Admixtures and Special Concretes

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Lecture -31

Mineral Admixtures: Electrical Conductivity method, Frattini test & Lime saturation method

Electrical Conductivity method:

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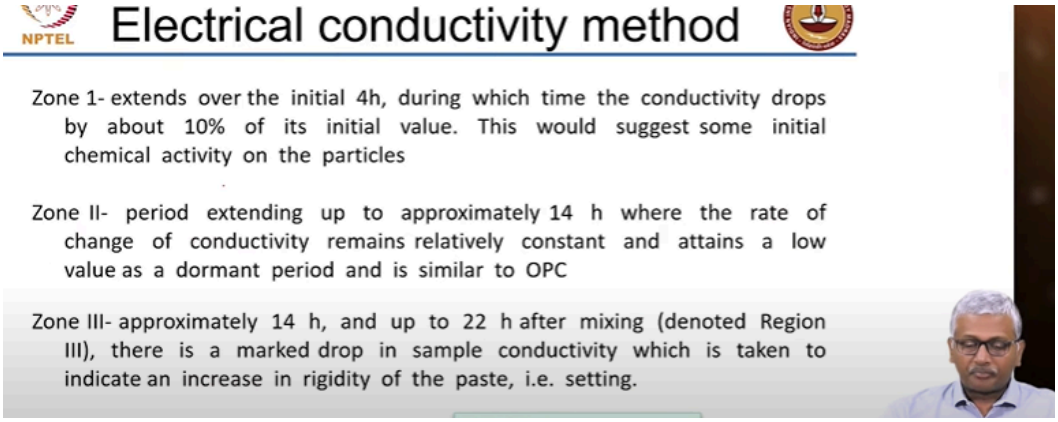

So, we were talking about how electrical conductivity determination can help us understand the contribution made by the mineral additive towards reactivity with calcium hydroxide and we saw that depending upon the type of pozzolanic materials like silica fume or fly ash or metakaolin the amount of calcium hydroxide consumed could be

quite different and that can be indicated as a steep fall in the conductivity in the zone 3 where we can actually take the rate of change of conductivity as a measure of the pozzolanicity index. Now of course this is just a description of the same thing that we talked about.

So this is an example of the electrical conductivity method being applied to sugarcane by gas ash as I said most of the results that I show you with respect to the activity determination is from the work of Dr. Bahruddin who worked on sugarcane by gas ash and this is an example of how the electrical conductivity method was employed. So you see here the mixture is getting prepared in a Hobart mixer, the material quantities have been proportioned appropriately and then you have a cube or cube mold in which you attach electrodes to the ends and then this LCR meter was employed to actually determine the resistance and convert that to resistivity. Now LCR meter as the name implies L for inductance, C for capacitance, R for resistance. What it does is it applies an alternative current but here only at a fixed frequency not across a range of frequencies. You can do the same with an electrochemical impedance setup. That is a lot more involved and complicated and of course not just complicated it can also give you a lot more insight into the behaviour of the material but this is a simple LCR meter which can be used to determine the resistance or resistivity offered or resistance offered by a solid element. So in this case the setting material is offering that.

In this case the initial chemical activity may be very fine particles that would have immediately dissolved and started reacting. So some initial conductivity drop can be seen but beyond that you do not see much of a reaction. See this is quite similar to your heat evolution in cement wastes. There is an initial heat burst because of a very quick reaction on the surface of the particles but then after that the reaction slows down significantly. Similarly here, pozzolanic reaction also in stage 2 is nearly non-existent or it is happening at a very low rate so you cannot really see the change in conductivity. And yeah so this is essentially the LCR meter with which the test is being conducted on this material that has been freshly put inside a concrete cube.

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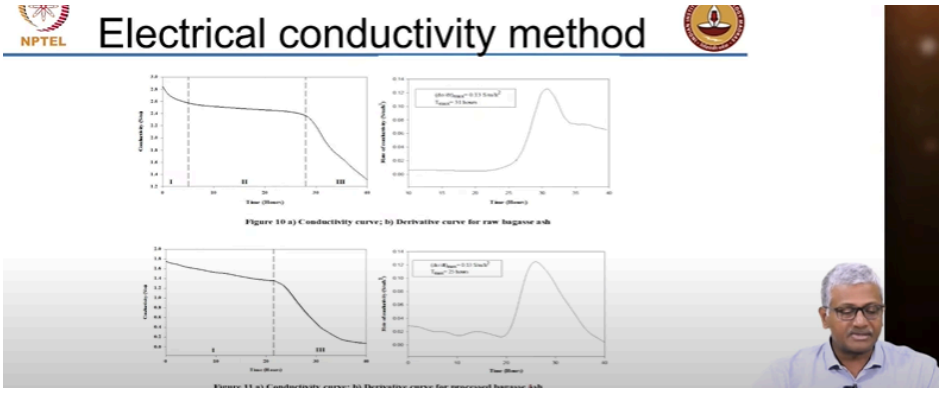

And these are the results as indicated in the paper by McCarter. You also see the same sort of zones here. You have zone 1 where there is a small drop in conductivity, zone 2 where the conductivity drops very slowly or almost remains constant and then zone 3 where you can then determine the slope as the conductivity. So these are the two different curves produced for raw bagasse ash and processed bagasse ash.

