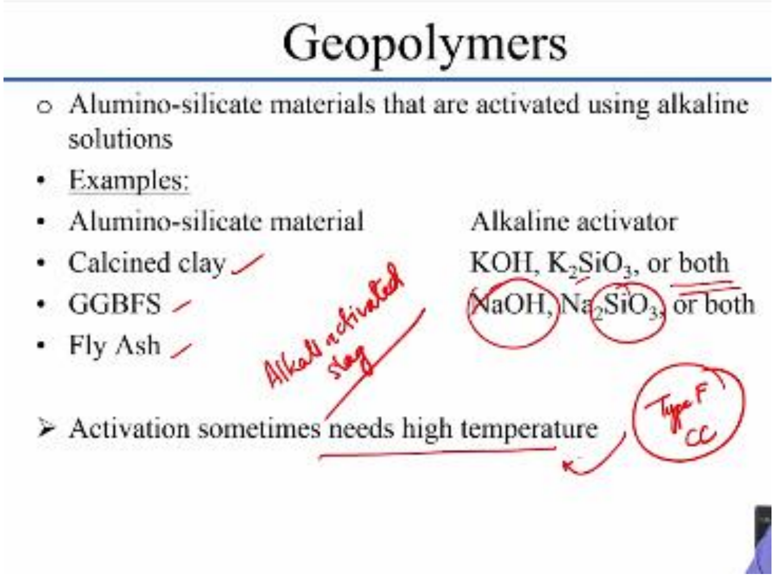
Advanced Concrete Technology
Dr. Manu Santhanam
Department of Civil Engineering
Indian Institute of Technology, Madras

Lecture – 24
Mineral admixtures - Part 7

So, good morning everyone, yesterday we were talking about different types of mineral additives that we used in concrete, we also looked at some specialty additives which were not really globally available but they could be made use of as local solutions to the shortage of cement clinker or to reduce the impact of cement clinker in concrete.

(Refer Slide Time: 00:37)



Geopolymers

- Alumino-silicate materials that are activated using alkaline solutions
- Examples:

Alumino-silicate material	Alkaline activator
Calcined clay	KOH, K_2SiO_3, or both
GGBFS	NaOH, Na_2SiO_3, or both
Fly Ash	

Alkali activated slag

➢ Activation sometimes needs high temperature

Type F CC

Today, we will talk a little bit about geopolymers not too much because I did not really think it was necessary to look at this to a very large extent at this stage. In general, geopolymers are alumino silicate materials that are activated using alkaline solutions, so one example of course we have looked at earlier is the fact you it can improve the hydraulicity of slag or rather the reactivity of slag by using some alkaline activators.

We saw that earlier that you call it alkali activated slag; alkali activated slag but what is happening in this sort of a system that alkali activated slag is basically using alkalis to increase the reactivity of the slag and introducing the hydraulic properties of slag, for example alkali activated slag leads to the production of CSH primarily because of the hydration of the slag, however when we talk about geopolymers, we are looking at some kind of polymerisation that happens in the structure of the inorganic materials.

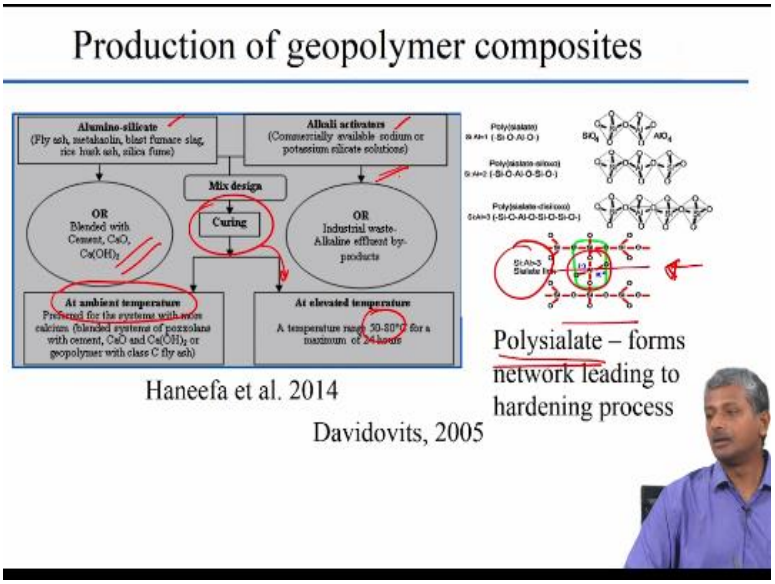
So, primarily these are alumino silicate materials, so the structure changes by the polymerisation of the aluminate and silicate and that forms some sort of a polymeric chain which leads to the hardening and strength development of these kind of concretes, so you have examples of alumino silicate materials like calcined clay, slag and fly ash but we generally exclude slag from geopolymers because we simply call it as alkali activated slag.

When we look at calcined clay or fly ash we call it geopolymers because there is some level of polymerisation that is actually going on, the alkaline activators generally are either potassium hydroxide or potassium silicate or generally a combination of both; potassium hydroxide and silicate, whereas the other kind of alkaline activators could be sodium hydroxide and sodium silicate or a combination of the two.

So, very often you see several research papers that look at only the hydroxide part to try and polymerise the inorganic alumino silicate molecules but sometimes what happens is the silica that is available in the inorganic material is not sufficient enough to cause this polymerisation to happened in a large way, so what is really happening is; you can add an extra source of silicate to increase the extent of that polymerisation.

So that is why people try to use combinations of sodium hydroxide and sodium silicate that seems to give better results as compared to just sodium hydroxide. Now, activation may sometimes need high temperature, the formation of the polymer chains sometimes cannot be accomplished at room temperature and needs a high temperature, so generally for the most part when you look at type F fly ash or even calcined clay, mostly what you will see is; you will have to perform your initial hydration process or initial polymerisation process at a high temperature.

(Refer Slide Time: 03:36)



Production of geopolymer composites

Alumino-silicate
(Fly ash, metakaolin, blast furnace slag, rice husk ash, silica fume)

Alkali activators
(Commercially available sodium or potassium silicate solutions)

Mix design

OR
Blended with Cement, CaO, $Ca(OH)_2$

Curing

OR
Industrial waste-Alkaline effluent by-products

At ambient temperature
Preferred for the systems with more calcium (blended systems of pozzolans with cement, CaO and $Ca(OH)_2$ or geopolymer with class C fly ash)

At elevated temperature
A temperature range 50-80°C for a maximum of 24 hours

Haneefa et al. 2014

Davidovits, 2005

Polysialate – forms network leading to hardening process

The high temperature promotes the linkage between the aluminate and silicate to form the network that result in the polymer formation. I will show what happens exactly here, so when you have alumino silicate sources plus alkali activators, when they are cured either at ambient conditions or at high temperature, what happens is at ambient temperature, what you are doing is; you are preferring this for systems that have a high amount of lime in them likes slag for instance.

Where hydration of the material actually happens and you end up forming some sort of CSH based products, so that is basically alkali activated system but when you do elevated temperature curing your form the geopolymer system, where a temperature range of about 50 to 80 degrees is typically maintained for the first 24 hours or sometimes I have seen research where they have done it for first 72 hours; 3 days.

So, about 50 to 80 degrees moderately elevated temperatures are used to end up forming structures that look like this; that look like this, so what is the structure now? So, we have the silicate chain and this is connected with an aluminate and this connection is promoted by the excess of the alkali ions. Now, what are the alkalis doing; the first step in the process is that alkalis have to help in dissolution of the aluminate and silicate components from the inorganic material?

So there is dissolution, there is nucleation and then there is polymerisation, so this basical element that leads to polymerisation is the formation of the polysialate network, so the sialate link is what is actually forming in these kinds of systems, where you have the silica chains attached with an alumina and this attachment is promoted by the presence of your alkalis, so when this link actually forms, this is actually the monomeric link, with time if you cure it at high enough temperature, you may end up forming this into a polymeric link.

That means, you have several such links in the chain that leads to the formation of the geopolymer, so again there is a lot of literature in geopolymer now, it seems to be the one of the buzzwords as far as research is concerned, lot of people are working in geopolymer and of course, what is it essentially ending up happening is that there is a lot of controversy whether geopolymers are really useful or not.

One way to look at it is that you are working with the system that does not have any Portland cement, geopolymers are typically made without any Portland cement but in some cases you may find that if you add either lime or cement to your geopolymeric mix, you may be able to actually get the polymerisation happening at room temperature, that means at ambient conditions, without the presence of lime or cement when you have inorganic alumino silicate like fly ash or calcined clay, which do not have enough calcium on their own, the reaction will have to be done at high temperature.

So when you to do the high temperature curing you are obviously giving an extra energy input to this process although, the range of temperatures that you have apply for high temperature curing is not very high about 50 to 80 degree Celsius but still there is a minor input of energy that you need to give to this system. So, now elevated temperature means giving an extra energy input.

