Admixtures and Special Concretes

Prof. Manu Santhanam

Indian Institute of Technology Madras

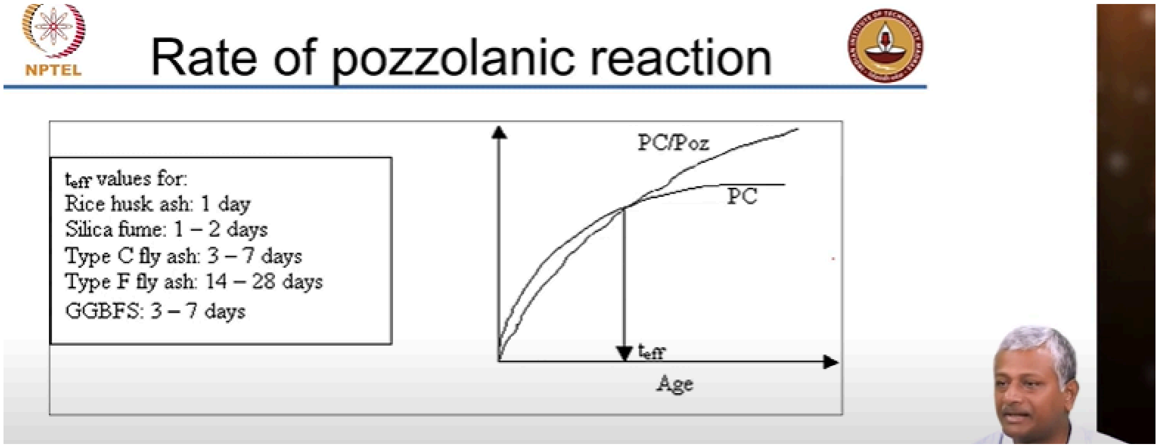
Department of Civil Engineering

Lecture -30

Mineral Admixtures: Pozzolanic activity

Rate of pozzolanic reaction:

(Refer to slide time: 00:20)



Rate of pozzolanic reaction

t_{eff} values for:
Rice husk ash: 1 day
Silica fume: 1 – 2 days
Type C fly ash: 3 – 7 days
Type F fly ash: 14 – 28 days
GGBFS: 3 – 7 days

Now, a very simple way to track the rate of pozzolanic reaction is to simply compare the strengths of these materials. So if you plot the relative strength, let us say this is the graph for strength development of Portland cement or cement mortar, Portland cement mortar or Portland cement concrete. So we know that at early ages there is a very quick reaction and this reaction slows down later and then you start going in more or less maximum strength will be reached and you will not really see major strength development after that. Now a system with Portland cement and pozzolan where partly the cement has been replaced by pozzolan of course the replacement levels will vary for the different types of materials that we are considering here for this kind of an assessment. This pozzolanic system because of the slow rate of the reaction will start off a little bit slower as compared to the cement but assuming you continue to cure, assuming continuous curing, you lead to a condition where the pozzolanic system exceeds the cementitious system in terms of the compressive strength. This is just in terms of relative strength. We can do this comparison with respect to other sorts of mechanical properties also but this is just a comparison with respect to this system.

So if you define the age at which this overtaking of the cement strength happens as t_{eff} effective, the values of t_{eff} for the different compounds are presented in this table. So rice as cash is generally quite highly reactive so this can happen within one day, silica fumes can happen within one or two days but generally when we are talking like this we are also talking about a certain percentage replacement of the cement by these materials. These normal t_{eff} numbers are given for 5 to 10 % rice as cash and silica fume, 5 to 10 % and for type C fly ash we are talking about 20 to 30 %, type F fly ash also 20 to 30 % and slag 40 to 60 %. This t_{eff} that I have given there are for specific percentage replacements, it is not true for everything. For instance if you replace type F fly ash or low calcium fly ash as 50% of the cement you are going to wait much longer for strength development, you are not going to get strength in like 14 to 28 days.

What does this tell you, it tells you that the speed of the reaction, pozzolanic reaction depends on the type of pozzolanic, silica fume and rice as cash being highly pozzolanic because of their high purity silica are able to react much faster because of which they are able to substitute cement and still produce the same strength at one day. Whereas if you use a high calcium fly ash the strength development will be slowed down to some extent and you will probably get the strength only by 3 to 7 days.

