

Advanced Concrete Technology
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Lecture – 19
Mineral admixtures – Part 2

Good morning everyone, in the last class, we were looking at how mineral admixtures make a contribution to sustainability by impacting all 3 major aspects of sustainability, 3 pillars which is economic, environmental and social, so all 3 pillars are affected by the use of mineral admixtures because of which they make a difference to the way that concrete construction is practiced and overall reduce the sustainability impact of the process or the product.

So, mineral admixtures are today probably used in all different types of construction in fact, even with ordinary Portland cement, you do not really get a true Portland cement clinker, you always get a performance improver which is added along with the OPC and that is typically fly ash sometimes but mostly, it is ground lime stone, please remember we talked about the fact that mineral additives could be also in the inert form.

So, we consider ground limestone to be mostly inert although, in some cases there can be some reactivity also expected from the limestone especially in a system that has reactive alumina inside, which we will talk about more towards the end of this chapter. So, the ground limestone is added as a performance improver up to 5% of the cement and cement clinker is only 95%. So, what you are essentially getting is a system which already has a mineral admixture inside.

And more and more, the focus of using different types of cements is shifted more from the OPC to the use of blended cements, so we are having increasingly more number of cements which have mineral admixtures in them today, apparently about 70% of our cement is actually, blended cement, 70% cement that is actually used is blended cement, so only 30% is actually ordinary Portland cement.

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Pozzolans

- Pozzolans are siliceous or aluminous materials, which possess by themselves little or no cementitious properties, but in finely divided form react with calcium hydroxide in the presence of moisture at ordinary temperatures to form compounds possessing cementitious properties (definition according to ASTM C595).

In fact, for all the residential construction market today, you do not get Portland cement you can only get blended cement. So, of course we know very well that the primary characteristic of the mineral admixtures that makes them effective is that Pozzolanic activity and pozzolans as per the official definition which is given in ASTM C595 are siliceous or aluminous materials which possess by themselves little or no cementitious properties.

But in finely divided form react with calcium hydroxide in the presence of moisture at ordinary temperatures once again, please remember this is all happening at regular temperatures to form compounds possessing cementitious properties, so again this is just rephrasing the previous aspect that we talked about, when we looked at different types of binders, the Pozzolanic binders are those which cannot react with themselves; by themselves with water.

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Pozzolan reaction

- $CH + \text{Reactive SiO}_2 \text{ (or } \text{Al}_2\text{O}_3) + \text{H}_2\text{O} \rightarrow \text{C-S-H (or C-A-H)}$
- Reaction is
 - Lime consuming ✓ \rightarrow pH high
 - Pore refining ✓
 - Interface refining (why?)
 - Slow (low heat of hydration)
 - Accelerated by alkalis and gypsum ✓



But they need the presence of lime for reaction to be completed and production of additional CSH. So, of course, just to reiterate, the Pozzolan reaction involves calcium hydroxide with reactive silica or alumina, sometimes the Pozzolan material may also have reactive alumina for example, we saw several types of Pozzolans like class F fly ash or metakaoline, they will also have alumina, which is quite reactive or amorphous.

Because of which you will end up getting some reactivity from the alumina also, so this will lead to the formation of calcium silicate hydrate or calcium aluminate hydrate or a mixture like what we earlier called as CASH; calcium alumino silicate hydrate, so that is what you are ultimately get with the reaction of these Pozzolan additives that have both reactive silica and alumina.

So, reaction obviously consumes the lime, we earlier said that lime although, it is good for the cement system, why is lime good for the cement system? It keeps pH at a high level, lime keeps pH at a high level, it also is a solid crystal and it occupies the pore because of which obviously it is contributing to the strength also but the problem with lime is obviously that it gets reacted very fast when there is an external attacking species like a chloride or a sulphate.

So, if you can convert calcium hydroxide into a more stable material like CSH, it will not have that issue, for example even when soft water passes through concrete, it can actually leach out your calcium hydroxide, soft water which is a neutral pH can actually leach out your calcium hydroxide

which is often why you see white patches on the surfaces of your brick walls or even sometimes concrete.

The white patches are basically, calcium hydroxide that has leach out and converted to calcium carbonate on atmospheric exposure. So, lime consumption happens, which makes the system a little bit more durable, it is refining the pores because you are converting a well-defined crystalline material into something, there is semi crystalline and occupies the very large surface area.

Because of that there is a large volume filling also that actually happens with the formation of CSH, so, the pores get refined, they become smaller, the interface also gets refined, again why does that happen, why does the interface get refined? There is more calcium hydroxide found in the interfacial zones, so obviously greater conversion of calcium hydroxide to CSH happens at the interface which leads to improved performance of the interface.

