Admixtures and Special Concretes

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Lecture -33

Mineral Admixtures: Fly ash - Part 1: Introduction

Mixture Proportioning:

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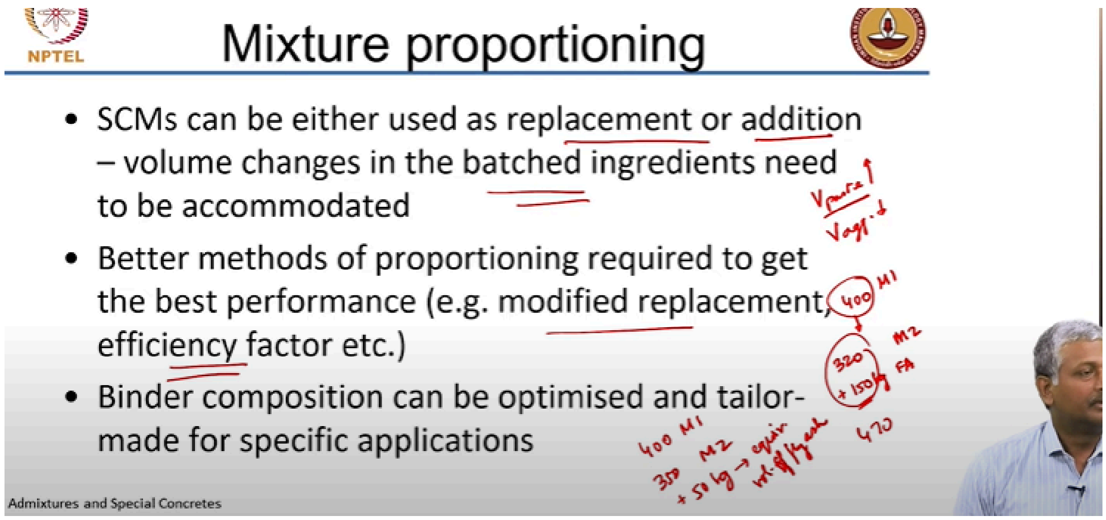

So in the last class we were talking about the different methods to actually assess the reactivity of supplementary cementitious materials and we finally discussed a little bit about what happens when you replace cement partially in concrete with these mineral additives, what kind of compensation we need to make for the change in volume that actually happens in the system and how does that affect the overall performance characteristics. Moving on, there is generally a need for exploring new materials depending upon where you are, which part of the world you are in because many of the materials may not be available worldwide, there are some local sources of materials that are perhaps making more sense in one part of the world as compared to another. For instance, we talked about sugarcane bagasse ash that is obviously going to be available only in those locations where sugarcane production happens in a large way, you cannot expect bagasse ash to be available around the world. So because of this one has to evaluate any such new materials with a systematic kind of a methodology and in this context there are actually standards available, there is an ASTM standard also which tries to understand the characterization scheme to be followed whenever a new material is taken up as a mineral additive.

One of our previous PhD students Dr.Bahurudeen actually had done a significant bit of understanding of what kind of characterization studies need to be done and proposed some sort of a schematic here.