So if you compare 1 day strength when cement is replaced by type C fly ash it may not be as good as plain cement strength. But when you compare the 7 day strength it is likely that you would have reached the same level of strength. Similarly with type F fly ash or low calcium fly ash before 14 days your fly ash system is going to lag your cement system significantly. But beyond that by 28 days you will see that more or less the strengths have come out to be equal. That is all assuming you are continuously curing. You are not going to stop curing in 7 days like you do in the field. This is for an ideal scenario and slag typically 3 to 7 days will be the time it takes to reach the level of a plain cement based mix. So this again tells you very clearly that when you are substituting cement by any mineral additive cure for a longer time. You need to cure for a longer time.

How long does the strength gain continue? See theoretically the strength gain should never stop because there is always internal moisture available which will continue to hydrate the system. But practically what happens is because of the barrier forming as a result of the hydrates you do not have waste for water to get in easily and then there is not enough space for your hydration products to form in your system. So oftentimes the reactions in your system will not proceed to completion even if you cure continuously. But for early ages like up to 56 days or 90 days the presence of curing is likely to keep on enhancing the reaction.

But in the long term you will certainly have a lot of cement or a lot of material that is unreacted because there is simply not enough space. The reaction becomes space limiting. We saw in the earlier discussion of cement chemistry that you are filling up the available space with hydration products and these hydration products were a lot more voluminous as compared to the initial cement grains. So once the space is not available you do not have space for these products to grow. So you are going to be constructing or restraining the extent of reaction that can further proceed. So all reactions are usually limited because of the lack of space.

So even though I have depicted a seemingly continuous trend of strength gain at some point it is not going to go beyond that. There is a lot of literature on that subject about how space becomes limited and then you really do not get too much more enhancement in your mechanical properties or improvement in durability beyond a certain point of time.

These are the effective times given for the typical dosage levels that we use. If you go to an RMC when you have a fly ash based concrete you will have fly ash typically at around 20 to 30%. If you choose Portland Pozzolana Cement it is likely that your cement has about 30% fly ash and slag cement is usually between 40 and 60% most of the time. There are cases where slag cements are more than 60% also used. So there you can imagine that you need to probably cure even longer. So it is very important to understand this. Very often when you see people on sites they really do not understand this concept well enough. They think that if cement is to be replaced by any other material you can still continue your regular processes and get the same effect. The issue with mineral additives is because of this speed of reaction getting affected you have to have a compensation by additional curing. But the amount of time and resources that you put in to do that additional curing will actually significantly enhance your long term service life and that is where you need to put all your bets to ensure that you get a long term performance from your concrete rather than worrying about extending some periods of working in the short term. So that is very important for us to understand.

So this is a very important concept because it tells you that for an early age when you are designing concrete let us say 28 days of strength you will be limited by the extent of mineral additives that you can actually put in your system.

Why do we talk about 28 days of strength? What is the reason? Why do we want this 28 days of strength? What is so significant about 28 days? Concept of 28 days came from 4 weeks or a month close to a month but in 28 days a significant portion of the loading transferred to the concrete element. Does the concrete element need to bear all the loads that are going to come to it during the lifetime of the structure as early as 28 days? So if I cast a beam for instance by the time the beam reaches 28 days is it going to bear the load that it is going to bear throughout its lifetime? You construct a column, you are continuously constructing. How much load does the column bear while it is getting hardened?

Mostly self-weight. Maybe in 28 days 2 additional floors may have been added so it is bearing somewhat additional load but in your building of 15 floors or 20 floors 2 floors is not going to be a significant part of the loading. So where is the need for this?

Jumping to get this early strength. On sites there is always a requirement to get the early strength and very often the reason why mineral admixtures do not get used to the extent that they should be is because of this over dependence on early strength for your construction projects. So your strength or the load transfer is executed over a long period of time. You do not transfer too much stress onto the concrete early in its lifetime.

So you have some leeway in doing a design where concrete strengths can be considered to be at later ages like 56 days or 90 days and that way you will be able to incorporate a lot more mineral additives in your system and that obviously makes the system more sustainable. You are reducing cement clinker usage by substituting more and more with mineral additives All this has to be carefully studied obviously but there have been several examples where 50% fly ash, 60% fly ash has been used, low calcium fly ash has been used as cement replacement and still those concretes are surviving and doing well. That is because when they were constructing the engineers saw that they could actually prolong the time of curing and wait for a strength at a later age because there was no need to load the structure early enough. In this era of fast track projects we often think that because we are speeding up the construction process our requirement of loading or requirement of the full strength at 28 days is a must. Truly speaking it is not.

