Admixtures and Special Concretes

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Lecture -34

Mineral Admixtures: Fly ash - Part 2: Classification and structure

Classification of Fly ash – ASTM:

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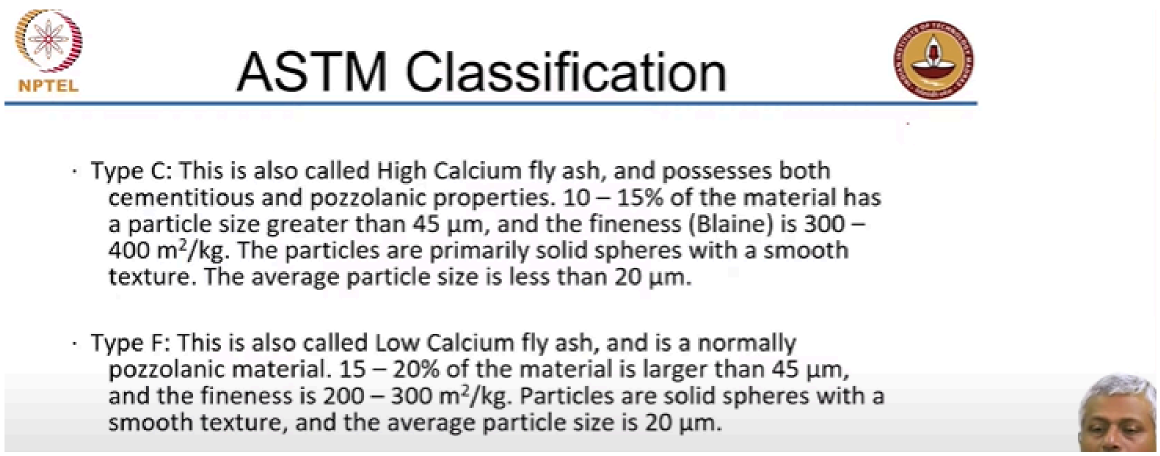

So, mostly we differentiate fly ash based on the calcium content as a high calcium fly ash or a low calcium fly ash. Usually they do not have too much difference in their appearance, they are both spherical particles of nearly the same size approximately similar to cement, but may be sometimes coarser than cement particles. Cement average size about 15µm here, average size about 20µm. Blaine fineness could depend, but generally ranges in the same order of the cement not much different. And again you can also test the particle size with respect to sieving through a 45µm sieve. So, generally cement has nearly 90% passing the 45µm sieve, fly ash will have about 80% passing the 45µm sieve.

So, solid spheres are the reactive silica particles that are found in fly ash, but it may not always be like that, there may be instances where bunches of these small solid spheres are present inside a glass or a glassy bubble which is simply containing these spheres and the bubble has to break for the spheres to get released. I will show you a picture of that in just a minute, but before that some more differences between the composition of the type C and type F fly ash.

Classification of Fly ash – IS:

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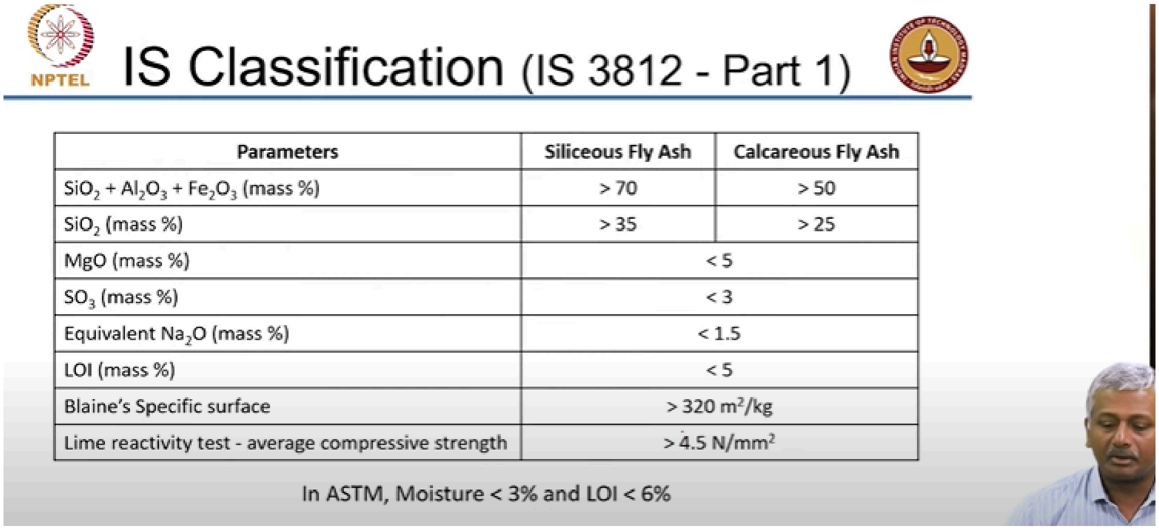