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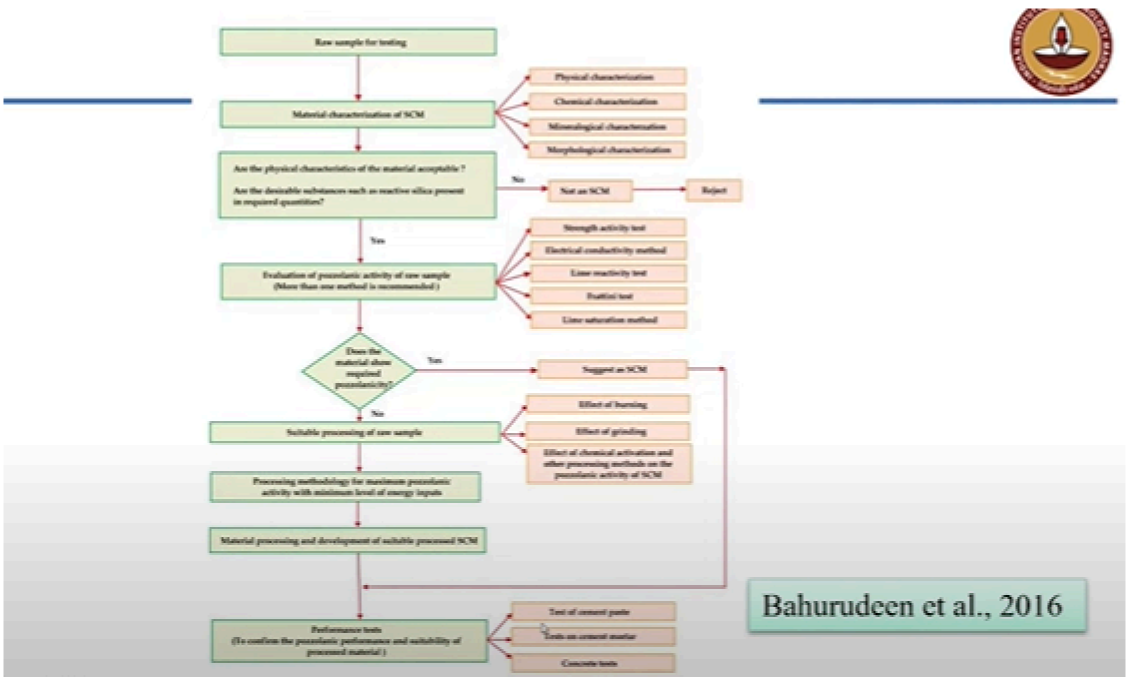

So you can see that this involves a mixture of the characterization of the material as such and then we determine the reactivity. Once the reactivity is determined and there is significant contribution that this material is likely to make then we need to understand what are the processing methodologies that need to be followed to get the material to a level which can perform suitably in concrete if there is a need for processing in the first place at all. For instance, fly ash you can use as collected also but then when it is processed it can actually get you much better characteristics. So, all that you need to work out and then finally it has to be studied with respect to performance tests on cement paste and concrete. This is a paper in the Indian concrete journal ICJ that appeared in 2016. It talks about why relying on a single estimate of the reactivity does not make the material suitable for use all the time. There may be other things that you need to look at. One aspect that specifically one has to address is the tests on cement paste that deal with compatibility of the cementitious system with chemical admixtures. We talked a lot about how the cement composition, the type of chemical admixture, the conditions of mixing, the temperature all of those aspects are actually affecting the way in which the cement interacts with the chemical admixture.

Now imagine that you are replacing part of cement and putting in a slightly different mineral or an amorphous material which may or may not have a well-defined composition. Composition may be variable, different aspects of the composition may be variable and so on and when these materials are used as partial replacement of cement you may actually further affect the compatibility with chemical admixtures. So one has to be very careful and not just assess the strength development with these materials but also look at compatibility issues. I have not specifically devoted much of our later discussions when we talk about chemical admixtures to compatibility problems but some of the aspects are quite clear. For instance when you are replacing cement with a much finer material you can expect that the super plasticizer demand will increase. When you replace cement with something which is nicely shaped like fly ash, when you have spherical particles of fly ash you can expect that the demand for super plasticizer is expected to go down. When you have calcined clay as a supplementary cementing material because of the structure of the calcined clay itself we saw earlier that your PCE molecules get intercalated they go between the layers of the calcined clay and that can lead to incompatibility when calcined clay is used. So you have to probably dose a higher amount of chemical admixture to get the same level of performance. So all of these aspects you need to be aware of because compatibility is complex as it is when you are actually complicating the cementitious material composition even more by adding further ingredients you can imagine that this scenario is going to get further worsened if you do not address it early enough.

How do you address it? By doing an assessment of the compatibility before the project so that during the project you do not have a problem of change in workability and inconsistent performance with respect to workability. You can read this paper on your own and get a much more detailed understanding. More or less it reflects what we have been talking about in this chapter but it is important for you to also read this.

Future without cement?