Secondly, there is also the filler effect of the mineral additives, so the fillers can actually go and block the open spaces available close to the interfaces, then this reaction is quite slow, it is much lower than your cement hydration because of which what will happen in the heat of hydration? It will get lowered. So, we talked earlier about low heat cement for instance. Now, for a cement company to actually produce a completely different brand of cement, they might need to open up new kilns to do that.

Because the maximum demand is still going to be for ordinary Portland cement, so if they cannot produce special cements then they need to manage all the special performance requirements with regular Portland cement. For example, the low heat requirement which is there for mass concrete, can also be obtained from a mixture of ordinary Portland cement and fly ash, you replace cement with fly ash, you can actually slow down the hydration and liberate much lesser heat.

We saw the examples of that in our discussion in cement chemistry, where we saw that colorimetric curves clearly show that when fly ash is added to the cement system or when fly ash is used as a cement replacement, you lower the heat of hydration, you lower the peak heat rate, you lower also the; you increase also the duration that the system takes to reach the peak heat rate.

So, we have looked at those examples earlier, now that is exactly because of the slow reaction that happens because of the Pozzolans, and this reaction is generally accelerated in the presence of alkalis and gypsum, where are the alkalis and gypsum coming from? From the cement clinker, the cement clinkers is actually or rather cement is contributing the gypsum and the alkalis.

So, in the presence of alkalis and gypsum, this reaction is much faster than it would be otherwise, so if you take a pure system of lime that is calcium hydroxide and react it with fly ash in the presence of moisture, your system will take a long time to attain strength, but in the presence of cement because the alkalis and gypsum are getting contributed by the cement, you actually can attain strength much faster even with fly ash based systems.

Now, some of you may have heard of this technology called FaLG, anybody as heard of FaLG? No, FaLG is a technology that is being used to manufacture bricks, low strength not as high strength as concrete but Fa stands for fly ash, L stands for lime and G stands for gypsum, this FaLG technology has been proposed by some researchers as an alternative to clay for manufacturing of bricks.

So, instead of burning clay, we say that we can actually formulate the bricks, mould the bricks with a combination of fly ash, lime and gypsum, approximately it has got about 65% fly ash, I think about 25% of lime and 10% gypsum that is the approximate formulation, although it may vary. So, what happens here is you are relying on the reaction between fly ash and lime and that reaction is accelerated by the presence of gypsum, just like what happens in the cementitious system.

Here, you have taken it out of cement, there is no cement in this case, you only react the fly ash with lime and accelerate that reaction with the presence of gypsum, so you end up obviously forming a structure like CSH and so on because the reactive silica from fly ash will react with the lime to produce a CSH. Now, of course, you also know that lime is used on its own as a binding material.

But it is usually confined only to heritage monument, we do not really use lime as much for regular construction except for whitewashing, we use pure lime for whitewashing. The advantage of using lime is obviously that it can take away the carbon dioxide from your environment and improve the air quality. So, if you talk to architects, lime is a preferred material of choice as far as the interior finishing is concerned.

Because it can also give you a lot of choices with respect to the kind of pigmentation you want to give and so on. Whereas, the cement which has got same grey colour always but lime because it is white, you can modify the colour suitably with the use of pigments. Anyway, we are not here to discuss about lime essentially, I want to bring to you information this technology we uses called FaLG, you may find some use of this in northern Andhra Pradesh close to vizag.

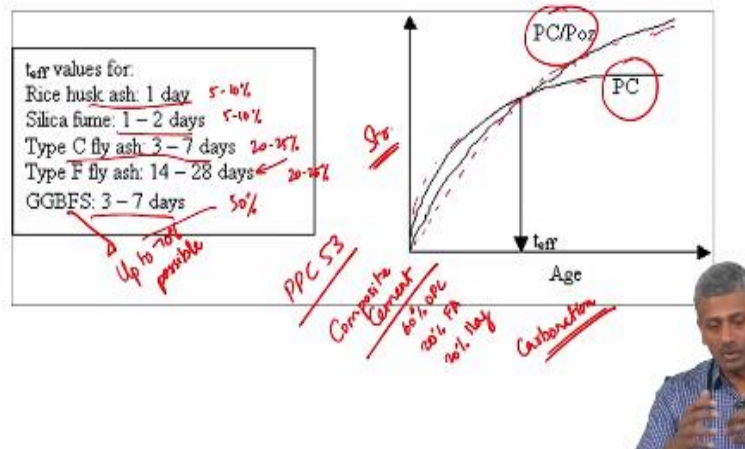
There are couple of researchers, who are base there, who are trying to promote this technology, a lot of FaLG is actually found there. The question is; is there any temperature limitation for the pozzolanic reaction? Now, generally pozzolanic reactions get accelerated when you increase the temperatures just like cement reactions, the pozzolanic reactions also get accelerated when you increase the temperature.