Parameters	Siliceous Fly Ash	Calcareous Fly Ash
$SiO_2 + Al_2O_3 + Fe_2O_3$ (mass %)	> 70	> 50
SiO_2 (mass %)	> 35	> 25
MgO (mass %)	< 5	
SO_3 (mass %)	< 3	
Equivalent Na_2O (mass %)	< 1.5	
LOI (mass %)	< 5	
Blaine's Specific surface	> 320 m^2/kg	
Lime reactivity test - average compressive strength	> 4.5 N/mm^2	

Here the IS classification is given IS 3812 for fly ashes, where the oxide content the silica plus alumina plus iron for fly ashes is defined in terms of percentage by mass, it should be greater than 70 % for siliceous fly ash and greater than 50 % for a calcareous fly ash.

So, if your material satisfies this particular quantity, then its composition can be deemed to be similar to that of a fly ash. Silica itself by mass should be more than 35 % in siliceous fly ash and more than 35 % in calcareous fly ash. So you have to be careful about when you receive the fly ash for evaluation, it has to satisfy these characteristics to be classified as a high calcium or a low calcium fly ash. Of course this is your low calcium fly ash and this is the high calcium fly ash.

Apart from the silica content and the aluminum and iron contents, you also have to worry about the MgO content, it has to be kept to less than 5%, why? You cause unsoundness because of the conversion of magnesium oxide to magnesium hydroxide which leads to expansion upon hydration and that should not be the case when you use this as a cement substitute.

Sulphate is also restricted to less than 3%, sulphate may be present in coal, there may be some sulphur that is present in coal but you have to ensure that your fly ash does not have too much sulphate, why? Because you are altering the sulphate chemistry of the cement while sulphates are essential at the same time excess of sulphates may lead to other problems in your cementitious material like your delayed retinoid formation and things like that.

Alkali content is also restricted to less than 1.5%. Now greater alkali content is permitted here than in cement. In cement composition we briefly talked about this that when you have alkalis more than 0.6%, you may if you have a reactive aggregate lead to alkali silica reaction. Now if you replace cement by fly ash your net alkali content is going up, if you are going to have a high alkali fly ash but whenever we use mineral admixtures fly ash or slag or silica fume higher alkali contents can be permitted because those alkalis are not free to interact with the aggregate lead to ASR. I will come back to that point later when we discuss that performance.

Loss and ignition should be less than 5%. Now why this loss and ignition test has been specified for fly ash? It may be organic matter, carbon bearing matter that is present in the fly ash because it is from coal there will be carbon definitely and if it is present in excess quantities it is going to interfere with your performance primarily with respect to air entrainment it may also affect your effectiveness of the super plasticizer, it may affect the overall strength gain characteristics and so on. So we do not want too much carbon in the system as far as possible carbon has to be removed from your system.

So how do you remove this carbon if it is in excess of 5% what will you do? If there is an excess of 5% carbon present in your fly ash what do you need to do? In the bagasse ash we saw that we could just sieve the carbon out because carbon was present as nice coarse particles and those could be removed but not in fly ash here everything is just a powder.

So you will have to burn it further, you will have to again burn it to remove the carbon but you have to burn it at a controlled temperature so that the silico aluminate that is amorphous in the case of fly ash does not start assuming some crystalline form. So you have to be careful about selecting fly ash carefully. The boiler characteristics have to be adjusted suitably so that not too much of the carbon is unburned. So you have to be extremely careful that is why this LOI has been specified very carefully at 5%. In ASTM they specify LOI as less than 6% so they give a little bit more leeway for the fly ash and moisture content is less than 3%. Where does moisture come from in fly ash? It is a fine material during storage. It may absorb some moisture that should not be more than 3% when you are actually using fly ash.