Raw bagasse ash refers to the material that was directly collected from the locations where bagasse ash had been dumped. I told you in the last class that sugarcane bagasse after extraction of the juice gives very good calorific value so it is burnt to obtain energy and after burning the ash that remains is usually dumped. It is not really utilized well enough. So that dumped ash we collected and we used that towards this pozzolanic activity test and the same ash was then processed. I will talk about this processing in a separate segment when we talk in detail about bagasse ash but what you see here is that the slope of the curve is getting changed because of this processing and it leads to a much more improved pozzolanicity performance when you actually get the material to be processed and get it to a stage where it can react better.

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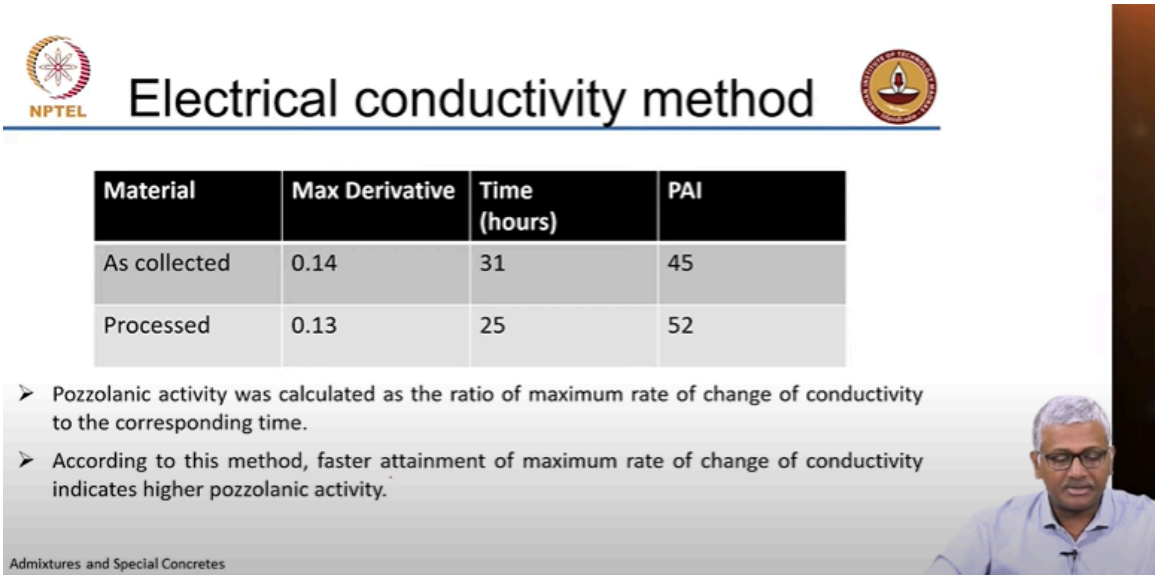

So this is the result of these because you need to divide the as per this equation pozzolanicity index you need to divide the maximum rate by the time and that is what is done in this case. The time it takes for the maximum derivative to be obtained is 31 hours here it is 25 hours so actually if you take the pozzolanic activity index as you do the processing it seems to be going up from 45 to 52. So ratio of the maximum rate of change of conductivity to the corresponding time at which that maximum actually happens. So where do you get that time? You get that from the peak of the derivative curve of the conductivity. So you can actually take a derivative so wherever this derivative curve is

maximum indicates the point at which the maximum transition is happening and or the slope is actually maximum and then you can take the derivative curve to determine the overall time at which this is happening.

Frattini Test:

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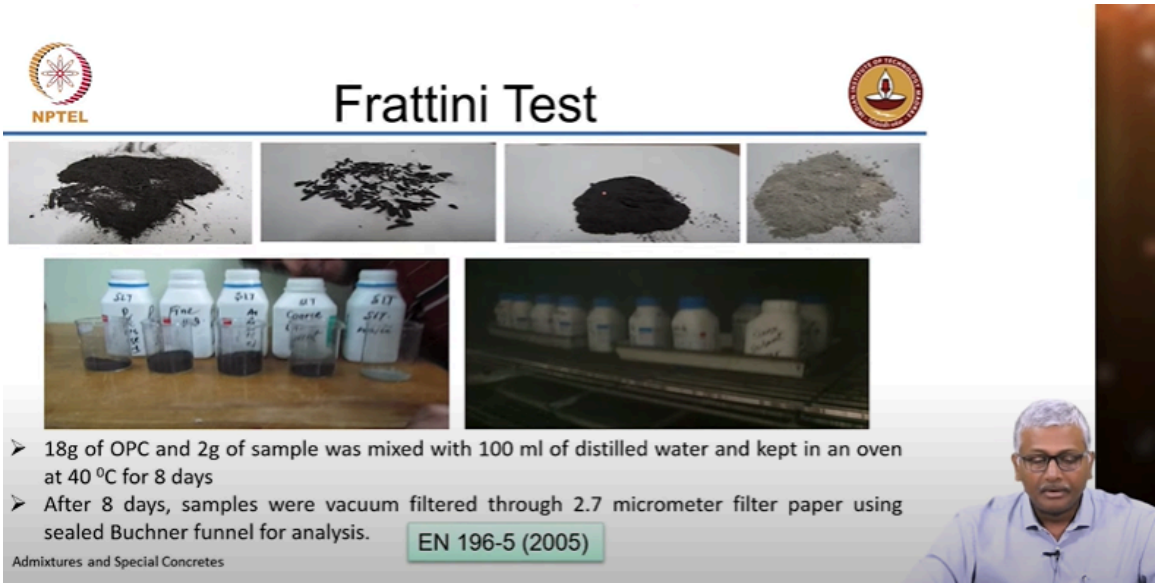

There is another chemical test called Frattini test where we mix the supplementary cementing material along with Portland cement and we put it in a container which has excess of water so in this case 100mm of distilled water is used to initiate the pozzolanic reaction between the calcium hydroxide that is getting generated from the cement hydration and the added supplementary cementing material and this is kept in an oven at 40 °C for 8 days. So you see here the same experiment being repeated with bagasse ash. Now with bagasse ash what we did was in this case separated out the very coarse fractions and the fine powder that is obtained from the as collected material. So this is the as collected material we have separated out using sieve analysis or using a sieve separation the coarser particles and the finer particles which are present within the bagasse ash and this is of course the cement particles that are used for this test. So these have been stored in an oven at 40°C for 8 days and after 8 days the samples are vacuum filtered through a 2.7 micrometer filter paper using a sealed Buchner funnel for analysis.