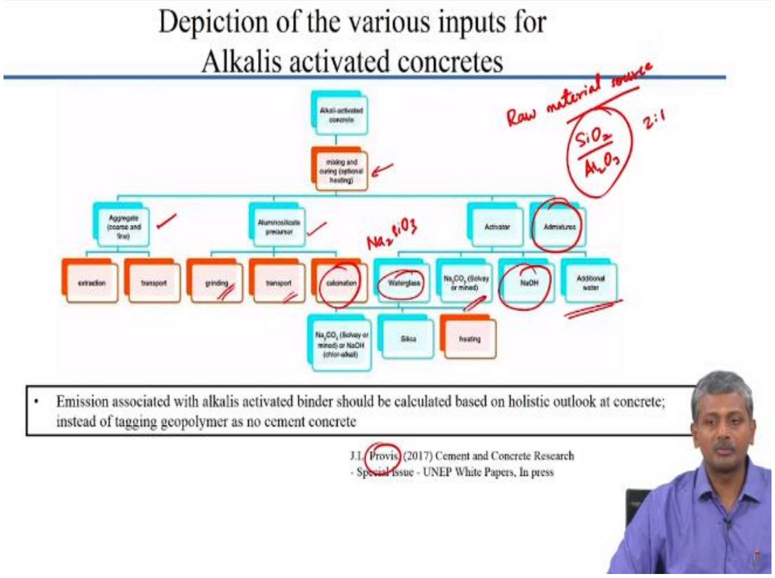
So that is a negative obviously, second is you are leading to a concrete whose performance is not very well known because again this is something which we have not looked at in the long term, what is the long term performance? There is research which looks at durability of course and there is enough research that shows that concrete with geopolymer based binders has comparable durability to the concrete with regular cement based binders.

Now, the positive side of it is that you have cement rather you do not have any cement in this kind of a system, so this kind of composites is being made without any cement at all, what is that mean? The CO_2 impact of cement is no longer going to be felt when you have geopolymer based concretes, but please remember one more thing that we are adding these alkaline activators, we are adding these alkali activators like sodium or potassium silicate, sodium or potassium hydroxide.

The incorporation of these activators implies that there is already a CO_2 footprint associated with the production of these chemicals that is something that you cannot neglect, very often you find in research studies that people simply neglect that and take the fact into account that there is no cement in this composite, so you have to remember that the alkaline solution also contributes extensively to the CO_2 emission.

And secondly, when you actually handle this material, it is quite dangerous because the alkaline activators like sodium hydroxide or potassium hydroxide are caustic, they are not very easy to handle, so you cannot think about this as being done on a regular on site application, this has to have very special control, so for precasting, geopolymer may be quite suitable but for RMC or on site concreting, geopolymer may not be a suitable solution for cement based components.

(Refer Slide Time: 08:33)



Depiction of the various inputs for Alkalis activated concretes

- Emission associated with alkalis activated binder should be calculated based on holistic outlook at concrete; instead of tagging geopolymer as no cement concrete

J.L Provis (2017) Cement and Concrete Research - Special Issue - UNEP White Papers, In press

So, essentially the hardening happens because of the formation of the polysialate network which is basically a linkage between the aluminate and silicate promoted by the alkali ions. So, again what are the various inputs for the alkali activated composites, you have of course, curing process that is extremely important, first of all you need to source your material properly, the raw material source should be perfect.

Now, in general what people have been able come to a conclusion about is the silica to alumina ratio that has to be maintained within a strict limit, and that is important because the kind of sialate network that you want to form depends a lot on the original alumino silicate material, it generally is preferred to have a silica to alumina ratio of at least 2: 1, so that you get substantial amounts of silicate or sialate network forming in the system.

So, again in terms of geopolymer concrete of course, you have the aggregates; coarse and fine aggregates, the alumino silicate precursor, we need to first grind it to really fine particle sizes, so that there is a faster dissolution just like cement hydration, the finer you grind your alumino silica precursor, the faster will be the dissolution rate, then of course, we need to transported to the place where you want to make geopolymer concrete.

Or sometimes we need to calcine it for example, when you have clay; clay has to be calcined to make calcined clay or metakaolin to really enable it to be used as geopolymer composites. The activator solutions include water glass which is your sodium silicate and then you have your sometimes you can add sodium carbonate and definitely need to have sodium hydroxide which leads to the very high pH conditions that are necessary for the initial dissolution of the alumino silicate components to happen.

In some cases, you may need admixtures or additional water to ensure that you get the degree of workability that you want one in the concrete, so what you need to do is; at each step of this process, we need to consider the energy input as well as the emissions in terms of CO_2 to really get to gauge the impact of this material on the construction process. So, again it is not very easy to associate the fact that this is a concrete without cement.

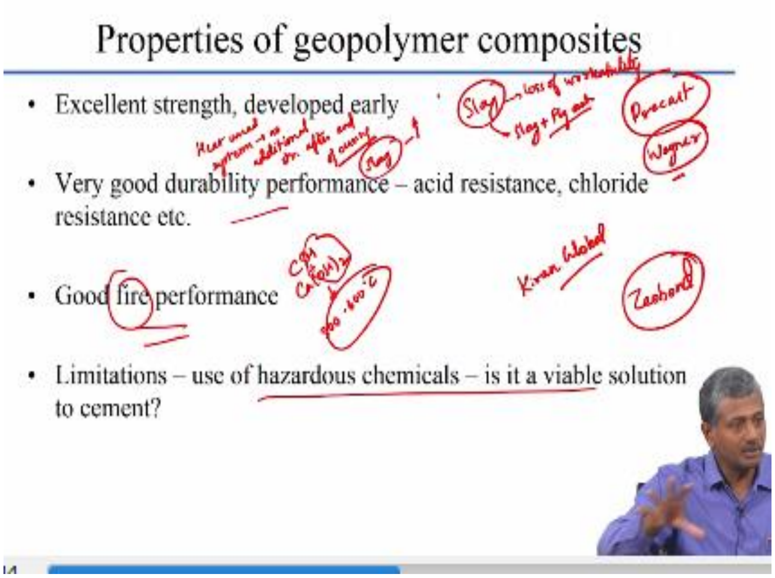
So, it must be definitely greener as compared to regular cement, you have to do an entire calculation based on the concrete itself and then try to understand whether it is actually producing a significant reduction in the CO_2 emissions and energy emissions. One prominent name that you will come across today is John Provis, he is based at the University of Sheffield and a lot of interesting geopolymer related work is being performed by John Provis and his group.

And that is probably, the leading group in the world now that looks a geopolymer research, so those of you are interest in this subject should definitely look up the papers of John Provis, the previous papers that you would mainly see are from a person named Davidovits, he is the French scientist and he was the one who have done some early work on geopolymeric systems as applied to concrete.

Interestingly, another controversy was created that the pyramids of Egypt which were built with huge stone blocks, what people started claiming is that those are not stone blocks, those are actually geopolymers which have been polymerised in moulds and then use directly on site because they try to show some examples that the nearest source of stone was quite far away from the site whether the current pyramids are.

So, they said that okay now, because of availability of the inorganic materials like clay, people started making geopolymer and that is what led to the formation of those large blocks but this theory is not really accepted quite extensively, so there is actually there is a site called www. geopolymer.org which may be interesting for you to go and look at it, the story of the pyramids is also there.

(Refer Slide Time: 12:23)



Properties of geopolymer composites

- Excellent strength, developed early
- Very good durability performance – acid resistance, chloride resistance etc.
- Good fire performance
- Limitations – use of hazardous chemicals – is it a viable solution to cement?

So, generally geopolymer composites as long as you are satisfying their curing requirements will end up giving you a very high strength early enough, especially with slag; the slag based alkali activated systems will give excellent strength at an early stage. The one drawback is when you use slag for geopolymeric systems or for alkali activated systems, you may end up losing your workability very fast.

So, there is a major loss of workability, when slag is used, in fact slag based geopolymer mixes are known to be stable only for about; or known to be workable only for between 15 to 30 minutes, so that serious problem if you are trying to do some large scale concreting, so what people have try to do is; use combinations of slag and fly ash, so fly ash will slow down the system.

And because slag is there, it will continue to hydrate for a long period of time and the strength will continue to develop for 28, 56, or 90 days. So, the fly ash basically will end up geopolymerising but that may take some time to happen because of which you can extend the time that you have for workability to be maintained for up to about 45 to 60 minutes, still not much more than that.

But at least 45 to 60 minutes gives you an enough window to do a fairly good pre casting operation, so it is usually suitable only for pre-cast application, for onsite construction, you need to be extremely careful with the kind of operations that you have in place because the loss in workability is rapid. In, Australia they have actually done some on site applications with the geopolymeric concrete, again not geopolymeric.

Again, mixture of slag and fly ash, alkali activator slag plus geopolymeric fly ash systems, so this is a company called Wagner, which does a lot of construction with geopolymeric materials in Australia, in fact there was also a company that was formed called Zeobond and this company manufactures geopolymer cement, so what they do is; they have the aluminate precursor or alumino silicate precursor and the alkaline activator which are sold either together or separately.

So, for example you will have a 2-part cement, you will have the inorganic alumino silicate in bag and then you may have a bottle of or a jug of the alkaline activator and then you may be asked to actually mix it and serve different kind of the proportions. In India also there was a company that was floated recently called Kiren global and this company has also come out with the geopolymeric cement.

Unfortunately, the uses and the applications are very limited; people have not been able to show this in a large scale yet, so there is still quite a bit of doubt about the long term performance of these kinds of systems. In general, from the research papers what you can get is that the durability performance is usually very good especially, in terms of acid resistance and chloride resistance.