Blaine specific surface now here this is a little bit of a concern it says greater than $320m^2/kg$ but this is a condition that is not always satisfied by most fly ashes that we use directly in concrete. For cement manufacture the fly ash is brought to this level but not for use in concrete because there is no way to exactly check this very carefully and this is IS3812 part 1 which means intended to be used as a pozzolanic replacement of cement. Part 2 is when fly ash is used directly as a mineral additive there we do not have this kind of restriction for the fineness. In the lime reactivity test the average compressive strength should be more than 4.5 MPa. So any material to be classified as a fly ash should produce that result of 4.5 MPa in the lime reactivity test.

But we saw earlier when we discussed the lime reactivity test that this can be actually a difficult target in certain cases. This could be a difficult target in certain cases because your lime reactivity test does not have the conditions that exist in the cement mixture. You do not have the alkalis that could contribute to the high pH which increases the rate of dissolution of the aluminosilicate. More pH, greater dissolution and greater ability for reaction or combination with the lime. So that is why we talked also about the modified R_3 test where we use a modified system not just lime but we also mix some alkalis sodium, potassium hydroxide and so on and sulphate and carbonate to simulate a realistic cementitious system so that that activation can actually happen in this pozzolanic material.

This is the fly ash that is intended to be used as a pozzolanic replacement of cement in PPC but in regular usage when you collect the fly ash to use in concrete this condition is typically not specified. If you look at IS 3812 part 2 it is not usually specified. So the fineness of fly ash is more or less similar to cement but it could be a little bit here or there depending upon whether you are using it as blended cement or using it as a mineral additive.

So typically when you do processing of the fly ash instead of just directly collecting and using it, if you collect it, process it and use it you would choose to make it finer because then you can control the rate of reaction. You can increase the reactivity by choosing a finer fly ash rather than using the full particle size range of fly ash. You are making sure that you are only using finer fly ash. In such instances use of particle sizes that could lead to such fineness can be helpful if you want a higher reactivity.

Type C v/s Type F:

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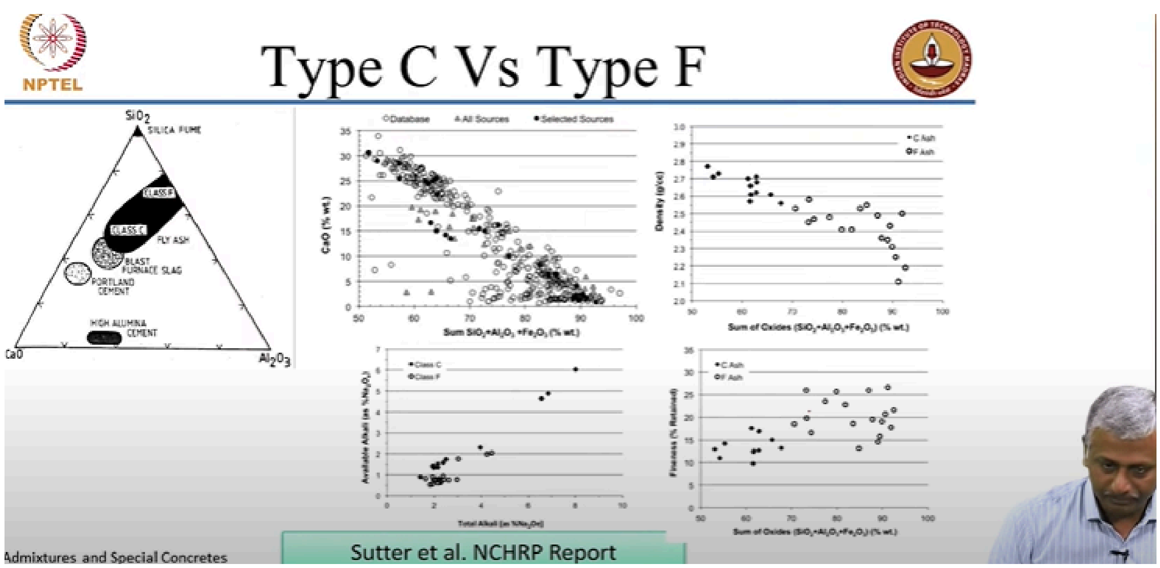

Now in the US they had this highway research program which funded this project at Michigan Tech University where they had looked at a number of different class C and class F fly ashes collected from different parts of the country and also a database that is being generated from other works that they looked at.