How much do you think is the maximum stress in the concrete as compared to its compressive strength in most conditions? How much maximum stress is taken by the concrete? You can always design with ultimate state, ultimate limit state but what is the stress level you think happens in concrete based on the loads that are given because you have so many factors even in the limit state design you assume material factors, you assume load factors. So very rare that your system will be getting loaded more than 50% or 60% max. Very rare. This is in full service.

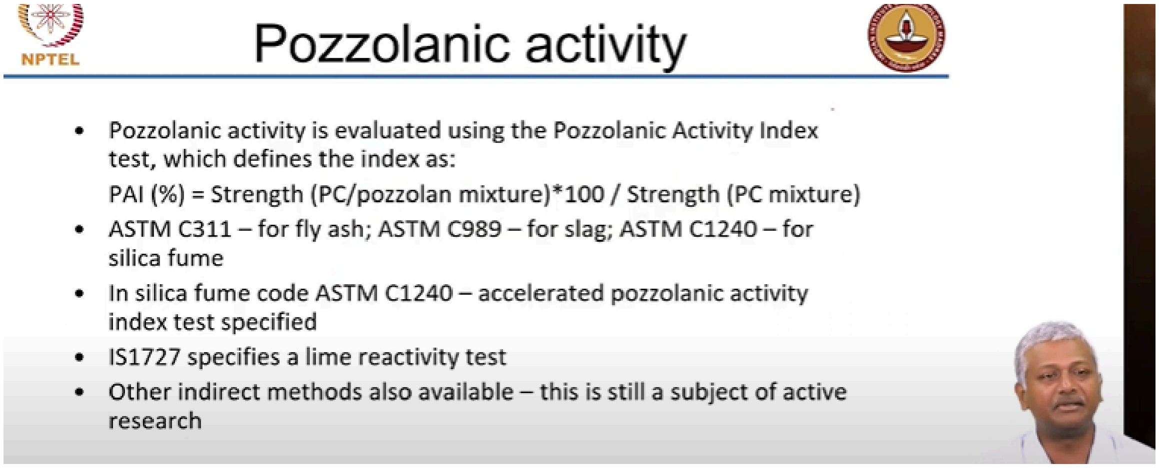
So during construction you can imagine that you have much greater leeway in terms of allowing for a greater strength development. So the reason I mean the very issue that leads to a slower reaction being slower as compared to hydration reaction that is the primary reason for pozzolanic concrete having a lower heat of hydration and that has its own advantages. Less thermal cracking, better long term performance and so on. Unfortunately because of that reason alone, because of the low rate of strength development alone a lot of the initial phase trials with pozzolanic cement were rejected by customers because they felt that the concrete was not getting strength fast enough or the concrete strength was getting compromised because the cement is slower reacting. Now what has to be understood in practice is that it is not the cement which is important, it is the concrete that needs to be designed for the strength.

If you need a 28 days strength with the fly ash cement you need to design it appropriately. You cannot design with OPC simply replace OPC with fly ash and then expect it to have the same behavior. It is not going to happen. So when you are designing for strength the cementitious content and water binder ratio that you need with plain OPC to produce a 28 days strength may be different as compared to the cementitious content and water binder ratio required for PPC. You may want a little bit higher cement and a little lower water cement ratio with PPC to achieve the same strength at 28 days. Some years ago instead of making the customer aware that it is a concrete they should be worrying about not the cement several cement companies went down the line of actually trying to make the Portland pozzolan cement start reacting faster and gaining strength as fast as OPC.

So what they started doing was crushing the PPC to much finer sizes and they even came out with the brand name of PPC 53. You know that OPC 43, 53 are grades of OPC which relates to strength attained by cement mortar at 28 days. So PPC 53 actually if you look at the standard for PPC it has to satisfy only 33 MPa at 28 days because you want the benefit from its low heat of hydration. But here they started grinding the cement finer and making it react faster. They totally shot down the major advantage of low heat of hydration. Problem what happened with them is that the bags they were using were similar to what they were using for OPC. So when you grind the cement finer the moisture effects are going to be more. So you saw the cement was getting hardened in the bags very fast very rapidly. So the life of cement was getting reduced because they were grinding it finer. So even today some cement brands are available with PPC 53 but it really does not make any sense. So one has to design the concrete to get the strength. It is not the cement strength that will dictate the concrete strength unless of course you are working at the same level of cement content and water binder ratio. This is a concept which not many people understand.