Why, because in regular Portland cement based systems, you end up forming lime, calcium hydroxide, and we have talked about this fact earlier that calcium hydroxide is the first to react with the external solutions like sulphates or chlorides or acids for instance, in the absence of calcium hydroxide and the absence of regular hydrated products like CSH, the components are not as reactive with the components of acids or other inorganic solutions like chlorides or sulphates.

So, generally the resistance to chemical attack is generally improved as compared to OPC concrete when geopolymers are used and the fire perform is also very good once again, because you do not have any lime, so this calcium hydroxide is what causes a major drop in the performance of cement concrete or CSH + calcium hydroxide, so what happens is between temperatures of 300 to 600 degree Celsius, you have a complete loss of the water from these systems.

And because of that your cement paste or cement based systems can actually lose their strength quite rapidly, in the case of geopolymer, you can expect that there is no such hydrated products which is present of course, we are talking about geopolymeric systems not the alkali activated slag systems, when you talk about slag systems, the fire performance will be quite similar to that of ordinary Portland cement concrete.

But here we are talking about geopolymer existence, so with slag systems, there is no difference with respect to OPC but with geopolymers you get much better fire performance. Again, the use of hazardous chemicals you need really evaluated very carefully to see whether it is a viable solution to cement, whether you can actually have the quantities of these chemicals which are required to make concrete on the scale that ordinary Portland cement concrete is made that remains a big question and it is not easy to answer that question.

So, again when you do it in a lab scale, the chemicals are quite expensive but when you do it on an industrial scale, it may be possible to bring down the costs but once again that requires a very careful analysis and people have not been able to provide that very easily because there is no major large scale applications that have been done. Of course, Wagner has done some airport taxiways with this kind of material.

But again, applications are too few and far between to really make a clear estimate of the costs involved. Well, slag based geopolymer systems in the lab we saw, we could easily achieve 70 to 100 mega Pascal’s without any problems and this was achieved within a matter of 7 days, so when you have fly ash based geopolymer systems if you cure them at significantly high temperature 60 to 80 degree Celsius, you may be able to obtain about 50 to 60 mpa at 7 days.

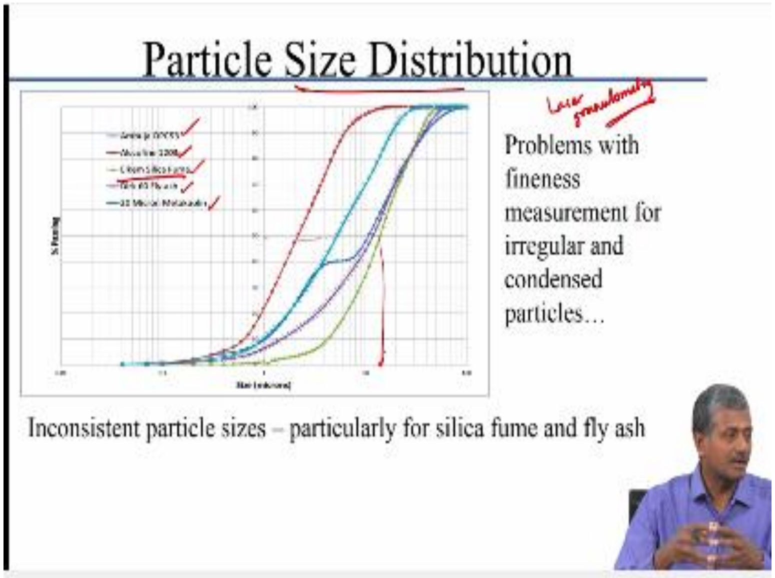
That again depends on the kind of mixture design that you adopt, with geopolymer systems after you finish the heat curing, there will not be much development in the strength, so again for heat cured systems, there will be no additional strength development or rather limited additional strength development after end of heat curing but for the slag based systems obviously, you can imagine that the strength keeps going up as long as there is moisture availability which continues to hydrate the slag.

For slag based systems, the strength will continue to go up with moisture availability, because slag based systems are hydrating, whereas fly ash or calcined clay based systems are polymerising, the polymerisation will stop after a certain period of time. So, heat curing tends to accelerate the hydration of ordinary Portland cement concrete and there is enough evidence to show that heat curing produces concrete which is generally of a poorer quality as compared to normally cured concrete.

But then again, the stoppage in hydration in OPC system happens because there is no space available for the hydrate products to form in group, like we discussed earlier that when mineral admixtures are used only a certain component of it can actually react not all of it because first of all there is lime availability issues, how much lime is actually available from cement hydration and how much space is available for this hydrate assemblage to actually form in fill up.

If there is lack of space, the hydration has to stop at certain stage. So having looked at different types of additive materials and also looked at some special combinations like geopolymers, let us take a look at certain issues that we may have with additive materials that are used in concrete.

(Refer Slide Time: 20:01)



Particle Size Distribution

Problems with fineness measurement for irregular and condensed particles…

Inconsistent particle sizes – particularly for silica fume and fly ash

The first and foremost is trying to understand the particle size characteristics because please remember one of the major advantages of using cement replacement materials is the fact that you can actually optimise the particle sizes to improve the pore filling ability of the cementitious particles. So, using suitable methodologies to determine the particle size distribution is very important.

Quite often, when we use a new material we try to develop a sense of what the particle size are based on either the finess measurements like blaine's air permeability or sometimes we do a sieving test, the amount that is sieving through a 45 microns sieve that is usually taken as an estimate of the finess of this material. Now, none of these tests come close to doing in actual particle sizing test, so particle size distribution needs to be studied using laser granulometry.

So, whenever fine powders are used in cementitious systems, you have to use laser based particle size analysis techniques. Now, having said that you need to ensure that your system is well dispersed for your particles to be detected quite easily, while that is not really a problem with most mineral additives, when you talk about silica fume, you may have serious problems because silica fume, I told you already come in a condensed form.

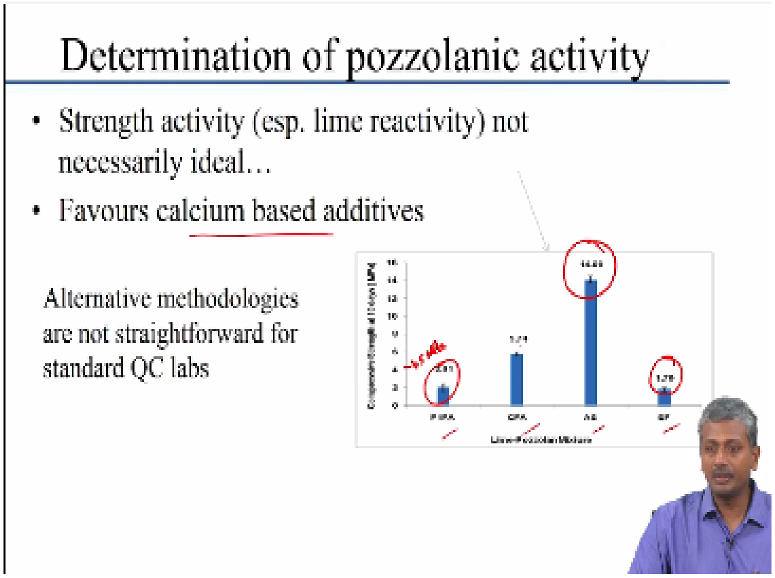
So, in the condensed form look at the particle size distribution, the green one is silica fume and you can see very clearly that it is much coarser as compared to even your cement, its coarser compare to fly ash, its coarser compared to ultrafine slag, here this is the brand name for ultrafine slag, that is basically 53 grade ordinary Portland cement that is silica fume, fly ash and metakaolin or calcined clay in this case.

So, you see very clearly that in the condensed form, the silica fume seems to have a problem as far as laser particle sizing is concerned, you need to develop a technique by which you can actually break the silica fume particles into their individual particles only then you can get the actual estimate of the silica fume particles, please remember we talked about this earlier that silica fume particle has an average size of about 0.3 to 0.5 micron.

If you look at this diagram the D50 for silica fume seems to be around 15 micron, which is not correct obviously, it is going to be much coarser than your cement and your fly ash that is not really what the actual silica fume will be like, so what you need to do is; develop a method by which you can break these agglomerates and then see the actual particle size because unless you really get an estimate of the particle sizes that are likely to be there in your mix, you can never gauge the impact of the filling effect of these materials very well.

Now, this is done directly on the powder, in concrete what is happening; there is substantial attrition between the aggregates that attrition-- usually helps to break down the silica fume particles and of course, you also have a super plasticizer in a concrete system, which can further disperse the individual particles and that will help you get better estimate of your overall particle sizes that you can get in the system.

(Refer Slide Time: 23:23)



Determination of pozzolanic activity

- Strength activity (esp. lime reactivity) not necessarily ideal…
- Favours calcium based additives

Alternative methodologies are not straightforward for standard QC labs

Unfortunately, with laser granulometry, you cannot do all that so, you might end up giving a very erroneous information with respect to the characteristics of this kind of material. Now, one aspect that we talk briefly about earlier is the determination of the pozzolanic activity, how do we accurately pinpoint how much of this material is going to react and what will that reaction contribute to the strength and durability development of the concrete?

So, strength activity tests are not necessarily ideal especially, lime activity because lime reactivity is done in unrealistic systems, we talked about this earlier that you are simply mixing your pozzolan with lime adding water and simply exposing it to a high temperature with a hope to accelerate the process but you do not have the kind of alkalis or sulphates that are contributed in cementitious materials.