So of course coming back to this ternary diagram we know that class C fly ash is more calcium rich, class F fly ash is more of a silica or alumino silicate so it is away from the calcium vertex significantly.

So what they are reporting here is the general composition and it seems to nicely follow a trend. The higher the sum of silica and alumina and iron oxide the lower is the calcium oxide content. It is a very interesting trend that they are reporting here that for most fly ashes they collected the calcium oxide by weight. If it is high then you have the lower content of the sum of silica plus alumina plus iron. Please note that it is always greater than 50 because otherwise it is not classified as a fly ash even for the high calcium fly ash the total oxide composition of silica, alumina and iron has to be at least 50%. 70% is the point for F fly ashes as you can see. Now of course the legend is showing the database and selected sources. Selected sources are the sources that they collected from different parts of the country. This is basically the data that they got from various published articles.

Interestingly they also see that the density of the fly ashes seems to reduce with increased amounts of the silica and alumina and iron content. So this indicates that when you have type C fly ash you may get higher density as opposed to type F fly ashes.

Similarly if you look at alkali contents, the total alkali and available alkali as sodium oxide, what does this mean? Total alkali present in the fly ash but the available alkali which is contributed to the system. Now for this what you need to understand is what is this alkali which is present in the bound form in the cement in the fly ash.

So some of the alkali may be present in a bound form and as you can see there are more alkalis in class C fly ash than in class F fly ash. So when you are using class C fly ashes you also have to be careful about the alkali load that they bring into your system. Now fineness it depends but as I said more or less type C and type F fly ashes are similar fineness but here you see that type F fly ashes that they collected had a slightly higher fineness as compared to type C but not that much. This is opposite, this is percentage retained on the 45µm C. So type C fly ashes have lesser percentage retained indicating that they are finer as compared to type F fly ashes. This is from the data that they collected from various sources in the United States.

Now interestingly the conditions are not that easy to predict. For instance if you go to Ennore thermal power plant north of Chennai they sometimes get fly ashes from multiple sources. They get fly ash from the coal fields in the main Goch Goch Bihar region or they can also get coal from Indonesia depending on what works out best for them economically. Interestingly it turns out the coal that we get from our Bihar, Jharkhand region seems to have the characteristics of a type F fly ash or seems to be the type that produces type F fly ash but when they get the same coal from Indonesia it changes the entire characteristic because it is a high calcium fly ash it also has a different color. So when the source of coal changes in a thermal power plant the fly ash characteristics may change significantly and what happens is when the cement companies go and collect this fly ash to make their PPC they could be getting a type F or a type C. The PPC still has to meet the demand of setting time, strength and so on and so forth. But the issue is the calcium content may not be the same between different batches of fly ash that they collect.

So the cement companies have to ensure that the net composition that they have for their PPC is closely maintained because they may be getting a type C or a type F fly ash or a mixture they are not very sure of. So again that leads to a slightly different kind of a characteristic if you do not exactly know where your coal is coming from because it turns out that shipping coal from Indonesia is cheaper than actually getting coal by road from Bihar or Jharkhand for a place which is on the port like Chennai. So economics obviously drives the kind of material that you collect. Nevertheless we have to ensure that the performance characteristics of cement are met irrespective of whether you have either a type C or a type F system.

Structure of Fly ash:

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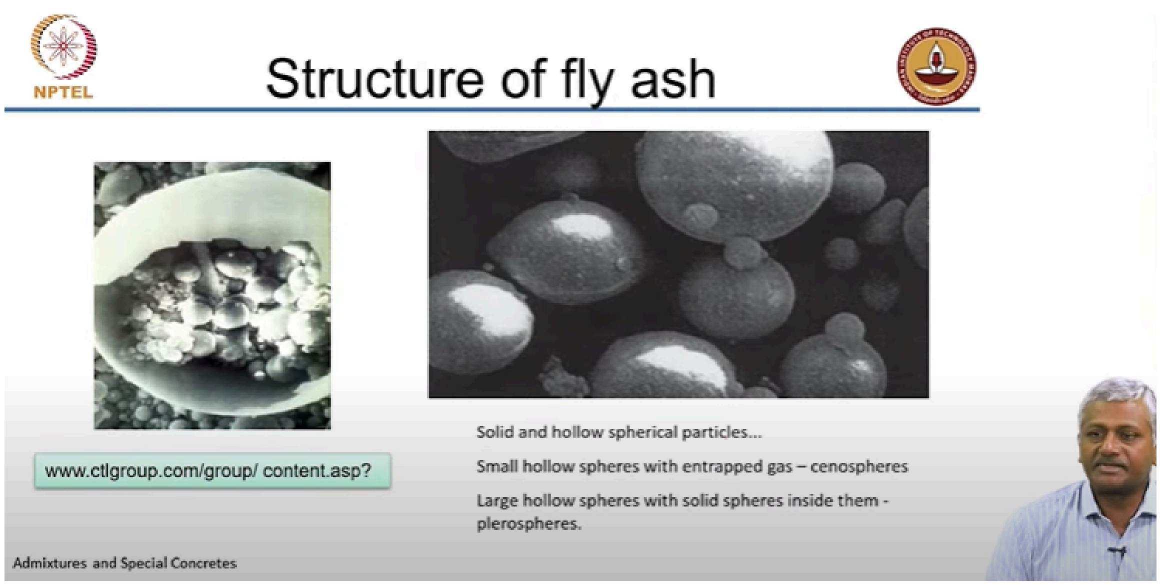