The idea is what is going to happen with time is that the silica from your supplementary material is going to start combining with the calcium oxide from your calcium hydroxide component or from the cementitious component you have the calcium hydroxide and that is where consumption of calcium oxide will happen to form the CSH.

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And these are showing you the basic results to determine the calcium oxide content from time to time we do a chemical titration based evaluation I will share the standard with you so that you can read this in more detail and based on that you can establish the hydroxyl ion concentration and the calcium oxide concentration at any given time and plot that in this graph. This graph basically is the calcium oxide concentration versus hydroxyl concentration. I will show you the graph in the next slide. So again calcium oxide versus hydroxyl ion concentration.

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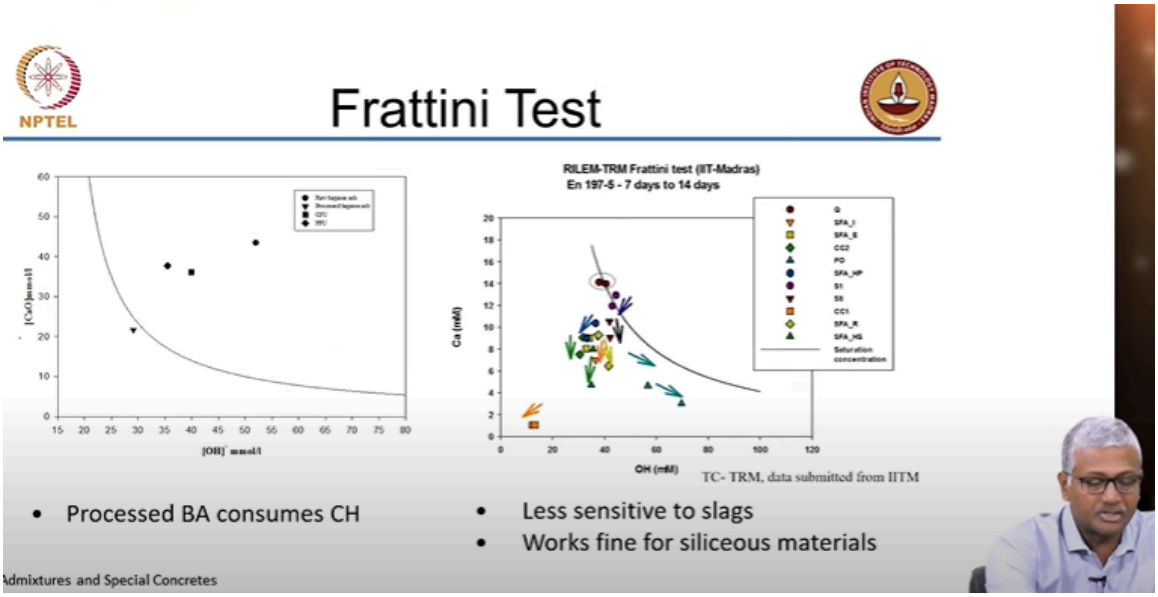

So this is actually the curve above which we can indicate that the sample is essentially non-reactive below this curve if your sample produces a calcium oxide OH^- content which is below this curve that means it is sufficiently reactive. So when you have a significant combination happening the amount of free lime available in your system is going to go down.

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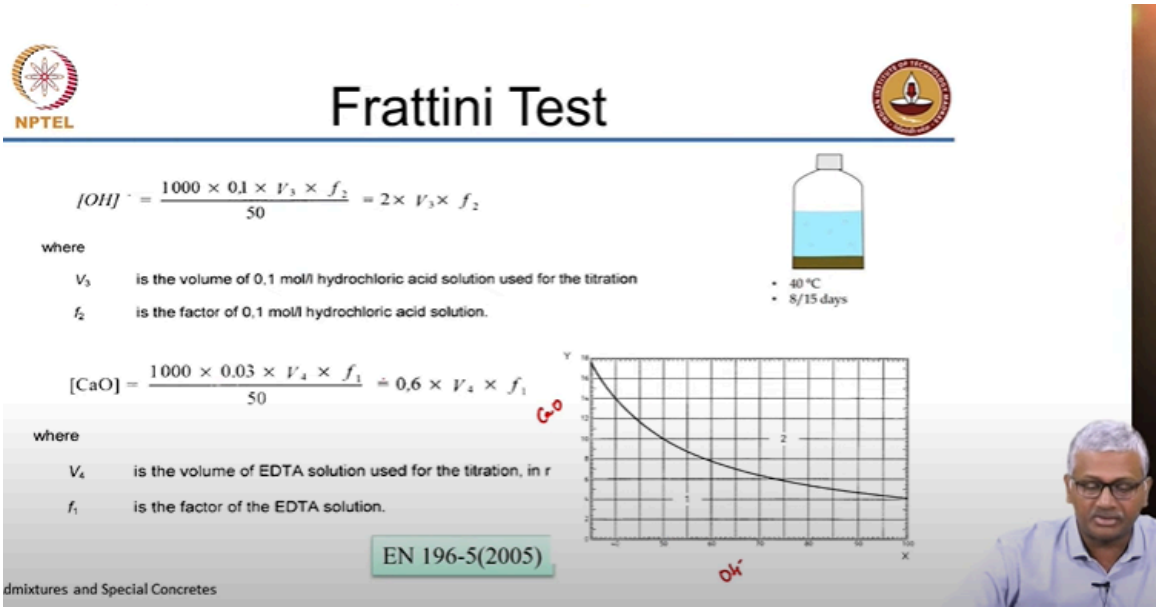