So, your system is not really ideal because it is not reflecting the actual scenario which happens in cement replaced systems, now when you do this strength activity tests as per the American standards, you are doing this with cement, so maybe it is a little bit better there but strength is only one parameter, it is not really telling you the whole part of the story, you are not really gauging any reactivity from that.

Because strength could be simply contributed by the fact that many of these additives maybe acting like fillers, so you do not really know what is a chemical reactivity which is happening in the system and interestingly lime reactivity test that at least from our understanding in our lab seems to be favouring the calcium based additives, look at this result here, this is type F fly ash that is type C fly ash, this is slag and that silica fume.

Now, lime reactivity test has to be done for fly ash and as per that the minimum strength you expect from fly ash should be 4.5 mega Pascal's, so in lime reactivity tests, you make the material, you make the mix and simply cast 5 cm cubes, which are tested at the age of 10 days after heat curing, so for fly ash to be qualified as pozzolanic material, it should have minimum strength of 4.5 mega Pascals, this is failing, type F fly ash is failing.

Whereas, type C fly ash is okay with respect to this, interestingly when you do the same test with silica fume, it is failing why, because you need to have certain amount of water in your system that is sufficient to produce a flow, many of these tests ask you to add water to the system which is enough to maintain the same flow as that of the controlled system, in the case of lime reactivity test, there is no control systems.

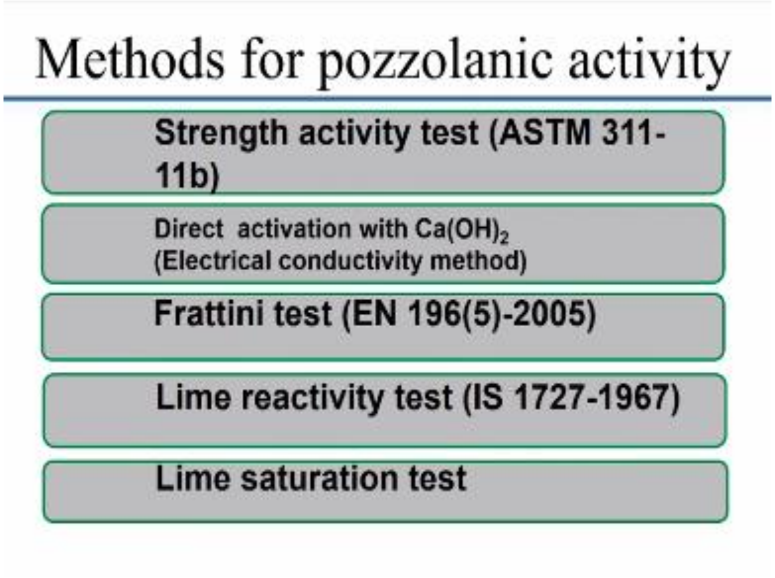
So, they asked you to maintain the flow in a particular range, so imagine you have silica fume obviously you need more water to get the same flow, so this additional water may end up actually producing much lower strength with silica fume based system, already lime is deficient, silica fume you are adding too much water to the system to increase the flow, you are obviously going to get lesser strengths.

With slag, you get extremely good performance with lime reactivity primarily because there is already an excess of calcium oxide present, so further you are doing heat curing, so on its own slag should be able to actually react and produce a much greater strength, so obviously it is not the surprise that all that you are getting such high numbers in lime reactivity test. The alternative methodologies that people are trying to promote to determine the pozzolanic activity are not very simple.

They are based on sophisticated analytical techniques like thermo gravimetric analysis, X ray diffraction all those is a quite confusing to an average quality control engineer, so the quality control engineer can understand strength quite easily but if you look at other techniques that are used to promote understanding of the reactivity is not going to be easy for a QC engineer to execute.

So, again that is something which is still not sorted out quite easily, so we need to arrive at some sort of estimate which can be obtained first of all quite easily and secondly gives a very valid representation of the extent of reactivity and the filler effect separately in your cement based systems.

(Refer Slide Time: 27:13)

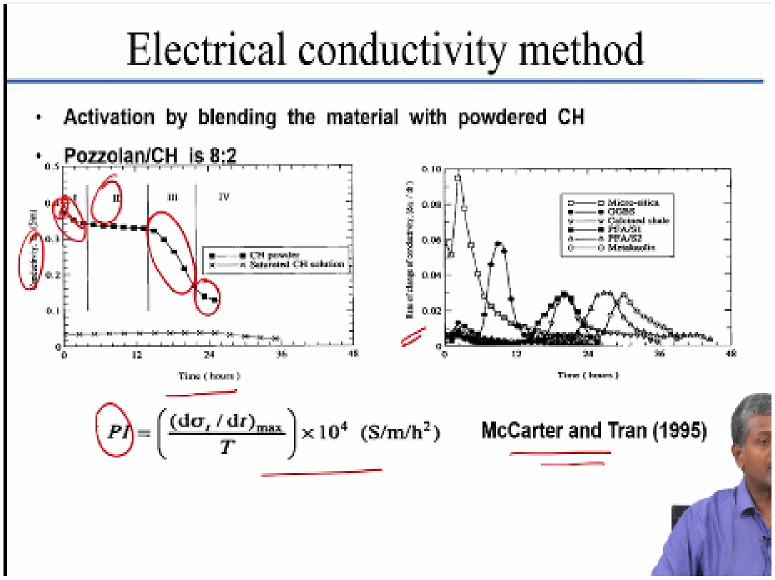


Methods for pozzolanic activity

- Strength activity test (ASTM 311-11b)
- Direct activation with $Ca(OH)_2$ (Electrical conductivity method)
- Frattini test (EN 196(5)-2005)
- Lime reactivity test (IS 1727-1967)
- Lime saturation test

So, again there are different methods, I am briefly presenting these, we are not go into details of these.

(Refer Slide Time: 27:20)



Electrical conductivity method

- Activation by blending the material with powdered CH
- Pozzolan/CH is 8:2

$$PI = \left(\frac{(d\sigma_t / dt)_{max}}{T}\right) \times 10^4 \ (S/m/h^2)$$

McCarter and Tran (1995)

You have the strength activity test obviously and then you have the electrical conductivity method, so what is happening again, when you mix your pozzolan with lime, because of the formation of CSH, your electrical connectivity of the system will continue to drop. So, what you simply do is; monitor the electrical conductivity with time and look at the drop in electrical connectivity and define stages of cement hydration based on that.

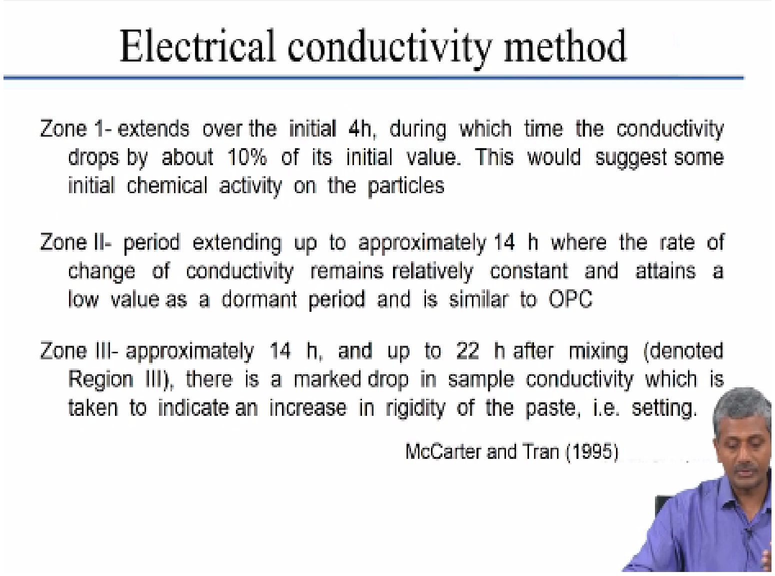
So, this is a classic paper by McCarter and Tran, which is quoted by people who are doing electrical conductivity measurements which says that the conductivity first has a minor rise, then it starts dropping, this minor rise may be because of ionic species that are there in your cement or cementitious system that start dissolving and increase the ionic concentration which leads to an enhancement of the connectivity.

Then, you start seeing a drop and that drop happens because of the initiation of your hydration reactions, that drop is quite rapid in this third stage and what should that correspond to after the final set, basically that is when your CSH hydration is reaching its peak or C_3S hydration is reaching its peak, so it is almost similar to your dominant period here, the second period is almost similar to the dominant period.

Because there is not much drop in connectivity in that stage, and then finally, there is a deceleration stage, where the reaction start slowing down and you start getting a drop in conductivity but very slowly, so what people have been able to do is; such systems have been able to depict much better the kind of pozzolanic activity that may there for your system. Secondly, they have also been able to relate conductivity measurements to the setting time of the concrete fairly accurately.

There are several papers on this, you can read this paper or there are additional papers also available which talk about this aspect, so using this derivative curve, the rate of change of conductivity curve, this kind of relationship was proposed for the pozzolanic activity index by McCarter and Tran.

(Refer Slide Time: 29:26)



Electrical conductivity method

Zone 1- extends over the initial 4h, during which time the conductivity drops by about 10% of its initial value. This would suggest some initial chemical activity on the particles

Zone II- period extending up to approximately 14 h where the rate of change of conductivity remains relatively constant and attains a low value as a dormant period and is similar to OPC

Zone III- approximately 14 h, and up to 22 h after mixing (denoted Region III), there is a marked drop in sample conductivity which is taken to indicate an increase in rigidity of the paste, i.e. setting.