As I said structure of fly ash essentially is composed of spherical particles but sometimes you may also get oblong particles not perfectly spherical but slightly elongated and oblong particles and you may also get a condition like this where you have this glassy spheres which are hollow which consist of these solid spheres inside.

These are all solid spheres. This is a closer image of a solid sphere that is present as a fly ash particle. So the glassy sphere is essentially like a gas bubble because of some condensation it forms a spherical surface but it is basically a gas bubble in which all these solid spheres are actually trapped. So that is essentially why the small hollow spheres are called. Some hollow spheres could also not be solid; they could be having an entrapped gas. Some small hollow spheres those are called cenospheres and if you have a very nice processing system you can actually separate by the difference in masses because these small hollow bubbles will be quite light and you can collect them separately in fact these are also sold cenospheres are sold as material for lightweight concrete. You can use cenospheres for lightweight concrete.

Large hollow spheres with solid spheres inside them like what is being shown in this picture here are called pleurospheres. So when you have an abundance of such pleurospheres in your fly ash you have to imagine that the fly ash has to first the material first has to get this glass broken to release the reactive silica particles that can actually do the reaction with your line. So there could be conditions like this also which may have a combination of particles embedded inside this gas bearing spherical particle.

Now a question may pop up as to what really happens when you make blended cement let us say when you are making Portland pozzolan cement if you are taking these spherical particles of fly ash mixing it with the cement where is the blending actually done where does the blended cement get created? In the ball mill right in the final stage of cement manufacture the cement and any other additives like gypsum or fly ash, whatever it may be, get crushed together in a ball mill or a horizontal roller press or a vertical roller press depending upon the type of cement plant that you're going to. So this crushing what do you think it is likely to do to this fly ash particle? First of all is silica easier to crush as compared to your cementitious particles that is calcium silicate which is harder which is softer the calcium bearing systems will be softer?

So when this grinding is happening in your system it is likely that the cement particles are getting ground the fly ash may or may not get ground but if grinding does happen of the silica and the fly ash what will that do? The shape will not be spherical anymore. So sometimes if there is over grinding in your system you may start getting angularity in fly ash particles also what would that do? It would go against your expectation of improvement in workability. So you have to be careful about the grinding process the other route to producing a blended cement is just blending you can just blend OPC and fly ash but for that you need to have a well-controlled fly ash in a silo that means you are controlling the composition and fineness carefully and then simply blending the material together.

How will they blend powders? How can you blend powders? You obviously cannot blend them in a wet state because cement will start hydrating what do you do? If you have a mixi you can do it but that is only for a small quantity. If you have to produce very bulk quantities like several hundreds of tons you cannot use a mixi so essentially it is similar to using a cyclonic system which can mix the powders well together. So inter blending can also be carried out however for Portland cement mostly it is going to be inter grinding but the fact that there is difference in the hardness of the clinker and fly ash particles and you lead to a preferential grinding of the clinker because fly ash is already available almost at the right size that you want. If you have documented that collection properly and if you are aware of the particle characteristics of the fly ash then the grinding is likely to grind the clinker and not the fly ash as much. So that is how Portland cement is created.