This is indicated by points that are lying below this solubility curve and that is what this is also indicating your OH^- ion concentration is determined based on the titration that you are doing and calcium oxide content is determined using the titration using EDTA ethylene diamine tetra acetate that is the typical reagent that we use and this is hydrochloric acid to determine the neutralization capacity which is offered from your OH^-.

So now using this approach what is being depicted here is that the raw bagasse ash which is this circle is somewhere out here that means you have a large amount of calcium oxide and OH^- available in solution. For process bagasse ash which is here it is below the curve indicating that it is exhibiting a significant bit of reactivity. On the other hand these fibrous particles that were extracted as I showed you that by sieve separation the fibrous particles that were present in the bagasse ash were extracted you again see that the same problem happens here also that the content of or the concentrations of calcium and hydroxyl are much greater than what is proposed by the solubility curve and based on that you can adjust that these materials are not really producing significant bit of reactivity.

Now the graph on the right essentially shows you the results of a test which is carried out with a number of different supplementary cementing materials. It was part of a RILEM inter laboratory study where IIT Madras also had participated. Here we were looking at many different types of ingredients including quartz, type F fly ash, limestone, natural pozzolan, slags, so several different types of supplementary materials were actually being used in this case and what we saw here was this test method obviously again this is the same solubility curve so all the points which are lying below this indicate that your materials are reactive.

Interestingly all your points involving quartz only the top two points are quartz that are lying exactly on that solubility curve. Slags for some reason this S1 slag and this S8 slag both of them are very close to this curve indicating that you are not really seeing a major reactivity being exhibited by the slags. Now this could happen because consumption of calcium hydroxide in the reaction of slag is not that significant as opposed to a pozzolanic reaction where principally you have a consumption of calcium hydroxide happening. In slag reaction you do not really end up consuming too much calcium hydroxide there is sufficient calcium available from the slag itself.

If you look at calcium clay you can see that you are almost at the bottom of this scale that indicates that the reactivity is extremely high. There is one more type of calcium clay CC2 which is here and the arrows basically indicate the change from 7 days to 14 days. So if I look at the arrows which are indicated in the curve 7 days to 14 days for instance if I take this triangular marker the decrease is from 7 days to 14 days. The marker basically shows that there is a decrease in the overall concentration of the calcium from 7 days to 14 days.

Lime Saturation method:

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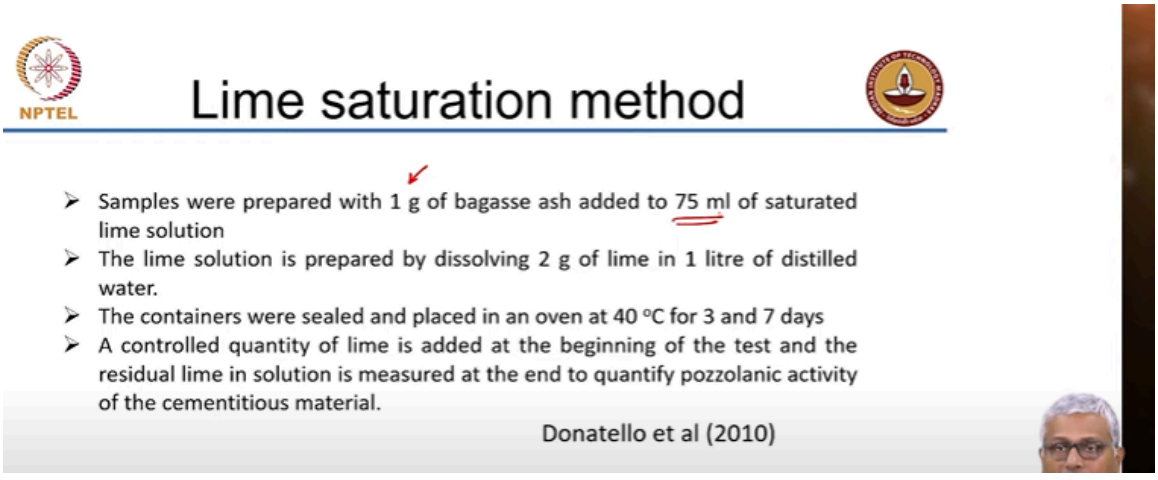

Now the other simple method is called the lime saturation method. So you take a small quantity of your supplementary material or supplementary cementitious material in this case just 1 gram of bagasse ash was taken and that was added to 75 ml of saturated lime solution. Lime is essentially calcium hydroxide.