McCarter and Tran (1995)

And of course, this is just describing what those zones that have just talked about are.

(Refer Slide Time: 29:31)

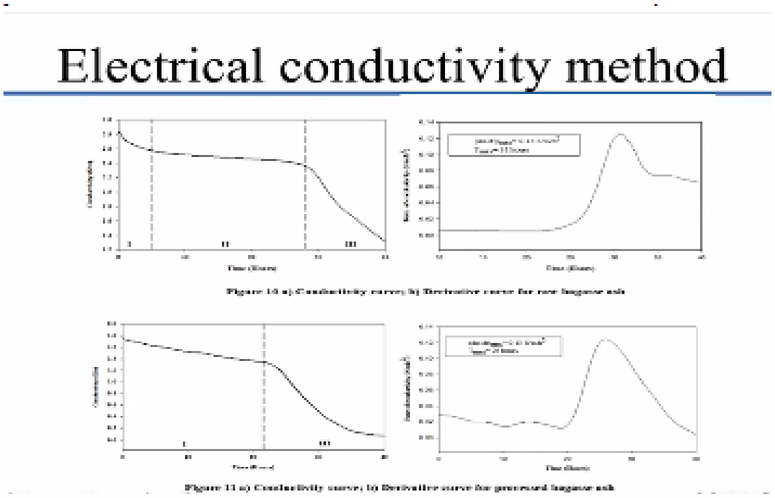
Electrical conductivity method

Again, this is the electrical conductivity test that was done in our lab for bagasse ash, so there is lime, that is bagasse ash and those were mixed in particular proportions, the proportions typically are 8:2, pozzolan to lime ratio, and then you do a mixing in the hobart mixer and that is your; this is the LCR meter which is used to determine the electrical connectivity of a cement paste system.

So, the cement paste was actually filled up into this cube and you had electrodes at 2 ends of the cube and the LCR meter is connected to these electrodes to determine the conductivity. Now, the problem with LCR meter is you have to operated at one particular frequency, so what people seem to prefer over this is the use of AC impedance, so AC impedance produces alternating current over a range of frequencies.

And you can actually test using that this kind of a system to determine the bulk conductivity of your concrete, so AC impedance spectroscopy is increasingly becoming very popular technique as far as construction materials research is concerned.

(Refer Slide Time: 30:42)



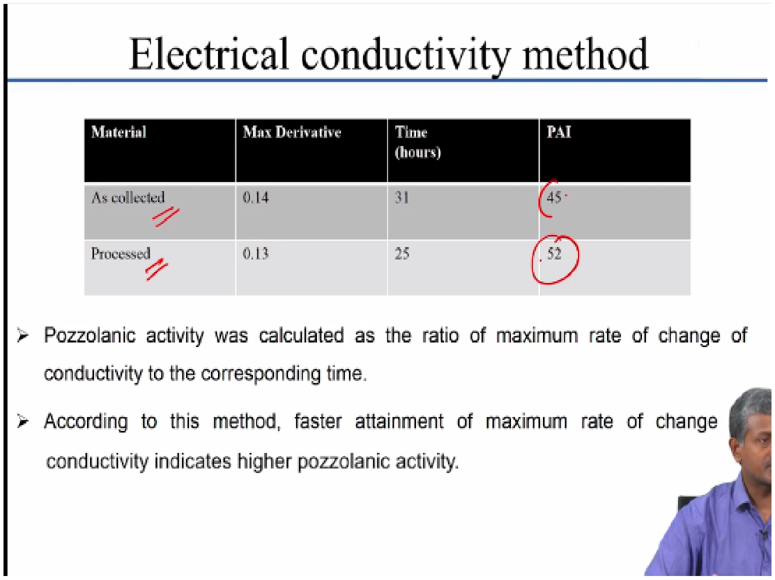
Electrical conductivity method

Figure 10 a) Conductivity curve; b) Derivative curve for raw bagasse ash

Figure 11 a) Conductivity curve; b) Derivative curve for processed bagasse ash

So, again we obtained the same kind of curves for this Bagasse ash based system and based on this, we were able to actually predict the pozzolanic activity.

(Refer Slide Time: 30:50)



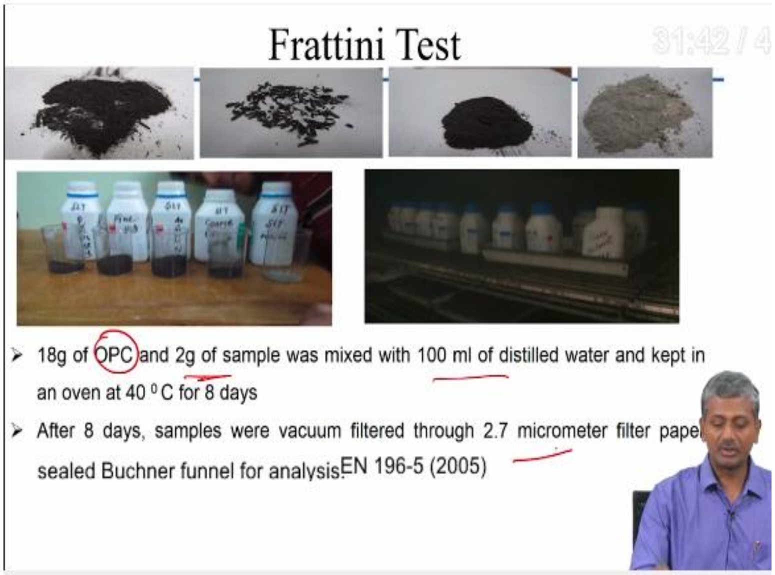
Electrical conductivity method

Material	Max Derivative	Time (hours)	PAI
As collected	0.14	31	45
Processed	0.13	25	52

- Pozzolanic activity was calculated as the ratio of maximum rate of change of conductivity to the corresponding time.
- According to this method, faster attainment of maximum rate of change conductivity indicates higher pozzolanic activity.

So, for example the as collected bagasse ash, please remember this is the bagasse ash that is collected from the site that showed an activity index only 45, whereas the process bagasse ash we talked about the fact that you sieve it and then you grind it to 300 squares meters per kilogram and that led to about 52 units of pozzolanic activity. So, again you obtained a better reactivity, when you are processing this material.

(Refer Slide Time: 31:14)



Frattini Test

- 18g of OPC and 2g of sample was mixed with 100 ml of distilled water and kept in an oven at 40 ^{0}C for 8 days
- After 8 days, samples were vacuum filtered through 2.7 micrometer filter pape sealed Buchner funnel for analysis. EN 196-5 (2005)

The Frattini test is the chemical test which is performed to see how much of the lime can be bound by your silica in the pozzolanic system, so again you can go through the details where you basically use a cement based system, 18 grams of Portland cement and 2 grams of your pozzolanic samples are used and mixed with 100 millilitres of distilled water and then after 8 days at 40 degrees, this sample is vacuum filtered through a filter paper.

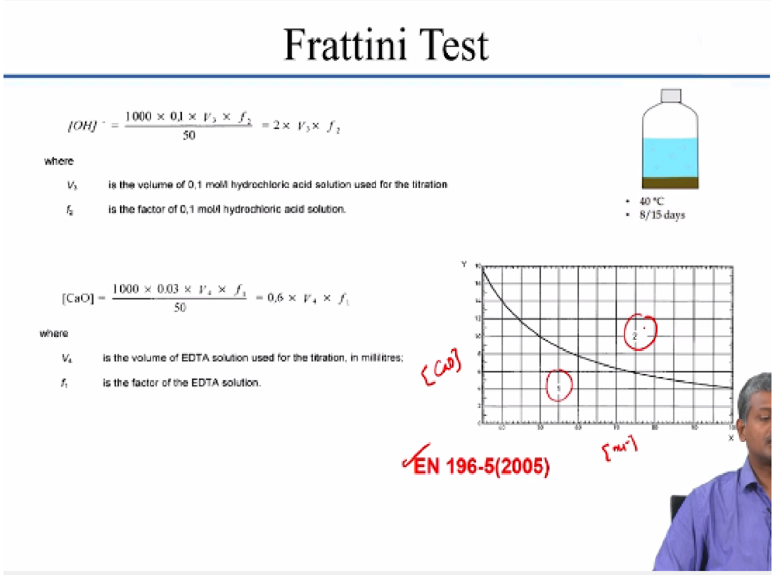
(Refer Slide Time: 31:44)

Frattini test

EN 196-5 (2005)

And then you determine the amount of calcium and hydroxyl ions in your solution.

(Refer Slide Time: 31:48)



Frattini Test

$$[OH]^- = \frac{1000 \times 0{,}1 \times V_3 \times f_2}{50} = 2 \times V_3 \times f_2$$

where

V_3 is the volume of 0,1 mol/l hydrochloric acid solution used for the titration

f_2 is the factor of 0,1 mol/l hydrochloric acid solution.