There is of course at low temperatures, even cement reactions are getting severely curtailed, so you can imagine that the pozzolanic reactions at very low temperatures may not happen at all, so especially when there is a chance of very low temperatures in the environment, you would not like to use pozzolanic materials like fly ash for instance, because fly ash however, reactive, the fly ash maybe, its reactivity is always going be lesser than cement.

So, if you have to cast concrete at freezing temperatures, then you tend to use normal Portland cement, unless of course you are doing heat treatment for the concrete, if you are subjecting your concrete to heat curing, then fly ash is an alternative that you can think of.

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Rate of pozzolanic reaction



Now, this is a very crude way of representing the kind of impact that the mineral admixtures are having on the strength development rate. Now, this may or may not be applicable in all instances but it is just a simple way of looking at things for example, if you plot the strengths; sorry, I make the mistake that I often accuse my students of doing not marking the axis, so here the axis; y axis should read strength and of course, the x axis is age.

So, strength development of Portland cement based materials is plotted here, so that is the strength development rate, so we know very well that by 7 days, you approximately get 70 to 80% of your strength, by 28 days 90, 95% of your strength is obtained and after that it is a very slow rate of increase provided you continue curing, always make sure that you understand that any strength development will take place only as long as you continue curing.

And then, why do we stop curing for concrete at 7 days? Yeah, generally by 7 days, we are getting nearly 70% of the target strength and in today's concrete, what happens is; 70% of target strength more or less matches with your characteristic strength of the concrete, for example if you are designing M30 concrete, your target at 28 days is around 38 to 40 mega Pascal's, by 7 days, you would easily reach around 30.

So, once you reach that strength, you do not really need to cure much more, but based on our discussion earlier, please remember that curing is very important from the perspective of filling up

of your porosity, so that you get less interconnected voids and you improve the durability of the system, always please look up on curing as a means of improving durability rather than attaining strength, without curing you may attain some level of strength.

But you will get very poor durability for your concrete, now all these continuous strength development patterns are drawn based on the assumption that you are continue to cure for a long period of time. Now, assuming that is the case when you have a Portland cement pozzolan system, you have a strength development rate which is slow in the beginning but eventually, has the potential of overtaking your Portland cement system.

And that is simply because the hydrates that are forming as a result of the pozzolanic reaction have a better volume filling ability as compared to the products of Portland cement itself. So, more volume if you fill up, the less porosity you have, the less porosity you have, the greater strength you will have, so potentially, I say potentially because you are assuming that there is sufficient moisture available, there is sufficient curing which is being done for these systems.

So, potentially the pozzolanic replaced systems have the potential of increasing or overcoming the strength of your Portland cement based systems. Now, the age at which this happens determines the; is determined by the reactivity of your pozzolanic material. For example, if you see rice husk ash, I told you earlier, it is about 90% silica, so it is a high reactivity pozzolan. So, it may take only about one day for the mix with rice husk ash to attain the same level of performance as your Portland cement mix.

Whereas, with silica fume, you may still be able to do this at one day itself; at one day itself, you may not have any difference between the Portland cement mix and silica fume mix and ultimately, you will get a much better strength development with silica fume because again the particle filling characteristics of silica fume are much better than that of cement. Type C fly ash, which is the high calcium fly ash, takes about 3 to 7 days to attain the same level of strength development as Portland cement.

And if you have a slag based system, again you take about 3 to 7 days to achieve the same level of strength as a Portland cement system that means there is the marginal reduction in your heat of hydration or marginal reduction in your rate of strength development, but with type F fly ash, you can be substantially delayed with respect to your strength development, you may actually be able to attain equivalent strength as a Portland cement mortar only between 14 and 28 days.

Now, all these numbers are given for typical replacement levels of these materials, obviously this would not hold good, if you keep changing the replacement rate, what are the typical replacement rates for slag? It is 50%, please remember we talked about Portland slag cement, where slag is typically around 50%, type F fly ash will be about 20 to 25%, type C fly ash again, same 20 to 25%, silica fume probably about 5 to 10% and rice husk ash also 5 to 10%.

So, those are the typical replacement rates of these materials, now why are these replacements restricted to these numbers, we will discuss that in some detail of course, you already understand about slag; the replacement level is high because it is hydraulic itself, it is able to have hydraulic reaction on its own, just that it needs some activation from the cement, so you can actually have a system which is rich in slag.

In fact, up to 70% slag is possible; with slag up to 70% replacement is possible and indeed has been done in real construction projects, but with fly ash, you rarely exceed 20, 25% unless of course, you have a high volume fly ash concrete application, I will talk about that little bit later, so these are assuming that you are replacing these materials at their conventional rates and that you do adequate amount of curing.