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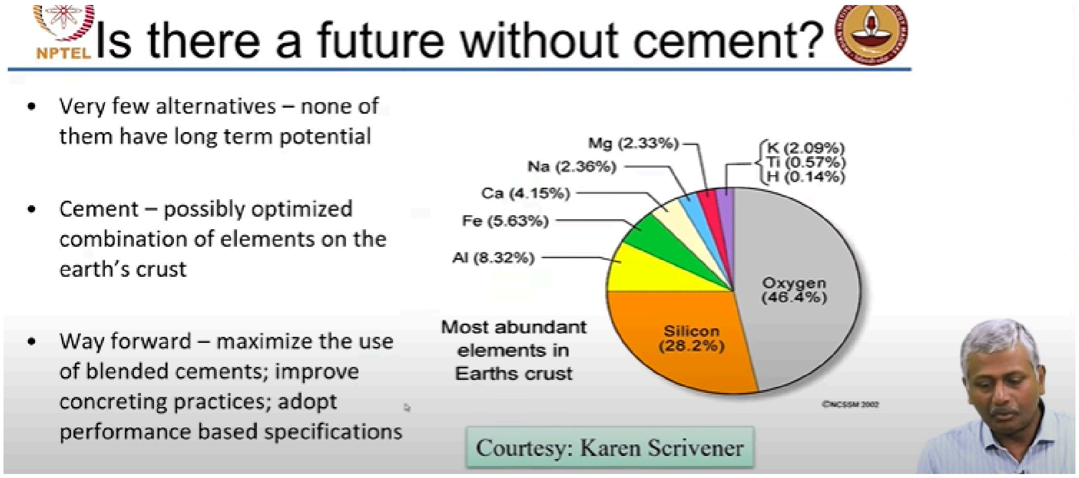

Now very often we come across articles where people are trying to attempt concrete systems without the use of Portland cement. The question to ask is then is there a realistic future where no cement is needed can we work without cement? So for that scientists have looked at the elemental makeup of the earth's crust that is where we are going to be mining for extracting the elements required to make any cementing compound.

So if you look at that you have silica and alumina as the maximum components I mean all these are present in the form of oxides, silicon dioxide, and aluminum oxide. The next is iron, calcium, sodium, magnesium and so on. Now if you really look at it cement is already a very highly optimized mixture of all of these. We up the calcium content in cement so that it becomes hydraulic and it is able to react on its own. If we go with the lesser calcium content we get a pozzolanic material which actually requires an excess of lime in order to get that reactivity. So our cementitious materials are already fairly optimized with respect to what is available in abundant quantities on the earth's crust.

You also have other cements which we had a lot talk about during this course but there are some special cements that are based on magnesium, magnesium phosphate cement, magnesium oxychloride cement and so on. The problem with those is then you really cannot manufacture those at any bulk level like you do for Portland cement. So it is not easily foreseeable that an alternative cementitious material could replace Portland cement for the kind of quantities that we use in.

How much cement do we use every year? About 4 billion tons, more than 4 billion tons. So we are talking about 4 gigatons of cement being used every year and for that kind of quantity you do not really have the raw material necessary to produce alternative cements as much in abundance. So cementitious or the compounds that are going to make cement are available in significant quantities so we can continue to produce cement and cement derivatives but if we really want to make a major impact to the environment then we have to start looking at how best to use blended cements which can reduce the quantity of cement clinker that is processed that contributes a lot to your energy and CO_2 in the concrete system. Improving concrete practices can also help to a large extent. We will see later when we discuss high performance concrete or special concrete that very often concreting practices can make a major difference not just for high performance but also for ordinary concrete. And again if you start looking at specifications that are performance based rather than prescriptive you will again further save the extent of material that you actually use in your system. So these are some strategies by which we can actually make do with the current cementitious materials that does not mean that you should pull the plug on any research that goes on about alternative cements that has to go on. As I said, one solution cannot apply everywhere in the world. There are zones where you can actually get a very good alternative solution working even better than Portland cement. For instance we talk about geopolymers.

What are geopolymers? Geopolymers are essentially the same alumino silicates which are activated using alkaline solutions. Now the same thing happens as a pozzolan also. What happens is that the alumino silicates which are amorphous are dissolving but then there is sufficient calcium available from the cementitious system to combine with the alumino silicates to form calcium aluminosilicate hydrate CASH gel.