- 40 °C
- 8/15 days

$$[CaO] = \frac{1000 \times 0{,}03 \times V_4 \times f_1}{50} = 0{,}6 \times V_4 \times f_1$$

where

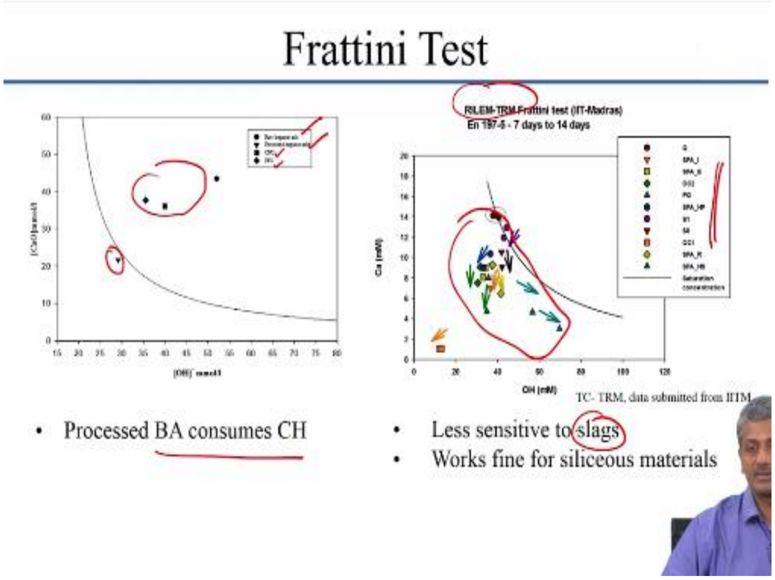
V_4 is the volume of EDTA solution used for the titration, in millilitres;

f_1 is the factor of the EDTA solution.

EN 196-5(2005)

There is a lot of chemistry here, you can read this on your own, the techniques are described quite well in this European standard EN 196-5 and what you do is; you plot on the y axis, the CaO concentration and in the x axis [OH^-] concentration, so you divide your pozzolanic material into the materials that lie below this curve or that lie about this curve. This curve is basically the solubility curve of calcium hydroxide.

(Refer Slide Time: 32:20)



Frattini Test

TC- TRM, data submitted from IITM

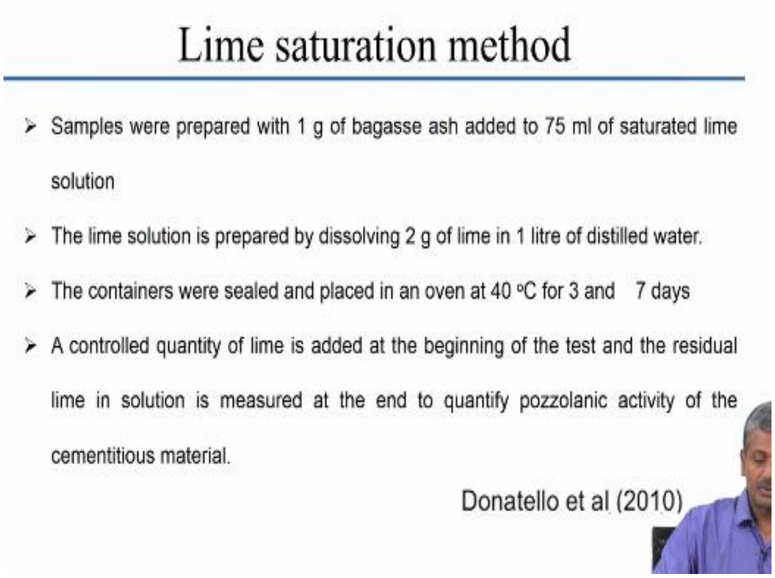
- Processed BA consumes CH
- Less sensitive to slags
- Works fine for siliceous materials

And the points that are lying below the curve depicts the points that are suitable to be used as pozzolanic systems, so that is processed bagasse ash here, whereas the other 3 systems; raw bagasse ash, the coarse fibrous and fine fibrous particles which were removed from the bagasse ash before you do the processing, those are producing pozzolanic activity there is not sufficient. So, process bagasse ash consumes calcium hydroxide and brings your overall concentration of CaO to below this; below the level predicted by the curve.

So, the large amount of data was collected by a special RILEM committee that was actually doing testing of the reactivity of different types of cementing materials, so here there was a range of different fly ashes, slags, calcined clays and all that were tested and they were able to see that a number of these were actually producing extensively good pozzolanic activity. Now, the problem is this test method is not as sensitive to slags.

And its works fine for regular pozzolanic materials whereas, your lime reactivity test seems to be favouring slag and does not work very well for the silicious materials.

(Refer Slide Time: 33:33)



Lime saturation method

- Samples were prepared with 1 g of bagasse ash added to 75 ml of saturated lime solution
- The lime solution is prepared by dissolving 2 g of lime in 1 litre of distilled water.
- The containers were sealed and placed in an oven at 40 °C for 3 and 7 days
- A controlled quantity of lime is added at the beginning of the test and the residual lime in solution is measured at the end to quantify pozzolanic activity of the cementitious material.

Donatello et al (2010)

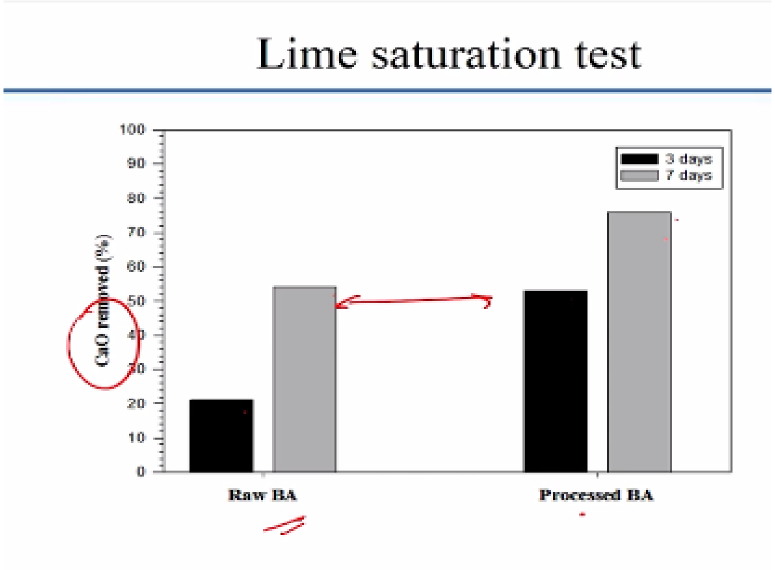
Okay, again lime saturation method is simply mixing your pozzolanic material with saturated lime solution and what you simply do is; you measure the lime remaining in solution because what happens to the lime because of pozzolanic reaction, part of this lime will start getting combined with the pozzolan and lime remaining in a solution can be measured, so that is essentially what is happening in the lime saturation test.

(Refer Slide Time: 33:57)

Lime saturation test

So, once again there is a chemical assessment that is done to determine the extent of lime remaining in solution after you keep the pozzolanic material inside the lime solution for a certain period of time.

(Refer Slide Time: 34:07)



Lime saturation test

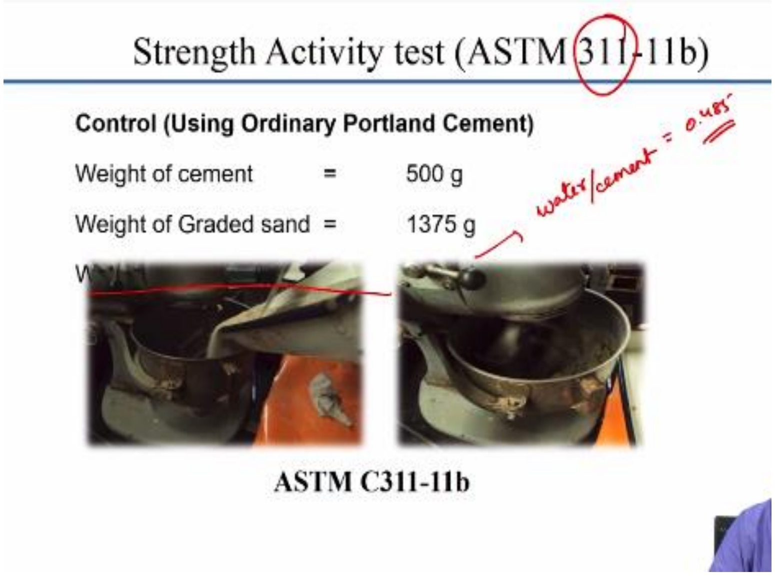
So, based on this, again the lime that was removed in raw bagasse ash at 3 days is only about 20%, at 7 days, it is about 53-54% and processed bagasse ash at 3 days itself, your almost equal to the 7 day performance of raw bagasse ash and by 7 days, you nearly reached 80% removal of the lime from the solution that means you got substantially good reactivity even as early as 7 days. So, there are several ways of looking at this.

So, you need to form a reasonably good estimate of what kind of reactivity your system will give, why is this important, why we are trying to do this, why not simply make concrete where cement is replaced with fly ash or bagasse ash and study these properties, why do we want to characterise the initial performance by doing the strength activity based determinations, why? The contention is that based on the reactivity chosen in the reactivity tests, we can do a much better mix proportioning for the concrete.

And that means what; better mix proportioning implies finding what; optimum levels of replacement of mineral admixtures in cement, we often do a trial and error method, we say okay, we will do 10%, 20%, 30%, 40% whichever gives us the maximisation of properties, we will use that but this is just helping us reach there without too many trials by simply understanding the fundamental characteristics of material.