Pozzolanic Activity:

(Refer to slide time: 15:34)



Pozzolanic activity

- Pozzolanic activity is evaluated using the Pozzolanic Activity Index test, which defines the index as:
  PAI (%) = Strength (PC/pozzolan mixture)*100 / Strength (PC mixture)
- ASTM C311 – for fly ash; ASTM C989 – for slag; ASTM C1240 – for silica fume
- In silica fume code ASTM C1240 – accelerated pozzolanic activity index test specified
- IS1727 specifies a lime reactivity test
- Other indirect methods also available – this is still a subject of active research

So again this entire debate on the extent of mineral admixtures and its effectiveness in a cementitious system leads us to understand very clearly the reactivity of the cementitious system. Now there is a lot more literature available as compared to what I am going to present to you here because this has been a subject of much research over the last 15 years. There is tons and tons of literature that has come out but I have kept it at a fairly simple level because there are a lot more important aspects that we need to look at from the aspect of usage of these materials in concrete.

But nevertheless we will talk about some of the activity determination tests. The simplest way to determine the reactivity of a pozzolanic material is to simply substitute cement by this material and determine the strength of a cement mortar. You make a standard cement mortar, make another mortar where cement is replaced partially by the mineral additive and then determine the strength. So that is called the pozzolanic activity index test, PAI. Pozzolanic activity index test where pozzolanic activity index is simply defined as the percentage strength of the pozzolanic mixture as a function of the plain portland cement mixture.

Now for different mineral additives like for fly ash ASTM defines the activity index test as per ASTM C311, for slag it is C989 and for silica fume it is C1240. There are some differences in these methods, I will let you read the standards and figure out what the differences are on your own. Now one principle difference that I would like to point out here is that ASTM C311 and C989 rely on producing mortar of the same consistency. So the water cement ratio is going to be variable. But when you use silica fumes, if you try to do the same thing because of the high water demand of silica fumes it may completely reduce the strength of your system. So what the standard permits you is to allow a super plasticizer.

So you prepare the cementitious system, you prepare the system with cement and silica fumes at the same water content but with a super plasticizer to get the same flow. Flow is measured by a flow table test which you typically do for cement mortars. So that is the primary difference between the silica fume code and the other mineral additive codes where super plasticizers are not actually permitted.

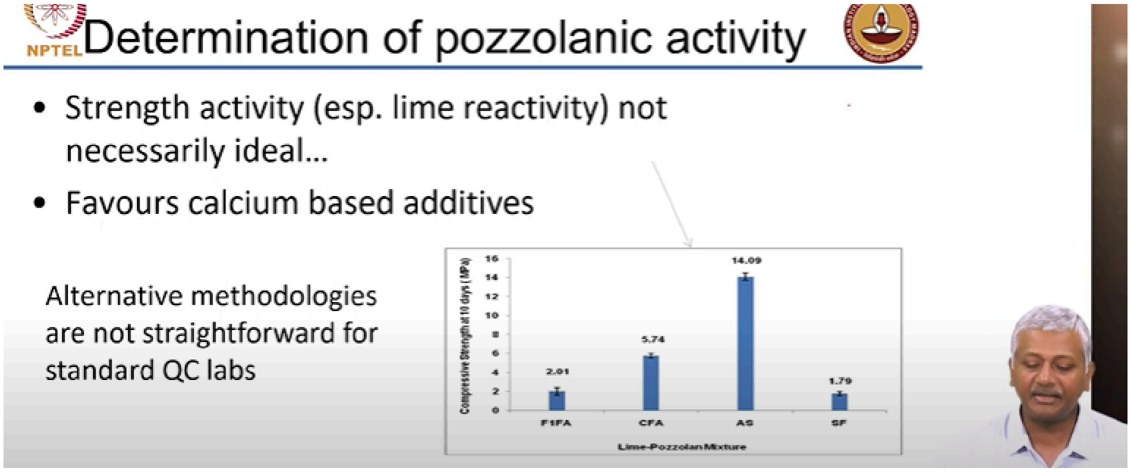
Now this is again a very common issue that we see between the practices in India and the practices in Europe for instance. So the strength of cement in India 43, 53 and all that, how do you determine the water content for those strengths? You determine from the standard consistency there is a formula that you need to apply 0.85 times. So you determine the standard consistency and use that to determine the water to binder ratio required for your strength test to cast the cubes. Now what happens is because of this aspect depending on the standard consistency of your cement the amount of water that you add in your system is variable for different cements. Even for the same 53 grade cement if there are different brands each one of them may have a different consistency the amount of water that you add will be different. As a result the water to cement ratio of your mix is going to be different. If you go to Europe the EN standard says that all mixes are to be prepared with the water to cement ratio of 0.5. So there they are comparing at the same water to cement ratio, here we are comparing at the same consistency. Now that produces a lot of different results, major differences in the results that you can expect from your strength tests. So you can't compare the way that grading is done in India to the system of grading that is done in Europe. So you need to be a bit careful when you look at the results and understand carefully what has been done. So even in the pozzolanic activity index test there are ways in which you can look at the system either with more water to produce the same consistency or with the same water content but with an added super plasticizer to produce the same consistency. So you have to be careful about what is the system being adopted in the study that you are reading about.