Now instead of cement, if you have an alkaline solution which has a lot of sodium or potassium what is going to happen is instead of calcium aluminosilicate hydrate you will form sodium or potassium aluminosilicate hydrate. The activator solutions will basically combine with the dissolved alumino silicates to form that the only difference being that calcium aluminosilicate hydrate is a small polymer short polymer there are not too many monomers in the chain of CSH whereas when we talk about geopolymeric systems like NASH sodium aluminosilicate hydrate that is like a 3 dimensional network that is what forms in a geopolymeric system. So you have to distinguish the way that that reaction happens with respect to the cement hydration. Now the only thing there you need to think about again is how easy it is to work with the alkaline solutions. You get sodium based solutions or potassium based solutions. You know that sodium and potassium are not as abundantly available as calcium.

People say that replacing cement completely by geopolymeric materials leads to a what we call as a green technology or sustainable technology but in truth you have to actually evaluate the sustainability impact not just from the point of view of not using cement but also what really goes into producing those alkaline solutions that are required to react with your alumino silicates to make the polymer network. The energy input for manufacture of these alkaline chemicals could be sufficiently high enough that you may not be able to justify them as a sustainable technology compared to your Portland cement based technology. So all that has to be evaluated very carefully.

So with that we will finish this first segment which had a general treatment of mineral additives. From the next segment on we will go towards understanding individual mineral additives like fly ash, slag, silica fume etc.

Fly Ash:

So I will go on to the chapter on fly ash. So fly ash is perhaps the most common mineral additive that is used around the world and for that we need to get into understanding what kind of sources does fly ash come from and how that does have an effect on its composition and how does the composition actually affect the properties of fly ash in concrete. So as I said we talked primarily about general mineral additives and types of materials and compositions. We looked at how to test the pozzolanic activity and what kind of issues we need to address with mixture proportioning of the concrete.

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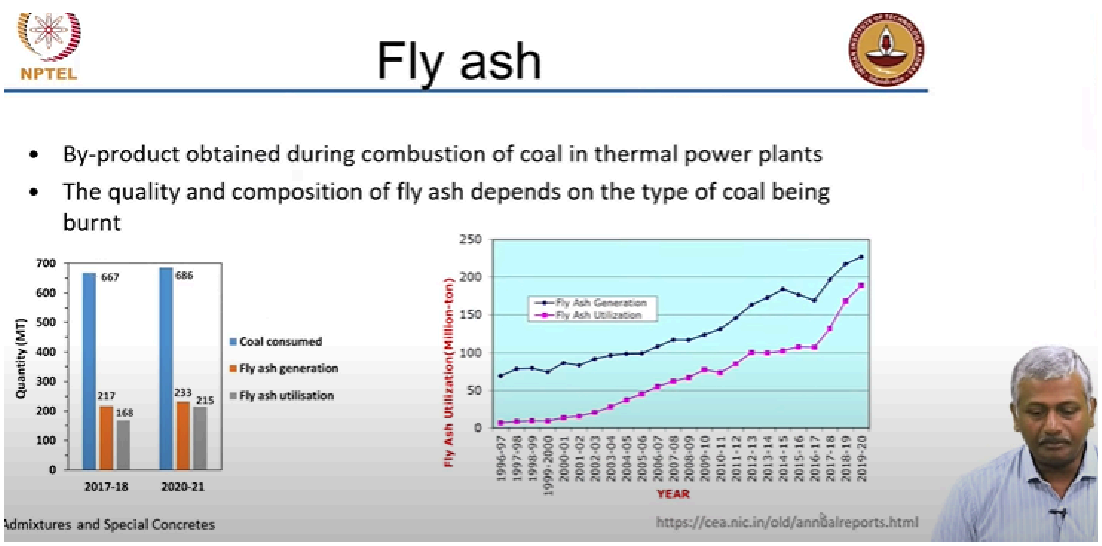

Now fly ash all of you know is obtained from thermal power plants wherever we are burning coal. So coal fired thermal power plants are producing fly ash and quality and composition of the fly ash obviously depend on the type of coal that is being burnt. So if you look at the generation of coal or coal consumption and generation of fly ash in India these are figures only from India. So we are burning or consuming nearly 650 or 700 million tons of coal every year. Coal fired thermal plants are supplying nearly 60% of India's power needs. So we are still relying heavily on thermal power plants unlike several other countries where thermal power plants have been closed down significantly owing to the fact that the release of gases CO_2 and your sulphur and nitrogen oxides into the atmosphere is causing pollution and for them to obtain credits using more greener sort of technologies which do not have so much emissions they have shifted to alternative sources of fuel instead of coal. Of course that is only dependent on what is available in your region if you do not have other sources of fuel you are done for you have to rely on coal.