For example, if you do not cure type of fly ash based systems for that duration of 14 to 28 days, it may never reach the strength of your Portland cement mixture, so if you do the same level of curing for fly ash based systems as we do for cement system, you may not get adequate strength development, so that is one thing that has sort of acted against the use of blended cements in a more, I mean widespread fashion in the industry.

Because the industry always believes in using cements that are gaining strength fast, so when you use blended cements, obviously your strength rate has to go down, so the customer always feels that okay, low strength developing cement may not be something that is good for their construction, they do not know any better that the low heat of hydration is actually promoting your durability, hence promoting the crack resistance in your concrete and so on.

So, because of this what cement company started doing some time back; because they had a mandate only to sell Portland pozzolana cement for the regular trade segment that is the residential market and so on, they had to sell only PPC, so in order to satisfy the customer's demands, they started grinding the PPC very fine. So, when you grind PPC fine what happens; the rate of reactivity goes up.

And they were actually able to grind it to such a fineness that the PPC was giving them a strength which is equivalent to 53 grade cement, in fact they started marking their bags as PPC 53, if you really look at the code for PPC, Portland pozzolana cement, you will actually find that the strength gain requirement only matches that of a 33 grade cement, for a PPC, the strength gain requirement is only that of the 33 grade cement.

But without applying their minds and just thinking about the customer's demand, the cement company started producing 53 grade PPC, so that defeats the purpose because you do not have the benefits of low heat of hydration anymore just in an attempt to achieve that high strength, you are trying to curtail the main importance of your product, so because of that they had some problems.

For example, when you grind cement finer, there will be a storage related problem, if you do not store it in ideal conditions, there will be moisture absorption, so people found that the cement in the bag itself getting pre hydrated, they were absorbing moisture and getting pre hydrated, the finer the material the greater the chance for pre hydration. So, because of all this cement companies realise their folly and started coming back to a little bit more conventional PPC.

Even though, still they still grind PPC a little bit finer than cement, here they grind PPC to the level of about 330 square meters per kilogram where regular cement is about 280 to 300, so some

level of increase grinding is still there, which may help but too much finer grinding will lead to more problems for storage and you are not really getting the best benefit out of these cements, so now finally the cement companies have woken up that they need to educate the customers.

And tell them that, the main benefits are in the improved crack resistance, long term durability and so on, so it is still taking a long time to sink in and at this stage what has happened is that the entire world is now talking about CO₂ reduction. When they talk about blended cements, the main impact is CO₂ reduction. Now, you try to explain CO₂ reduction to a regular construction customer, you will fall flat on your face.

They have no idea about what is CO₂ reduction is all about, if you do not construct fast then you have a loss of money that is all they understand, so to get them to realise the benefits probably will take some time because you have to wait for an instance where people start imposing taxes in you, if your technology is actually liberating too much CO₂, at that point people will start trying to educate themselves and bring themselves to the fact that we have to have been using blended cements for a very long time.

Anyway, let us hope that happens sooner than later, so that is a good question; can we combine these together, so very often when you produce very high grades of concrete like high strength concrete, high performance concrete you can get significant benefits in combining more than one type of mineral admixture. For example, if you are using it; if you are preparing high strength concrete, you obviously will be using one of the finely divided mineral additives like silica fume.

But we know very well that when you have too much fines in your system, your water demand will go up, your workability may be affected and so on because of that the ternary combination or 3 triple blend combination of cement, silica fume and fly ash or cement silica fume and slag is often utilised to produce high grades of concrete. The other condition is also there that sometimes when you are not able to use too much fly ash, what you can do is combine fly ash with slag and use that at a higher level of replacement.

Today, there is a new cement which is come up, in Indian standard also it is called composite cement, that is a new cement standard in India now, composite cement, I do not know the standard number, so here we are essentially talking about 60% cement about 20% fly ash and 20% slag, so this is combining fly ash and slag in the formulation, so there are benefits to be obtained from this obviously your chloride durability will be very good without any doubt.

Your heat of hydration also will be lowered because if we simply replace cement with slag, you do not get that much benefit in your heat of hydration reduction but in combination with fly ash, you can actually significantly reduce heat of hydration, your strength gain will not be severely affected because you only have 20% fly ash, your slag does not affect strength gain rate tremendously.

Now, while in all those characteristics, the composite cement is very good, the one problem which can occur in composite cements is a higher rate of carbonation, now I am not talked about this earlier but we will talk about this in more detail in the durability chapter that the carbonation rates when you replace cement in large quantity by mineral admixtures can get to be quite high, and what is the reason for that?