IS 1727 which is actually a specific standard applicable to pozzolanic materials, a lime reactivity test is specified. So what does the name imply? Lime reactivity. Lime reactivity simply means you have a mineral admixture, you add lime and determine the strength that develops as a result of reaction of lime with the pozzolan. So this basically is expressed, reactivity is expressed as the strength in megaPascal. We will look at this a little bit later in more detail. Lime reactivity is simply expressed as the strength of the cement mortar prepared by putting together a mixture of lime and the pozzolan and then determining the strength and the strength in MPa is the lime reactivity not a percentage. Pozzolanic activity index test describes the percentage, sometimes it is also simply called strength activity index test.

There are other indirect methods as I said this is the subject of a lot of research. In fact there are people who are going on developing new tests just from the point of view of being more relevant than the others but you have to take everything with a pinch of salt and ensure that you understand what is going on in each of these tests, what are you actually measuring is very important to really understand.

Strength activity test:

(Refer to slide time: 21:44)



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

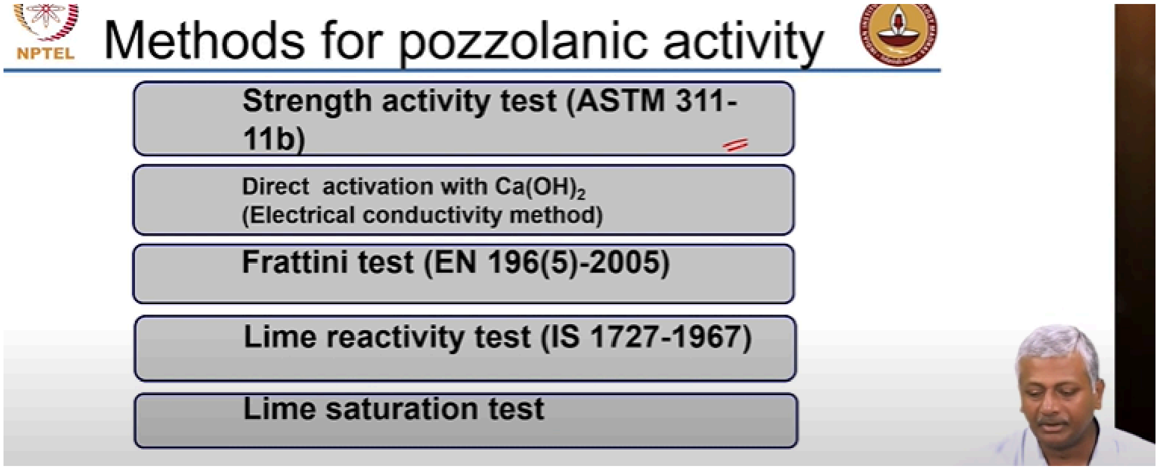
Now strength activity, especially your lime reactivity tests, is not necessarily ideal. Now why is that? Because in the lime reactivity test you add the lime and the pozzolan and then you expect it to form CSH but this is not really reflecting your cement system. Why? You have alkalis, you have gypsum present in the cement which is further going to contribute to the reactivity of your pozzolan. You are not capturing that in the lime reactivity test and because of that what happens is sometimes not every time but sometimes depending on the nature of your material it may work out less in favor of the silica bearing systems.