How do you saturate a lime solution? You keep adding calcium hydroxide in water and stirring it beyond a point it will not dissolve further because it would have already reached its solubility limit. Now beyond that point your lime excess will simply settle and would not get dissolved in the water. So that is a lime saturated solution. So you can be clear that the quantity of lime that you have in your solution is beyond the maximum solubility of the lime in water. So the lime solution here is prepared by dissolving 2 gm of lime in 1 liter of distilled water. So that is already saturated at that level. So that indicates that you cannot really be dissolving much more than that at a given temperature. Now once the supplementary material is put into the lime solution the containers having this solution basically are shifted to an oven at 40°C for 3 and 7 days.

What will happen with time? What is going to happen with time? If the pozzolanic reaction happens the lime content will reduce. The lime content has to be reduced. So what we essentially do is the residual lime in the solution is measured at the end to quantify pozzolanic activity of the cementitious material. This is from a paper by Donatello et al. So again the same approach is given. So the same titration is performed to really get an estimate of the lime content of the solution.

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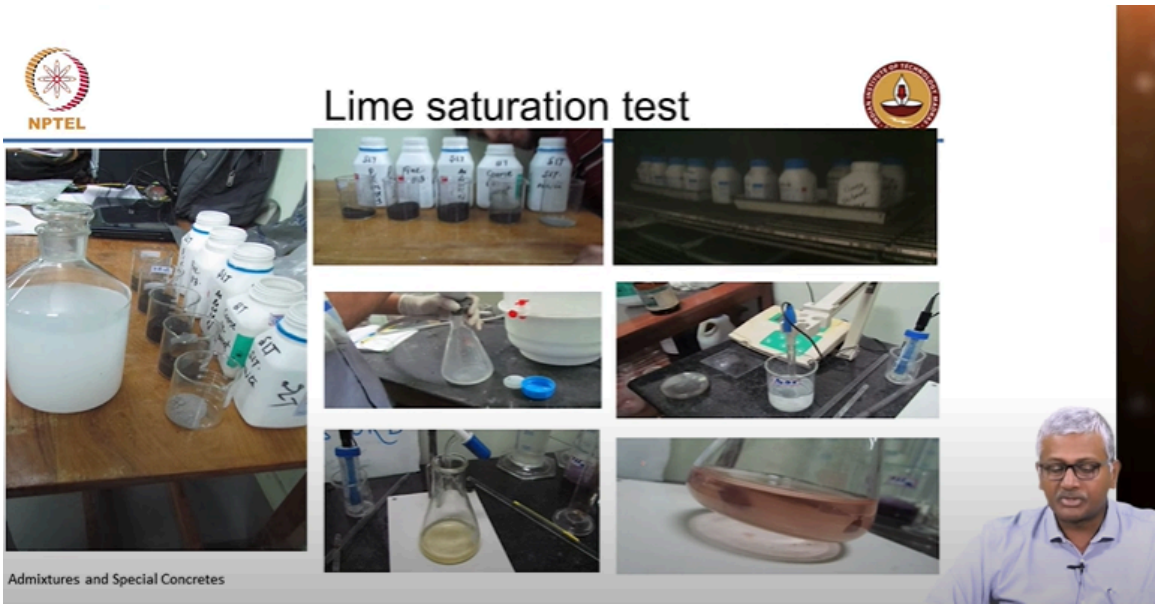

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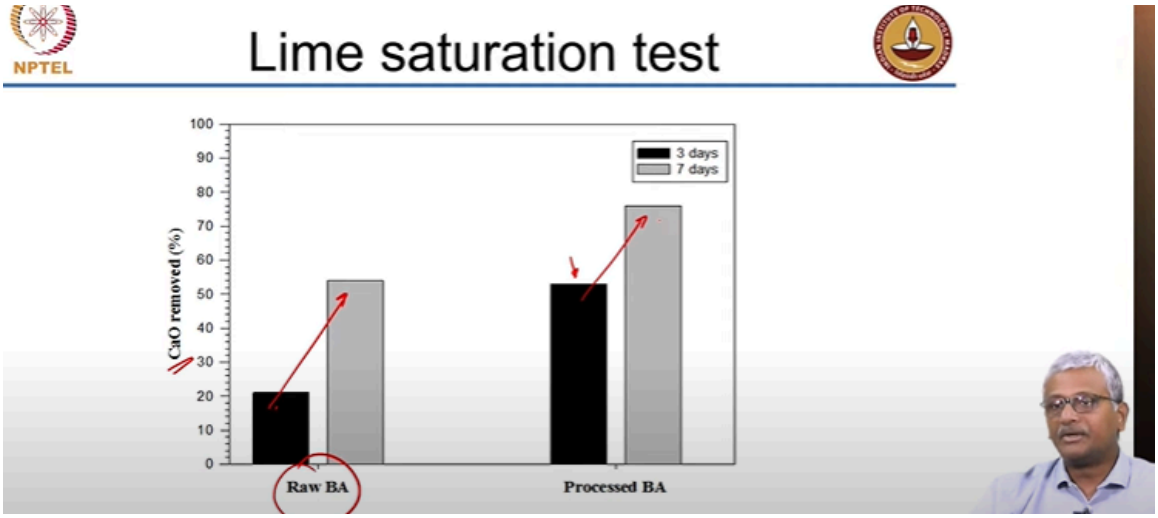

And based on this the extent of lime removed from raw bagasse ash at 3 days and 7 days is presented. Of course by 7 days much more lime gets removed because of more pozzolanic reaction. But at 3 days itself for the process bagasse ash you get significant lime removal which only increases further at 7 days to about 80% lime removal. That indicates that process bagasse ash may have significantly higher ability to react.