But increasingly world over people are shifting towards non-conventional sources for instance in India we are moving a lot towards solar and wind. Wind power generation in states which are on the coast has increased tremendously. There is also investment in nuclear plants for generating power. So a lot of alternative sources will come but for us in India to actually completely get rid of thermal power plants will take a significant bit of time. Even as we debate on the demerits of thermal power plants there are still new plants being built across the country because as I said earlier India is going to be hungry for more and more power. Their power demand is only going to go up with the increasing urban population that we have in our country.

Now the fly ash that is getting generated from this coal being burnt is nearly one third of the quantity. 217 million tons in 2017-18 and 233 not that much of an increase but still significant quantities are produced in 2020-21. Interestingly if you look at the data here it seems to indicate that there has been a significant uptick in the utilization of the fly ash. So if you see across the years from 1996-97 to 2019-20 you see that the gap between the generation and utilization is getting reduced.

So currently we are at a state where nearly 80% of the fly ash is getting utilized now this possibly talks only about the fly ash that is collected from the electrostatic precipitators. There is a lot of waste fly ash and bottom ash that is also getting dumped in fly ash ponds. This does not indicate fly ash. This is only the fly ash that is generated of a quality that is suitable to be used and much of this utilization is happening where? Obviously in the cement industry as a substitute for cement because as I already told you the commercial segment in India you only get Portland pozzolan cement and the commercial segment utilizes nearly 70% of the cement demand in our country and you can imagine if 70% of the overall demand of cement in our country is about 300 million tons in a year that is 210 million tons is Portland pozzolan cement.

If you make a cement with 30% fly ash then 210 million tons means 30% is about 65 million tons of fly ash is getting consumed just in the manufacture of cement. Apart from that fly ash is also sold for mineral additives and concrete directly and then fly ash is used a lot for soil stabilization for making embankments and so on. It has got a lot of geotechnical applications also. So there is significant usage of fly ash in our country. We are doing a great job and that is because of government initiatives like the fly ash mission that was set up in the early 2000’s that really identified the niche areas where fly ash could be applied in large quantities and since for the last 20 years we have done really well as you can see clearly from this graph. So 21 data says 92% utilization so that is quite significant.

Types of Coal:

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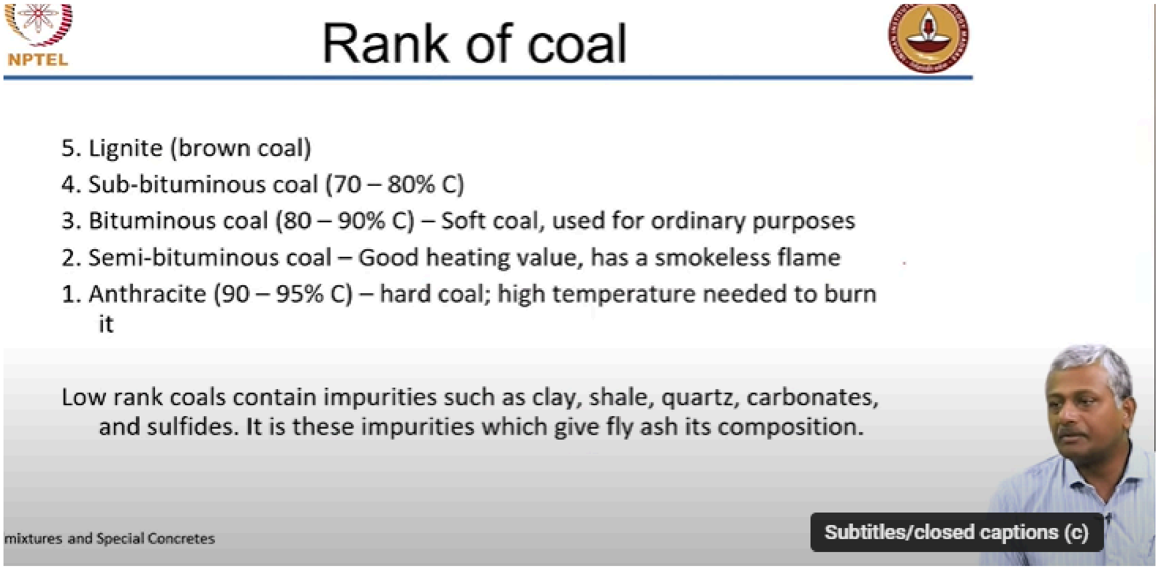