And see how much it will be actually able to contribute to the development of your structure in actual concrete, so all these tests, please remember are done either on cement paste or mortar, so the amount of test time and material is reduced significantly as opposed to doing test directly on concrete. So, wherever possible, if you can devise your test methodologies to work at the cement paste or mortar level, it helps in reducing the extent of time it takes to proportion your concrete properly.

(Refer Slide Time: 36:04)



Strength Activity test (ASTM 311-11b)

Control (Using Ordinary Portland Cement)

Weight of cement = 500 g

Weight of Graded sand = 1375 g

W

water/cement = 0.485

ASTM C311-11b

ASTM strength activity test is quite good because it uses cement and the sand and your mineral admixtures typically, in 20% replacement, I am sorry that the water part is going out of here, it is not there in the thing, so water typically is; so, water to cement ratio for these kind of; for the ASTM based mixtures is typically 0.485 that is the water cement ratio that is typically used for the cement based systems that is the controlled system.

So, when you replace cement with fly ash or with other mineral additives, I told you that ASTM C 311 talks mainly about fly ash, so you usually will replace about 20% of the cement with fly ash. Now, the problem here is when you replace it 20%, you may expect a change in your workability, so what ASTM tells you is that you maintain the workability by adding either less or more water to get the same flow.

That means you are doing this test not at a constant water cement ratio, you are varying water cement ratio to get the same flow in your system, now because of that you may get some differences in performance. So, generally, in fly ash based systems, the fly ash is of a good quality that means, it has got good spherical particles, you may actually end up improving the flow characteristics you may actually need lesser water for the fly ash based system to work.

(Refer Slide Time: 37:31)

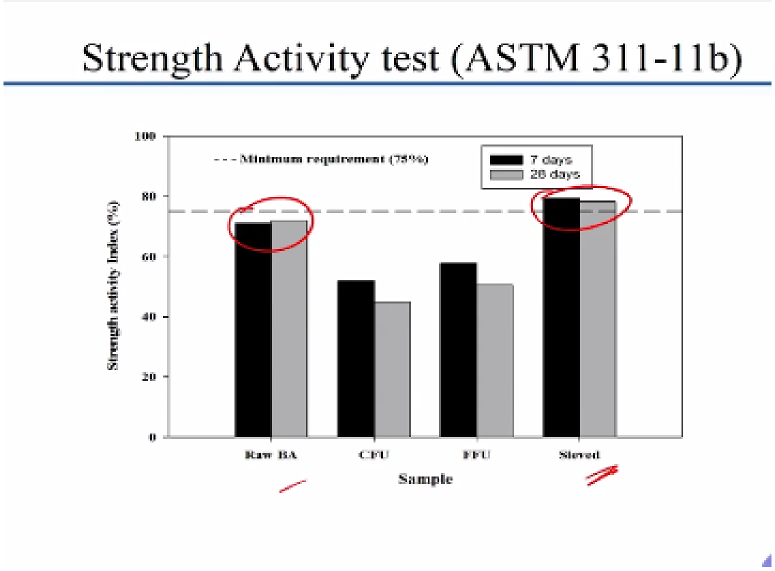
ASTM C1240

ASTM C311-11b
&
ASTM C1437-07

And that will end up producing an effect on the strength also, so the strength activity test, again the flow determination is done with the controlled system and with the blended system and finally, you produce a 5 centimetre cubes and test them for compression. In silica fume based determination, what you do is; replace cement with silica fume then you add a super plasticiser to the silica fume based system to ensure the same flow as your cement based system.

Silica fume is basically ASTM C1240 that covers the determination of activity of silica fume, now there you are actually going to be testing at equivalent water to cement ratio and not at equivalent flow, I mean, of course you make the flow equivalent by adding a super plasticizer to the silica fume system and added to that fact for dispersing silica fume, you do need a good super plasticizer, so it is not correct to do the test without a super plasticizer.

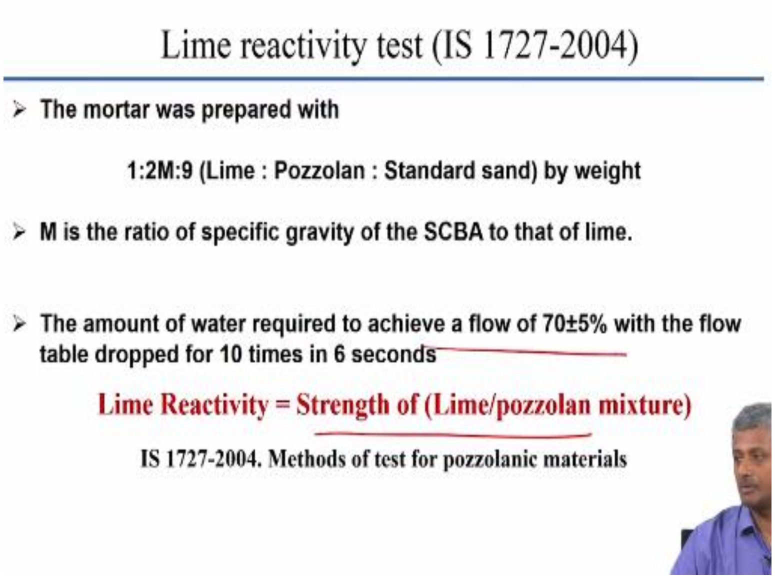
(Refer Slide Time: 38:22)



Strength Activity test (ASTM 311-11b)

So, again this is the result as per strength activity test for raw bagasse ash, it is much below the requirement of 75% for the sieved material, I have shown you this before that we have already reached about 80% and with the sieved and ground material, we were able to reach more than 100% reactivity in this case.

(Refer Slide Time: 38:39)



Lime reactivity test (IS 1727-2004)

- The mortar was prepared with

  1:2M:9 (Lime : Pozzolan : Standard sand) by weight

- M is the ratio of specific gravity of the SCBA to that of lime.

- The amount of water required to achieve a flow of 70±5% with the flow table dropped for 10 times in 6 seconds

Lime Reactivity = Strength of (Lime/pozzolan mixture)

IS 1727-2004. Methods of test for pozzolanic materials

Lime reactivity, I have already talked about you mix the lime pozzolan and standard sand and lime reactivity is nothing but the strength of the lime pozzolan mixture, the amount of water required to achieve a flow of 70 plus or minus 5% is what is taken for obtaining the consistency of your mix and at that consistency, you make 5 cm cubes and test them for compression.

(Refer Slide Time: 38:58)

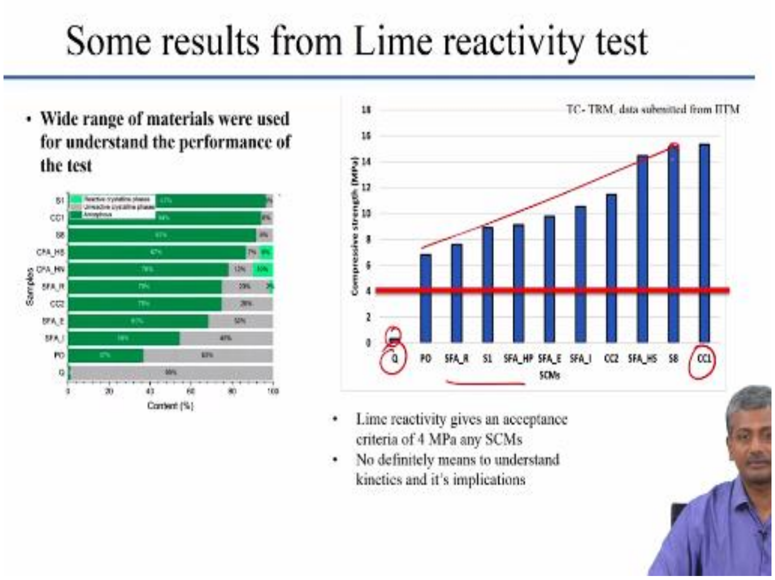
Lime reactivity test (IS 1727-2004)

- Average crushing load for raw and processed bagasse were observed 2.14 kN and 5.52 kN respectively
- Lime reactivity of raw bagasse is lesser than sieved sample

IS 1727-2004, Methods of test for pozzolanic materials

Again, the exact process actually shown here and you show the result in terms of the actual strength obtained itself.

(Refer Slide Time: 39:09)



Some results from Lime reactivity test

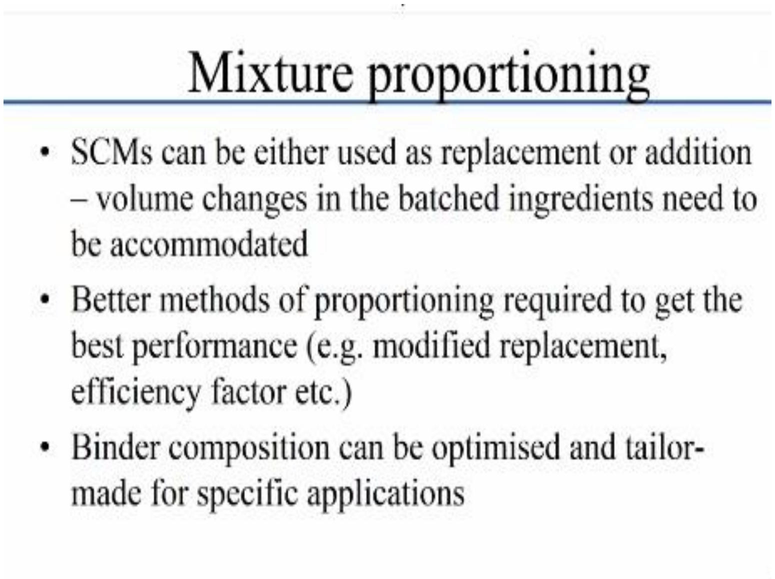
- Wide range of materials were used for understand the performance of the test

- Lime reactivity gives an acceptance criteria of 4 MPa any SCMs
- No definitely means to understand kinetics and it's implications

So, some results from lime reactivity tests are shown here, so this is again part of a large group of laboratories that are involved around the world in doing round robin testing of several different types of mineral additives; slags, fly ashes, type F, type C fly ashes, quartz, calcined clay, several different types of systems are being used in this case. So, here you can see that when you use quartz nothing is happening why, because there is no reaction at all.