So you see that there are different types of tests given. One is where you are assuming that this cement will produce the calcium hydroxide, your bagasse ash or any other supplementary material will react with it and slowly consume the extent of lime. In this case you are putting the material in excess of a lime solution. So that means there is a sufficient amount of lime available for reactivity to happen. This is not indicative of a true mixture of a true cement supplementary cementing material mixture. In that case you do not really have this kind of an over saturation of the lime available. You only have some amount of lime which is why in spite of very high reactivity a lot of your supplementary material may still remain unreacted in your system. Not all of it will react. So these tests are just designed to understand the potential reactivity but that does not indicate that all these systems are going to react completely in a mixture with cement.

Strength activity test:

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Now this is again just for completion. I also wanted to show you the result of bagasse ash in a strength activity test done with the method that is used for fly ash. This is the fly ash standard ASTM C311 where the control mortar is prepared using 500 grams of cement, 1375 grams of graded sand which means a mass ratio of 1: 2.75 and a water content of 242 which indicates a water to cement ratio of 0.485. So it should be technically 242.5 but just for rounding off it is being written as 242 and this mixture is prepared and then you prepare this in cube molds and test the strength of the concrete of the mortar at 7 days and 28 days.

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So to ensure that you have the same flow you need to adjust the water content of the mix with the pozzolan. You do not have the same water to cement ratio for the mix with the pozzolan. You adjust the water content to get the same flow. This is the flow as per the flow table test. So when you make the pozzolanic mixture, adjust the water to get the same flow. Then you prepare your cubes, store the cubes in a saturated lime solution. You can see the cloudy white solution, basically it is a saturated lime solution.

Any idea why we want to store it in a saturated lime solution? What will happen if I store cement based materials in plain water like it is done on site and site we have a curing tank, we have plain water inside we just dump the cubes inside that. What is going to happen? There will be leaching happening from the cement to the surrounding solution. Why should leaching happen? Because the concentration of ionic species in the pore solution of cement is much greater than what is outside. So you have a lot of calcium, sodium, potassium and so on. It is going to start moving outside. Leaching will continue to happen until the solution outside stabilizes in respect to the pH with the material itself. So if you actually measure the pH of the surrounding solution it will quickly go from if it is distilled water it will quickly go from 7 to 12 or more than 12. At that point of time leaching may stop. So that is why for curing it is very often recommended that you put calcium hydroxide into your curing tank to ensure that the leaching of at least calcium can be avoided.

But even in this case leaching of alkali is still going to happen. Your sodium potassium from your system is still going to start leaching out. So deciding on a very accurate solution to store your specimens is quite tough because in most laboratories what we do is we store concrete in a moist curing chamber. We put that in a chamber and simply spray moisture in it so that there is no driving force to leach out the material. So water or fog is essentially there in the system.So you maintain a 100% relative humidity atmosphere and if you want to see a curing chamber you can go to our concrete lab. We have a big room where we can actually do the curing at 100% relative humidity.

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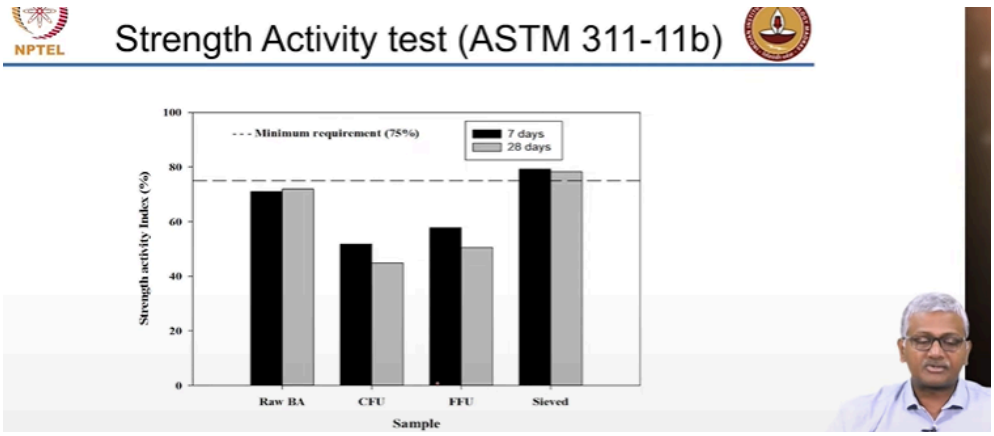

Anyway just to come back so here the test is performed at 7 days and 28 days and based on the test result we calculate the strength activity index which is the ratio of the strength of the pozzolanic mortar to the strength of the plain cement mortar expressed as a% age and for fly ash the minimum requirement is 75% that means the strength of the pozzolanic mortar should be at least 75% of the strength of plain cement mortar. Now mind you in this test the extent of replacement of cement is 20% that is prescribed in this test. Cement mortar is prepared by using 420 grams of cements and 80 grams of pozzolan. You have 20% replacement. Now at that 20% replacement you are allowing up to 25% lower strength because the test is getting conducted at early ages 7 days or 28 days.

So here raw bagasse ash was able to get you a strength of nearly 70%, not too bad. These fibrous materials, What are these fibrous materials in bagasse ash? What could it be? So bagasse is extracted from sugarcane. So what could remain in the system? Molasses essentially is the overall material but what is the element you think which is available in these fibrous particles? They are all organic particles. So carbon essentially they are carbon bearing. Maybe your strands of cellulose which are there in your bagasse may remain just as such which did not get burnt completely. So they came into your ash and then when you remove them they are showing that you absolutely produce no pozzolanic activity because you are getting only 50% of the strength. But then when you sieve it to remove these fibrous materials you are crossing this 75%limit without any problems. That means sieved bagasse ash where you can remove this organic material that is still remaining in the burnt bagasse ash. If you remove it then you can get some fairly consistent performance from your system. We will come back to this to look at other approaches for processing also but the idea was to just show you a comparison of the results from different activity methods.