For instance this one work that was done by one of our students here which showed that the lime reactivity of products available in the market low calcium fly ash and silica fume the lime reactivity is not up to the mark that is very surprising. Usually you do not expect that. You expect that products available in the market will be having significantly high lime reactivity. But the same thing for type C fly ash and for slag the lime reactivity obtained using the same lime reactivity test was significantly high and was able to meet the standard level and that shows that it seems to favor the systems which already have a high amount of calcium present in them. But it does not reflect the reality of a cementitious system. So there are alternative methodologies prescribed but they are not as straightforward for standard QC labs. In typical QC labs they are okay to do strength tests. Any QC lab will have a cement strength test so the same thing can be applied for a pozzolanic strength test also.

Usually the lime reactivity test also needs an oven at 50°C to speed up the reaction but that is not really a problem. Usually for QC labs you may have ovens available for aggregate moisture determination and so on. So that is not really an issue for QC labs but when we talk about other reactivity tests as I will show you they are not as straightforward for QC labs. So let us look at some of these tests. Of course we already talked briefly about strength activity tests but we will take a look at the mixture design in just a minute.

Methods of Pozzolanic Activity:

(Refer to slide time: 23:54)



Methods for pozzolanic activity

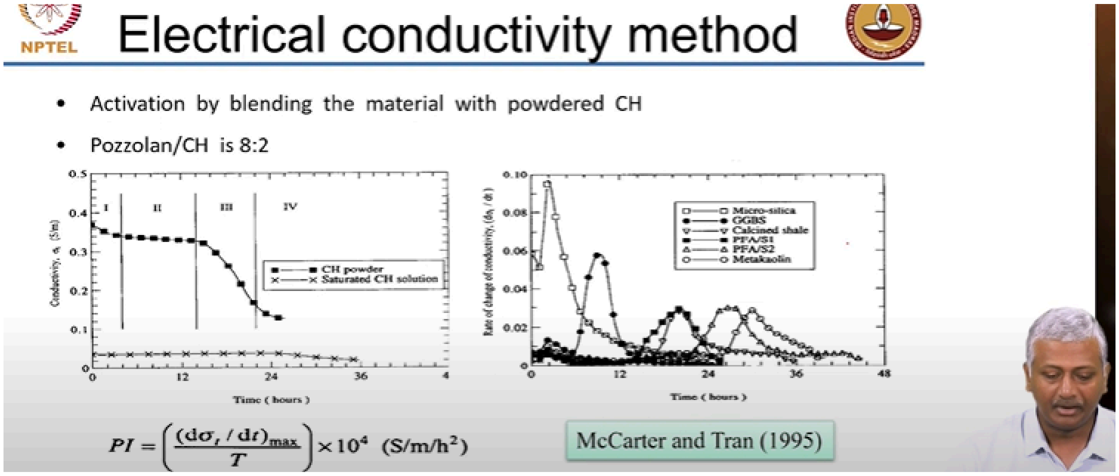
- Strength activity test (ASTM 311-11b)
- Direct activation with $Ca(OH)_2$ (Electrical conductivity method)
- Frattini test (EN 196(5)-2005)
- Lime reactivity test (IS 1727-1967)
- Lime saturation test

We also have the electrical conductivity determination by a direct activation with calcium hydroxide. There is a more chemical test called the Fretini test and then of course the IS lime reactivity test which is also a strength activity type of determination and lime saturation test. Let us look at these briefly and most of the examples here are from the research work of a student of mine who worked on sugarcane bagasse ash. So many of the data that are shown in the next few slides are from that work so you will see bagasse ash as the mineral additive in that case.

What is bagasse? So after you crush the sugarcane and extract the juice the fibers that remain are called bagasse. Bagasse has a very good calorific value so they burn it for producing electricity or producing steam for your sugar mill and so on but after they burn it the ash that remains is dumped because it is of no use after that. But then it turns out it has good silica content in it and that silica is what we are trying to use.