Structure of Fly ash:

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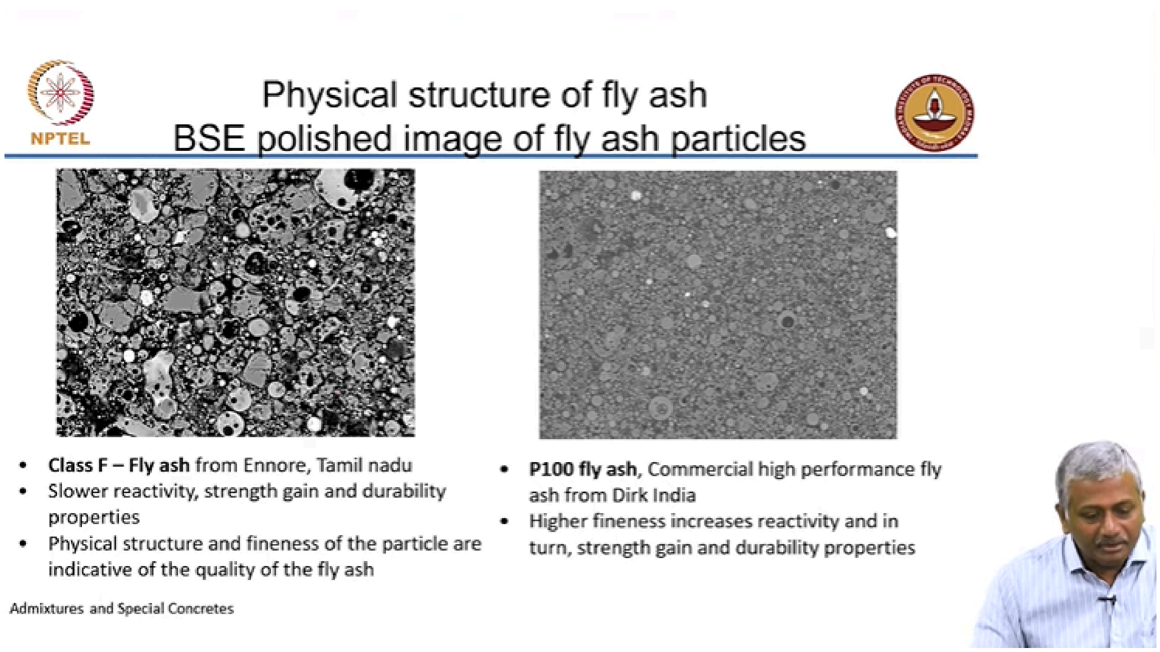

As u can see here if you just take a bunch of fly ash particles and want to image them under the microscope they may have very different characteristics. So here for instance this is class F fly ash collected from Ennore on the left. Both these are viewed under a scanning electron microscope not under an optical microscope but scanning electron microscope. For that the fly ash particles were first embedded in an epoxy then the epoxy was sliced to reveal the surface of the fly ash particles and polished so that you could actually view it under the high reflectivity conditions required by the backscattered scanning electron microscopy. But anyway we are not interested in the technique. The idea is to look at what kind of particles are available in the system of fly ash.

So this is class F fly ash from Ennore that means just collected directly from the thermal power plant. It is generally slower in its reactivity, the strength gain is slow and of course durability assuming you do sufficient curing will be quite good no doubt. You can see very clearly there are several of these hollow looking spheres which have been broken because of the polishing because of slicing and polishing you are exposing the hollow surfaces but then there are also these solid spheres in between.

Interestingly there are also these sand type particles which are seen inside almost looking like sand that is your quartz. Quartz is present here as an impurity or sometimes you may have other crystalline phases like mullite you may have quartz or mullite as typical crystalline impurities present in your quartz in your fly ash. But what we are essentially looking for are these spherical grains of silica that are what we want in abundance. Sometimes you have a collection like this loosely held together and so on. But you see that there is a lot of seemingly junk like substances that you find in your collected material. But when you are processing this is P100 fly ash which is process fly ash they call it a high performance fly ash of course it is from Dirk India now I think it is owned by your ACC Ambuja which of course is now owned by Adani so I am not sure what to call it now I do not know what they if they have changed the name of this product at all earlier it was called Dirk fly ash.

So here you can see that most of your particles are these solid spherical particles which are much smaller all these particles are extremely small they have and you have some coarse particles which are having these empty sort of a more or less like an empty shell some particles are like that but mostly you have the solid small spherical particles. So there is a difference in the performance obviously because of the higher fineness more reactivity comes in and in turn your strength gain is better, durability can be achieved faster and so on.