Quartz is not reacting with calcium hydroxide, you do not expect any major strength development at all but when you use any of the other pozzolanic indicators, you get very high levels of lime reactivity from this round of testing, so again lime reactivity has been used quite extensively to determine the pozzolanic activity index of different types of mineral additives.

(Refer Slide Time: 40:00)



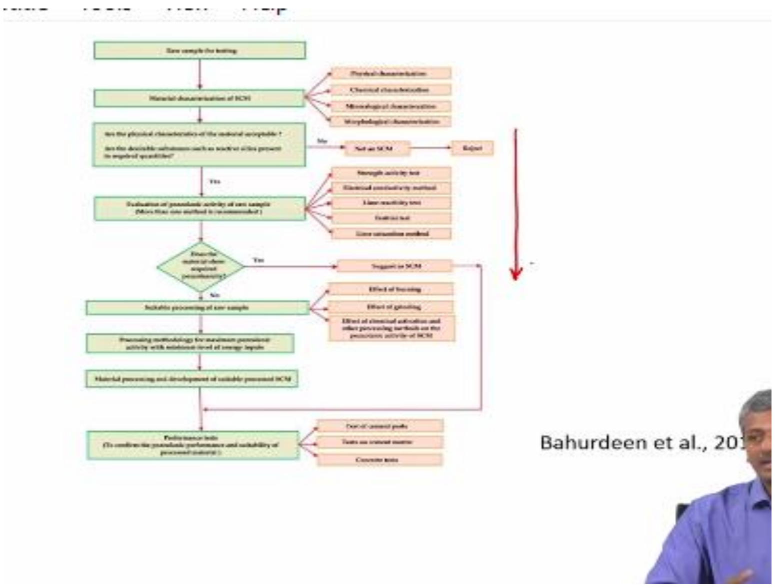
Mixture proportioning

- SCMs can be either used as replacement or addition – volume changes in the batched ingredients need to be accommodated
- Better methods of proportioning required to get the best performance (e.g. modified replacement, efficiency factor etc.)
- Binder composition can be optimised and tailor-made for specific applications

Mixture proportioning of concrete with SCM can also be a little bit tricky because we talked about this earlier that many mineral additives are having a specific gravity lower than that of cement, so choosing to do a mass replacement or volume replacement can end up giving you very different kind of performances. So, we need better methods of proportioning required for best performance.

We will talk about using these mineral admixtures with an approach of particle packing, when we come to the next chapter on high performance concrete mix proportioning, so again this is something that you need to keep in mind, while designing concrete with mineral admixtures, you need to optimise the mixture to obtain the desired characteristics of workability, strength and durability.

(Refer Slide Time: 40:53)

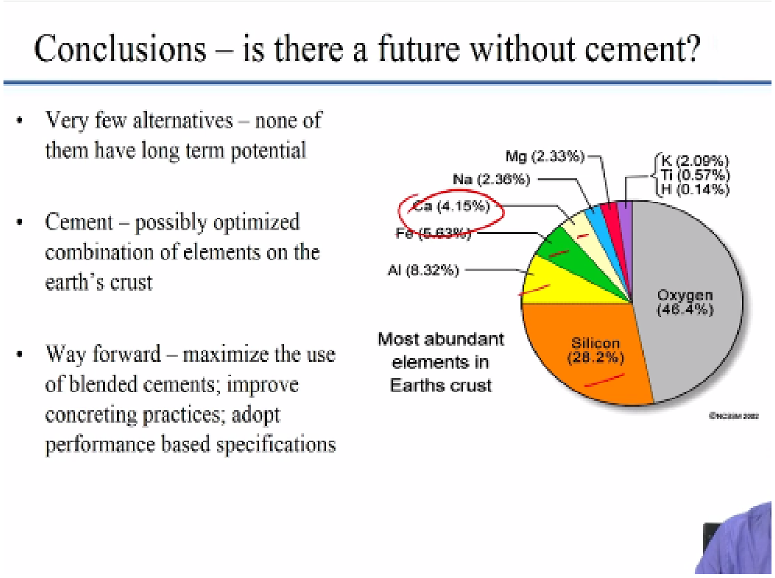


Bahurdeen et al., 201

And for that understanding the aspects we discussed earlier the actual reactivity, the actual filler effect that is very important. So, again we have done extensive study on how to do the initial characterisation and produce the kind of result that we need for different types of mineral admixtures. So, this is a very systematic methodology that was developed based on one of our research papers.

And if you read through this paper which I will share with you on online, you will be able to get a much better picture of what are the problems ailing the current mix design philosophies and how we can better improve the approach to characterisation of mineral additives and then use them for determination of concrete characteristics.

(Refer Slide Time: 41:26)



Conclusions – is there a future without cement?

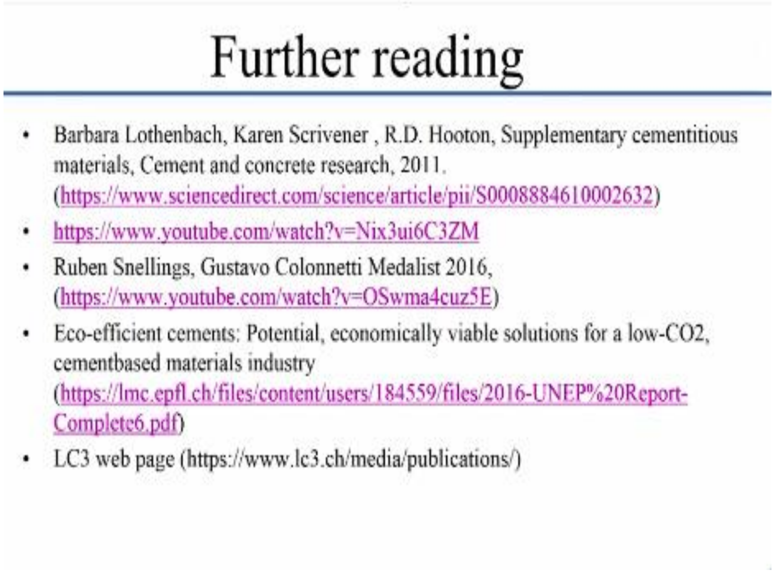
- Very few alternatives – none of them have long term potential
- Cement – possibly optimized combination of elements on the earth's crust
- Way forward – maximize the use of blended cements; improve concreting practices; adopt performance based specifications

So, to conclude is there a future without cement, now that something which we keep asking ourselves whether we can make concrete without cement, the research in geopolymers getting popular primarily because people want to use concrete that do not have cement but truly speaking if you look at the distribution of elements in the Earth's crust, there is already a fairly good understanding that cement is optimising what is actually available on the earth's crust.

Why is that because cement has silica, it has got aluminium, iron, calcium, these are the 4 major elements in the earth's crust. When you make systems rich in silica and less in calcium, we do not get the hydraulicity from these systems, so obviously we need to have calcium based systems as the primary precursor for any hydrating system. So, cement is possibly an optimised combination of elements on the earth crust.

So, the primary way to reduce the impact of cement clinker usage in concrete is simply to optimise the use of blending materials and also adopt performance specifications, very often our projects with mineral admixtures do not move forward because they do not allow the use of mineral admixtures based on initial choice of materials, if they look at the performance requirements in terms of durability, long term cost, maintenance and so on, they will find that it is definitely much more profitable to use cement replacement materials.

(Refer Slide Time: 42:49)



Further reading

- Barbara Lothenbach, Karen Scrivener , R.D. Hooton, Supplementary cementitious materials, Cement and concrete research, 2011. (https://www.sciencedirect.com/science/article/pii/S0008884610002632)
- https://www.youtube.com/watch?v=Nix3ui6C3ZM
- Ruben Snellings, Gustavo Colonnetti Medalist 2016, (https://www.youtube.com/watch?v=OSwma4cuz5E)
- Eco-efficient cements: Potential, economically viable solutions for a low-CO2, cementbased materials industry (https://lmc.epfl.ch/files/content/users/184559/files/2016-UNEP%20Report-Complete6.pdf)
- LC3 web page (https://www.lc3.ch/media/publications/)

So, with that there is lot of further reading that you can do, you can have a look at some of these websites and also the textbooks that have been published by several different authors, this is a subject that is extensively being studied all over the world because people realise that reduction in carbon emissions in construction or in cement usage or concrete usage is primarily possible only with the replacement of cement with mineral additives. Thank you all.