Lime reactivity test:

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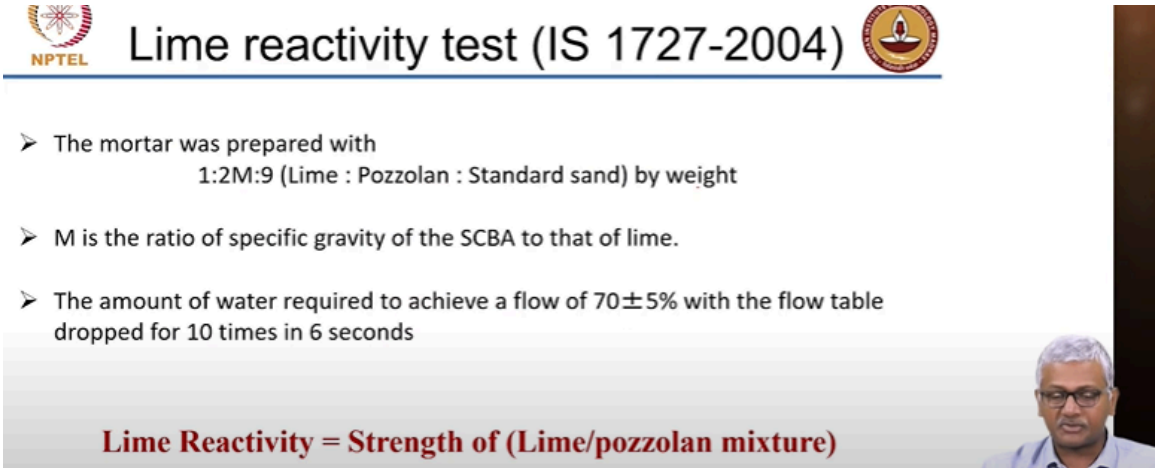

Now in the lime reactivity test which is specified by AS 1727 the mortar is prepared with one part of lime to 2M of the pozzolan. 2M means ratio of specific gravity of the not SCBA of any pozzolan SCBA sugar and bagasse ash but it could be any other pozzolan to that of lime. So let us say pozzolan has a specific gravity of 2.5 and lime has specific gravity of 2 then this would be 2 into 2.5 by 2 or 1.25. Ratio of specific gravity of the pozzolan to that of lime is to 9 parts of standard sand.

What is standard sand? Ennore sand we call it ennore sand because standard sand as per Indian standard specifications is taken from Ennore which is just south of Chennai and that is where they get the sand and it is usually available in 3 size ranges. So you take equal portions of each size range and then prepare this mixture. So mortar is prepared with one part of your lime to 2 parts of your equivalent pozzolanic material to 9 parts of sand. Now water has to be added to achieve a flow of 70±5% with the flow table test. So again water is not constant you need to control it based on the flow. So between different pozzolanic materials you may get different quantities of water. So again this flow table is dropped 10 times in 6 seconds as per this standard. So that when you drop it, it causes the material to flow out. You need to get a flow of 70±5%.

That means that if the initial diameter of the cement mortar was 100mm you need to obtain a final diameter of 170 millimeters. So 70% flow is defined like that. Now there are some issues here. You have lime then you have the pozzolan. We know that pozzolanic materials depending on their reactivity will take a long time to react with this lime. So this mixture essentially is subjected to a high temperature curing. So it is subjected to 50°C curing for 10 days. That is the curing specified in your IS standard. So again this is the same. So the mixture is prepared you check the flow and then do the test after 10 days but the curing is done essentially with 50°C. Now while you are curing at 50°C it has to be in a water bath because otherwise it will start or rather sealed because otherwise you are going to start removing the water from your system. You do not want to do that. So it has to be sealed to prevent any water evaporation from your mortar.

Now after curing at 50°C for 10 days you take the cubes out and determine the strength. So lime reactivity is simply taken as the strength of the mixture that is it. There is no comparative strength that you do with just lime. So the strength of the mixture in mega Pascal is your lime reactivity.

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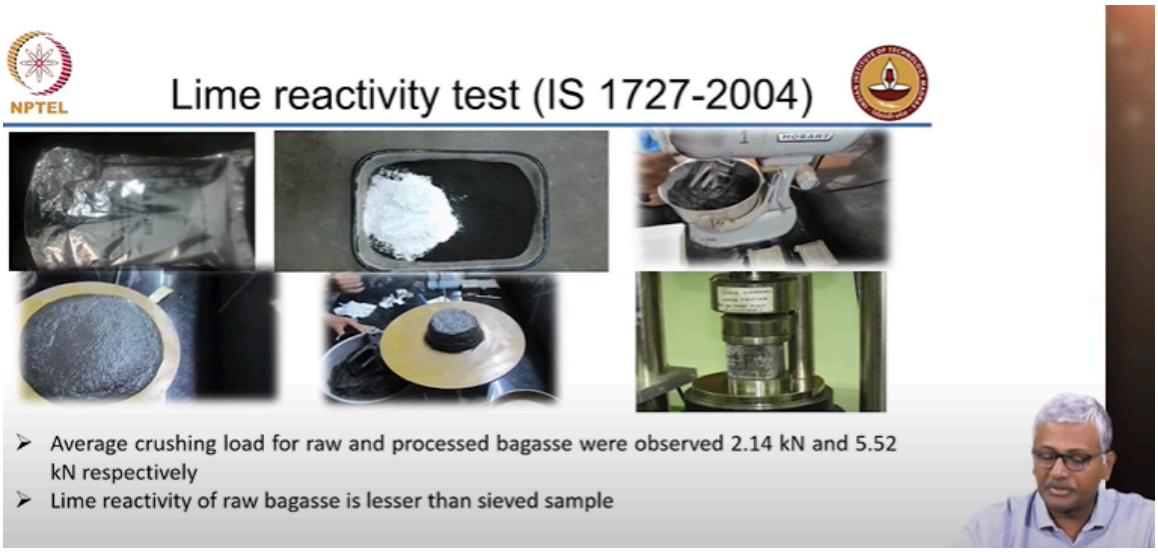