The reason is this reaction here, the pozzolanic reaction, now you know that when cement hydrates it produces a lot of lime, calcium hydroxide is a plenty because primarily it is C_3S in cement and you know that C_3S produces very large amounts of calcium hydroxide, this calcium hydroxide provides a nice alkaline buffer, it provides a good buffer and when an external chemical like a chloride or a sulphate or a carbon dioxide enters the cement, it starts first reacting with the calcium hydroxide.

So, in a plain cement system, this carbon dioxide comes in, reacts with calcium hydroxide leads to the formation of calcium carbonate, calcium hydroxide + CO_2 will give you calcium carbonate ultimately, there is a sequence of reactions that happens but ultimately, you form calcium carbonate. Now, this calcium carbonate in regular cement densifies the external surface of your cement mortars or cement concrete.

Now, when you densifies, the rate of penetration of CO₂ will become lesser and lesser with time, so as age progresses, CO₂ progresses into the concrete at a very slow rate, now the real impact of CO₂ attack on concrete or carbonation on concrete is that it converts your alkaline system into a less alkaline system not acidic yet but it lowers the pH to about 8 to 9 and that level, your steel becomes unstable and starts to corrode.

So, that is a primary effect of carbonation, the effect on the cement paste is actually more positive because formation of calcium carbonate densifies the structure and strengthens it. Now, in mineral admixture based systems you are removing your lime, you are removing this buffer which was otherwise there to content with the incoming agents, and then you are producing CSH.

Now, what happens in the case of mineral admixture mixtures; is that since you do not have sufficient calcium hydroxide available, the carbon dioxide can now directly attacked the other calcium bearing products like CSH, your CSH starts getting attacked directly and when that happens, you have a possibility of a more porous network forming in the system, whereas the attack on CH leads to formation of more dense concrete, attack on calcium silicate hydrate may actually create a slightly more porous network in your system which further propagates the carbon dioxide into the concrete system.

So, when you substitute cement with mineral additives, you will definitely get greater propagation of CO₂, so without a doubt, any concrete where cement has been replaced by mineral admixture will lead to a higher rate of carbonation that means, you are increasing the risk of carbonation induced corrosion. Now, where does that lead us? I mean, we are talking about the fact that we should now move only to blended cements.

But now we are saying that carbonation is a problem, so what do we do, how do we avoid the problems due to carbonation? So what you can do is; when you use mineral admixtures, you improve the; increase the grade of the concrete that is required because if you have a higher grade concrete, you will have a lower water cement ratio in the system because of which your system will become less permeable first of all.

So, rate of diffusion of carbon di oxide is going to get reduced because of that, so that is a general way of accommodating this issue is that with mineral admixtures, it tends to increase the level of your strength grade of the concrete. Now, we will look at these options when we actually discuss durability much later but essentially, what you are saying is; do not replace mineral admixtures at the same water cement ratio.


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Pozzolanic activity

- Pozzolanic activity is evaluated using the Pozzolanic Activity Index test, which defines the index as:

$$PAI (\%) = \frac{\text{Strength (PC/pozzolan mixture)} * 100}{\text{Strength (PC mixture)}}$$
- 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
- (S172) specifies a lime reactivity test
- Other indirect methods also available – this is still a subject of active research

Handwritten notes:
 - Red circle around (S172)
 - Red arrow pointing to the formula: "Strength (PC/pozzolan mixture) * 100 / Strength (PC mixture)"
 - Red arrow pointing to ASTM C311: "75%"
 - Red arrow pointing to ASTM C989: "80-100" and "100-120"
 - Red arrow pointing to ASTM C1240: "It can be used to keep flow constant"
 - Red arrow pointing to (S172): "C1240 Acc. by high temp. → Fly Ash LR 74-142a"
 - Red arrow pointing to "Other indirect methods": "this is still a subject of active research"



When you are replacing mineral admixtures, lower the water cement ratio, if you want to improve your resistance to carbonation, so we will talk about that a little bit later. Now, when you have a new pozzolan to be used in concrete, you can not simply put that as a replacement of cement and concrete and do 100's of trials, you need to be as; you need to ascertain whether this pozzolanic material has any reactivity which can contribute to the development of the microstructure in concrete.

For that there are several types of test called pozzolanic activity tests. The most commonly used test is a regular strength test, you prepare a mortar with plain Portland cement, you prepare a mortar, the same type of mortar at the same flowability with the system which has the Portland cement replaced by a certain percentage of your mineral additive, and then you represent the pozzolanic activity index as the ratio of the strength of the Portland pozzolan mixture to the strength of the plane Portland cement mixture.

Generally, for fly ash; this ASTM C311 is the standard that is typically used and as per that your pozzolanic activity index with fly ash should be greater than 75% that means, when you replace cement by 20% fly ash, when you replace cement by 20% fly ash, your strength of the fly ash cement mix at 28 days should be at least 75% of the strength of the plain Portland cement mix.