Electrical Conductivity Method:

(Refer to slide time: 25:15)



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)

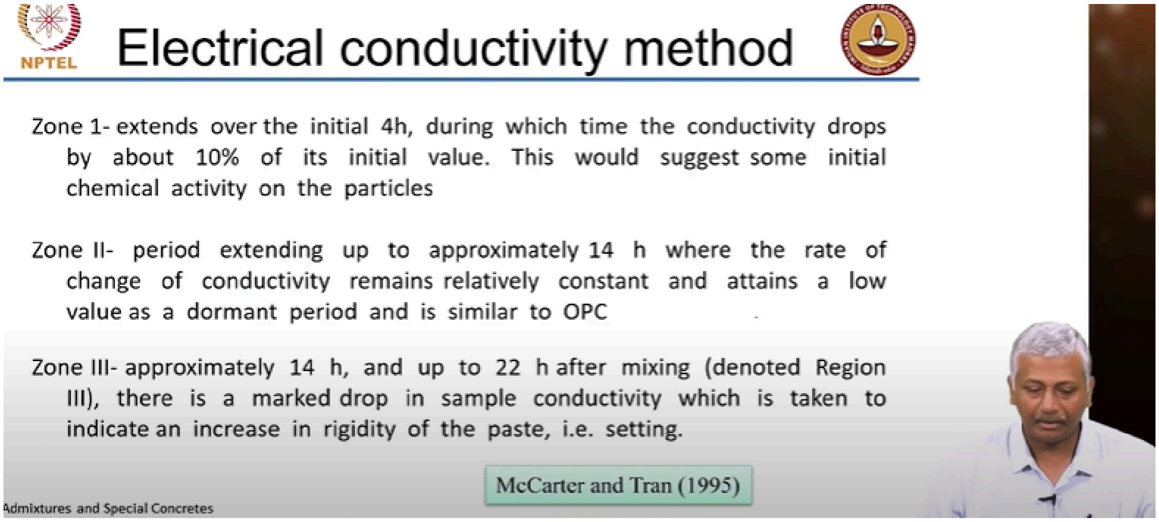
So electrical conductivity method, so here what you do is you blend the material with powdered calcium hydroxide. The pozzolanic material to calcium hydroxide ratio is 8: 2 or 80 to 20% if you will and you prepare a mixture with different amounts of water and what you are simply trying to do is measure the electrical conductivity of the system.

Why will that help? Why will the measurement of electrical conductivity help? Initially of course the system is wet so the conductivity will be high or low? It is going to be high as the hydration products form your conductivity will start getting lowered. Usually the work was done by McCarter who is one of the very well-known research scientists working on electrical methods applied to concrete. So here there are several regions of the conductivity curve that are seen. You have region 1, region 2, region 3 and region 4.

Region 1 you see a slight loss in conductivity but then in region 2 you have almost a steady conductivity value that means the reaction is not really happening at a fast rate. Initially there is some reaction which reduces conductivity but then your conductivity is almost steady. Stage 3 you have a major decline in conductivity that means this is the stage at which a bulk of your reactivity is happening and then stage 4 the reactivity slows down. More or less similar to what we see with our cement heat curve, the calorimetric curve of cement is more or less similar to that. Now here the pozzolanic index is defined as the maximum rate of change of conductivity over the time over which it happens.

So this is expressed in s/m^2/hr^2. Now this is only a definition just simply taking into account this stage 3 where the pozzolanic activity is maximum. In using this they are able to define of course the pozzolanic activity of several different compounds that they have investigated including micro silica or silica fume, slag, calcine shale, fly ash and metakaolin. So you have different results available here. As you can clearly see for micro silica the rate of change of conductivity in that zone 3 is the highest that means you have the highest rate of reaction. Then it turns out it is for slag. Interestingly for metakaolin they seem to have very slow reactivity. I do not know why because they may not have used a very high reactivity metakaolin in this case.

So what they are observing is very clearly you can distinguish the pozzolanic activity of the system by simply measuring the electrical conductivity of the system. So you can measure electrical conductivity quite simply. You can put your freshly mixed material in a cubical container and at two ends of the cube you put electrodes and then you can either do an AC based system or a DC based system. AC is preferred, we will talk about that later. Alternative current is preferred and then at a specific frequency you apply a voltage and then determine the current and change that to conductivity value.



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)

Admixtures and Special Concretes