So that is what is shown here. The compression test is done. The crushing load for raw and processed big ash is 2.14 and 5.52 kN. So what is going to be this is a 5 cm cube. So what is going to be your lime reactivity in this case?

So just by processing you are able to extend the lime reactivity from 0.86 to 2.2. The problem here is for qualifying as a fly ash the minimum lime reactivity your material should have should be 4 MPa. For classifying as a fly ash. So when you do the lime reactivity test with fly ash you need to get at least 4 MPa only then the fly ash is adjusted to be reactive enough to be used in concrete. So LR should be greater than 4 MPa for fly ash.

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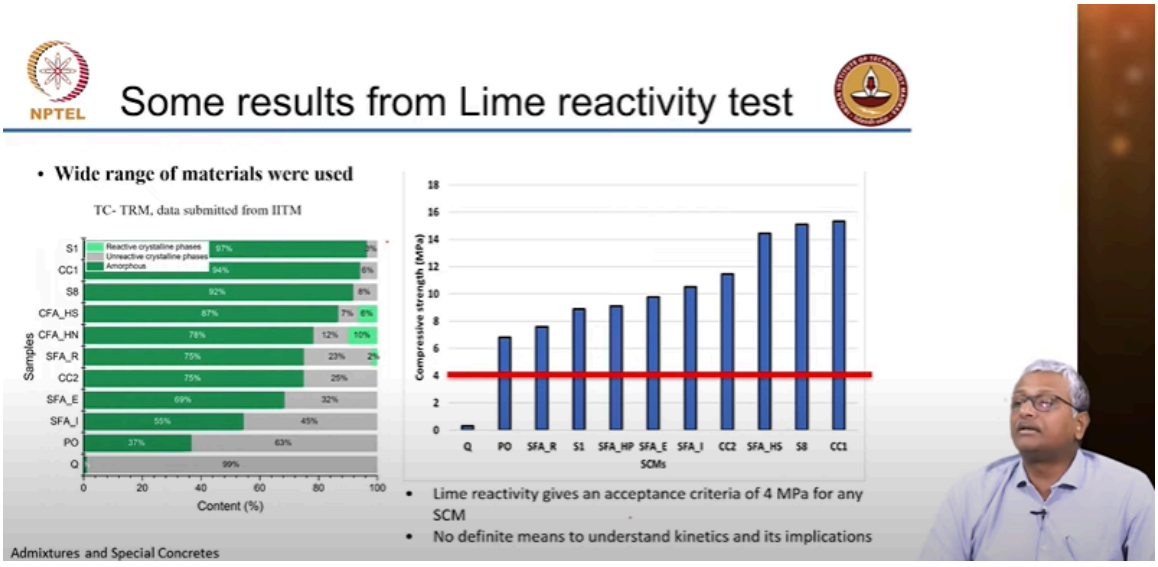

Some results are given here for the same inter laboratory study that was being done. The data from IITM is shared on the left. So you see here that the samples from different materials like you have slag, calcined clay, another slag and so on type C fly ash, type F fly ash and so on. So what is provided here on the left side is the extent of amorphous and reactive crystalline phases in the overall system. So green indicates an amorphous phase. In quartz you can imagine that the amorphous phase is nearly 0. Quartz is almost a pure crystalline material and it also has absolutely no reactivity. The crystalline quartz exhibits very little reactivity.

But when you go to type C fly ashes there may be some phases like calcium silicate that may be present because it has got a high amount of calcium in it. Apart from the amorphous siliceous material that is present you may also get some calcium silicates and type C fly ashes. That is why you see some reactive crystalline phases also present in type C fly ash. So but for the most part what you see is the extent of amorphous phases is varying from nearly 0 all the way up to 97% among all the materials that have been supplied for this test. And what you clearly see is the compressive strength in MPa as exhibited by the lime reactivity test for quartz. It is almost nothing, it is less than 0.5 but all other pozzolanic materials are crossing this 4 MPa mark. All of them are crossing the 4 MPa mark. The highest being exhibited by the calcium clays, the slag and for some reason this one of the type F fly ashes that was also considered where you can see SFAHS which is the one which has very high amorphous content.

So if you do a plot of the amorphous content versus the pozzolanic reactivity you will generally get more or less a linearly increasing trend. The greater the amorphous content the greater will be your pozzolanic activity in this test. So again what you have to do is ensure that you understand how the chemical composition of the metal admixtures will play a role in your overall reactivity. How that reactivity is going to affect the performance of the system in concrete is what is most important.