If it is anyway greater than 75% then that fly ash is suitable for use as a pozzolanic material, other materials which are similar to fly ash like bagasse ash, type C fly ash all those are also judged by the same standard. For slag, there is a separate standard because again here the percentage substitution is a lot higher as compared to the fly ash. Now, slag because it is hydraulic and it is highly reactive, we use a slightly different means of classifying the type of slag.

Slag is classified into different grades; 80 to 100, 100 to 120 and so on, so that means that the strength of the slag mixture is at least 80 to 100% of the strength of your ordinary Portland cement mixture and 100 to 120 means, the slag mixture has a strength which is greater than your Portland cement mixture that means, you have a very highly reactive slag in your system and for silica fume, we use a slightly different standard, there is a reason for that.

In your ASTM C311 standard, we adjust the water to get the same flow that means, if I am replacing cement with fly ash and my water requirement is higher to obtain the same flow, my fly ash mixture will actually have a greater water content than the cement mixture or alternatively, if my workability improves with the addition of fly ash, my water requirement for the fly ash system will be lower.

So, my water cement ratio for the fly ash system will be lower than that of the cement system, with silica fume you know very well that because of the very fine particle sizes, you may actually end up increasing water demand tremendously, so here a super plasticizer can be used to adjust; to keep flow constant, so that means you have a constant water to cement ratio or water to bind the ratio and you add a super plasticizer to maintain the same flow.

So, you are testing different mineral admixtures with respect to their own categories of pozzolanic activity, again that is what I mentioned here also and in the silica fume system, it is an accelerated

pozzolanic activity test, where you actually subjecting your mortar to a high temperature during the setting phase, during the hardening phase, because of that the strength gain rate is much faster and I think you can get the result in about 7 to 8 days in this case.

In the fly ash system, you have to wait the regular 28 days before you can actually get the result. Now IS standard; IS1727 which is a standard which talks about replacement; pozzolanic replacement for cement, it specifies a lime reactivity test, now please remember, we talk about this earlier that if you react the system with lime itself it will still produce CSH, so here that is what is done.

You basically combine calcium hydroxide + pozzolan, and then that gives you CSH and this reaction is accelerated by high temperature. If you look at IS1727 that is the kind of reaction that they have, they directly react the lime with the pozzolan, now obviously there is a problem here know, what is the problem? It is not reflecting the true system; in the true system there are alkalis in the system, whereas gypsum in the system which is going to promote this reaction to happen faster.

But in the absence of those, you do not get a perfectly good reaction in this case. Now, as per IS1727, for fly ash, so lime reactivity test is only measuring the compressive strength of cubes prepared with these mixtures, if you look at that standard, I will tell you exactly how much lime you need, how much pozzolan you need and so on. So, for fly ash to be qualified as a good pozzolan, the lime reactivity should be greater than 4.5 mega Pascal.

So, here the units are just the strength of the cube, when you test the cubes of fly ash, there should at least, they get a strength of greater than 4.5 mega Pascal's, again high temperature because of that you are; I think the entire tests gets done in 8 days to some extent yes but it will be good to also have the real system like the presence of alkalis and gypsum, so people have proposed modifications in this test.

They have some sort of a model system in which they have lime, pozzolan as well as some added alkalis, so again this is a; as I said this is the subject to active research to actually find the real

contribution of mineral admixtures in a reactive system. How much of the mineral admixtures actually react? Now, this is important to understand what would be the optimum percentage of replacement with different mineral admixtures.

And you will find that because lime is only available to a certain limit, lime will only be available as long as cement is hydrating, so the reaction of the pozzolan is severely restricted by the presence of lime, so if you do not have sufficient lime in the system, the pozzolanic reaction will ultimately stop and at that point of time, you would not have the required rate of strength development.

For example, with silica fume mixtures, the reaction of the pozzolan is so fast but then the lime availability from the cement is not matching that reactivity that is why the silica fume system still take some time to reach the level of a cement system. So, if you can accelerate the generation of lime from cement, then you can accelerate the pozzolanic reaction that is why high temperatures generally tend to improve the rate at which your pozzolanic system will react.

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Source

- By-product obtained during combustion of coal in thermal power plants
- The quality and composition of fly ash depends on the type of coal being burnt

So, now let us take a look at individual mineral admixtures, we will we talk about their sources, we will talk about their reactivity and ultimately what effects they have on fresh and hardened concrete. Fly ash; your all know very well, it is obtained during combustion of coal and thermal power plants and the quality and composition of fly ash obviously depends on the type of coal that has being burnt.

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Rank of coal

3. Lignite (brown coal)
4. Sub-bituminous coal (70 – 80% C)
3. Bituminous coal (80 – 90% C) – Soft coal, used for ordinary purposes
2. Semi-bituminous coal – Good heating value, has a smokeless flame
1. Anthracite (90 – 95% C) – hard coal; high temperature needed to burn it

Low rank coals contain impurities such as clay, shale, quartz, carbonates, and sulfides. It is these impurities which give fly ash its composition.

You have learnt before that coal is divided based on the extent of impurities in it into 5 different types, you have the most impure form this just called lignite or brown coal, you have sub bituminous coal which is about 70 to 80% carbon, bituminous coal 80 to 90% carbon and that is the basics soft coal used for ordinary purposes and then you come to more purere forms of coa; which is semi bituminous or anthracite.

The problem is; we often do not find these sources easily and then burning requires a lot of energy to be given to the system, so generally for most part, the bituminous coal or sub bituminous coal is burnt and of course, we get lignite in certain parts of the country. So, from lignite, from all these coals, there are several impurities that may be present in coal and these are present in the form of clay, shale, quartz, carbonates and sulphites.

So, the impurities are the ones which give fly ash the composition because any carbon in the coal, we will get burnt off, all the parts that do not get burned will be the impurities which will be the SiO₂, the calcium oxide, the iron oxide, aluminium oxide again, the components that essentially make up your cement and these are the ones which fly off with the flue gas and are collected as fly ash.

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Collection of fly ash

- During combustion of coal, 75 – 80% of the ash flies out with the flue gas, and is thus called 'fly ash'. The ash that doesn't fly out is called 'bottom ash'. This can be processed as aggregate, but is generally not used in concrete.
- Most fly ash – dumped directly in ponds (as slurry)
- Collection is typically done in electrostatic precipitators

*Fly ash ponds
of
Bottom Ash*

So, during combustion about 75 to 80% of the ash flies out with the flue gas that is why it is called fly ash, the ash that remains is called the bottom ash because it is too heavy to fly out and the bottom ash is sometimes processed as an aggregate, although there is a lot of issues with use of bottom ash as aggregate also but generally it is not used in concrete, most of the ash so collected is dumped by the thermal power plants in fly ash ponds.

You know very well about fly ash ponds, very large area of a thermal power plant is occupied by fly ash ponds, so what they do is; simply collect the fly ash, if they are not able to sell the fly ash in the cement companies or other users, they collect all the fly ash and the bottom ash and mix it up as slurry and dump it in a pond, so several acres around the thermal power plant can be actually covered with a fly ash ponds.

And so, ultimately if you really want to make a difference in society, you should actually promote the use of pond ash that is the ash that you take from the pond in a wet state, you dry off the water, remaining ash which is a mixture of different types of impurities that are coming from the coal burning system, if you can actually promote that as an additive to either cement or to make synthetic aggregate and that would be a real contribution.

In our lab, Professor Ramamurthy's student have actually done some work on retrieval of pond ash and conversion of that into a sintered fly ash aggregate, so they actually palletise it and sinter

it into the aggregate size and they been quite successful at obtaining pond ash aggregate with this, so that is a very interesting way of looking at things, the only problem is when you turn it to aggregate, you need to give a lot of energy input into the system.

And that may sometimes act against your intentions of actually using this fly ash, so you have to then start understanding which one has the greater environmental impact, the amount of energy you put to process the material or the land use that you have in dumping this material, so you need to arrive at a proper arrangement to understand which is a better sin; which is the better sin.

Now, the issue is when you leave it in a pond, what may ultimately happen is that, there may be some heavy metals present inside the fly ash which may start seeping or leaching out into the ground water like arsenic for instance, that is often present in fly ash and because of that a lot of thermal power plants in the US had to be closed because of the dangers of arsenic pollution from the fly ash ponds.

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Electrostatic precipitator

The image contains several components related to an electrostatic precipitator (ESP):

- Schematic:** Shows the flow from **Combustion** to a **Steam Generator**, then to a **Precipitator**, and finally **Cleaned Gas** exiting through a tall chimney.
- Internal Diagram:** A detailed cross-section of the precipitator showing:
 - 1** Inlet ducts with a negative charge.
 - 2** Collecting plates with a positive charge.
 - 3** Discharge electrodes.
 - 4** Precipitator housing.
 - 5** Precipitator outlet duct.
- Photograph:** A large industrial structure, the physical ESP unit.
- Video Inset:** A small video frame showing a man in a blue shirt speaking.
- Handwritten Notes:** Red text annotations include "Super-Condensation", "Finely Suspended Pt", "Induced Dry Draft", and "Draught".

Detailed info at: <http://www.researchgate.net/publication/261010101>

So, again there are lot of issues with dumping of fly ash, so because of that in spite of the higher energy required to actually convert them to useful resource materials like aggregates, many people are still in favour of doing that. So, most fly ash as I said is dumped directly in ponds as slurry and collection of the actual fly ash that flies out is done in electrostatic precipitators, you saw that

electrostatic precipitator in the cement plant also right after your cement clinker cooling unit, where all the gases from the cooling of the clinker are coming out.

And these gases are carrying particles with them, these particles get trapped by electrostatic precipitators and then they are collected separately. So, ESP is nothing but a set of charged plates these are plates which are charged, oppositely charged, so any particles or the stream of gas that is flying between these plates, the particles get attracted to the charged plates.

While the gas goes out, the particles get attracted and usually, you have some fans which introduce the draft necessary to carry these gases between these plates, those fans are called ID fans; induced draft fans, so induced draft means they are inducing the flow in the gas because otherwise, if the gases do not have sufficient energy to flow out, they will not be able to come out properly.

So, you need to actually push them out by an induced draft fan, I think it is not draft, it should be drought probably, anyway essentially, you are pushing the gas out between the electrostatic precipitators plates and the particles get trapped, the gas goes out. So, these are; the picture which you see at the bottom here that is a set of electrostatic precipitators, so there are 4 of them in sequence.

So, what will happen is; the particles will be of different sizes, so the finer particles we will get charged and attracted to the plates more differently as compared to the coarser particles, so what will happen is as you moving from this end to this end, you will collect different levels of fineness of your fly ash, different levels of fineness of the fly ash and sometimes actually, even that collection may not be able to bring out the best of the particles in your fly ash, the most reactive particles in your fly ash.

You may want to do some further classification which is again called so, they call it super classification that means they further take this powder wherever facilities available, they can further take this fly ash particles that are actually coming out and getting trapped in the ESP and further process it to actually get very fine particulate materials from it and in fact today, there are

categories of fly ash available which are classified fly ash that means, they classified into different sizes.

And make it available as a much more reactive material, what you will find is; in some countries they actually use very finely classified fly ash and that can be as reactive as silica fume, in some countries they have such extensively good system for classification that they can actually get, very finely classified fly ash and use it even in applications which demands the silica fume, you can actually produce the same kind of improvement in your strength and durability as a regular silica fume particle.

And in fact, in India also, there are lot of companies that are involved in collection of the fly ash and classifying it based on the size but what you get from thermal power plant will be a mixture of different sizes, the cement companies simply we will go to the thermal power plant, collect the fly ash and bring it to the cement company, they may do some additional processing in terms of again classifying the sizes before it deemed suitable for use as fly ash.

Now, the problem is, that fly ash that you get if it is used directly in the concrete like in an RMC you have no control on the quality, one day you may collect fly ash that has certain quality, another day you may collect something completely different but if you are buying it from a supplier who does processing by classification, then you can demand a certain quality of fly ash each and every time.

So, to me this is the biggest barrier to the use of fly ash that we do not have a system where we can actually get the same quality fly ash day after day and that leads us to some problems with respect to the control of concrete which has fly ash, especially in RMC situation where you are getting directly from suppliers who are collecting and then distributing the fly ash to the RMC's, you do not really have a control in the fly ash properties.

In a cement plant on the other hand, the cement company can put in some conditions to check the quality of the fly ash and adjust it before they mix it with the cement to produce the PPC, so in India in general, it is often better to use PPC rather than fly ash as a mineral admixture in your

concrete because your variability will be much lower with the blended cement as opposed to the concrete which has fly ash.

Unless of course, you are buying a fly ash which is processed, there are processed fly ash also available in India but again you need to pay a heavy cost for it, so while in reality when you collect fly ash from the thermal power plant, all you will be paying is a transportation cost or little bit more than a transportation cost, it may cost less than 1 rupee a kilogram actually ultimately, but when you buy it from a processing plant, you may actually end up spending 4 rupees; 3 to 4 rupees per kilogram of fly ash.

So, on a tonne per ton basis, you will probably spend a lot more for process fly ash but the kind of quality improvement you get in your concrete, the kind of consistency you get in your concrete may sometimes you worth it to actually get the processed fly ash, it is still not propagated much in India, the use of processed fly ash. If you go to the west, you actually get fly ash in bags just like cement.

Fly ash is also obtained in bags, typically 25 kilogram bags, you can get fly ash in bags and bulkers as just like you get cement but in India it is still not reached that kind of a level, although there are Indian companies which sell the kind of fly ashes that go abroad for example, all these companies that manufacture the process fly ash sell it to customers abroad mostly in the Middle East and Southeast Asia and so on. So, we will stop with that and resume our discussion on Tuesday.