Now fly ash is obtained from coal and coal itself is of different types. You know very well that impure forms of coal like lignite which are also called brown coal are formed in specific geographical areas. In India primarily we obtain lignite in Nevely which is about 200 km from Chennai and we also get lignite or brown coal in Rajasthan. So the type of fly ash that you get from lignite or brown coal has got a significant amount of impurities. There are a lot of impurities in lignite and the fly ash that is getting produced from this is generally high calcium fly ash. That is what is produced from lignite.

When you go to purer forms of coal you go to sub-bituminous and bituminous coals which have lesser content of impurities and your bituminous coal and sub-bituminous coals are the ones which are most often utilized for thermal power plants and that is what gives us our low calcium fly ash. You get high calcium from lignite and low calcium from the purer forms of coal. When you go to the purest form that is anthracite it is very difficult to actually burn it. It is hard coal, it is not that easy to actually burn this kind of coal.

The impurities are present primarily in the form of clay, shale, quartz, calcite, calcium carbonate and sulphides. All of these minerals that are constituting these materials basically give the composition to fly ash. Again in terms of oxides we still have the 4 primary oxides that were present in cement also except that the order is flipped. In fly ashes we have more silica, then we have alumina, iron content and then finally calcium. If it is type C fly ash we have silica, alumina, calcium and then iron. So that is the order in which the composition is flipped. Of course calcium can also be more than alumina in type C fly ashes depending upon the source and depending upon the composition of the coal.

Collection of fly ash:

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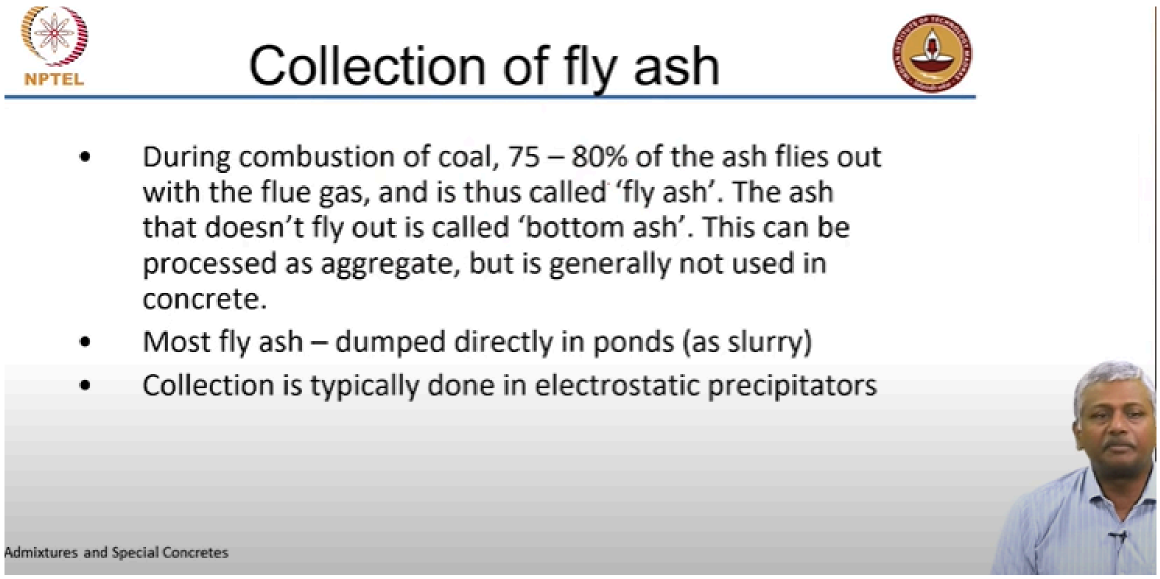

Fly ashes are collected typically with electrostatic precipitators. This is the ash that flies out. So you burn the coal in the boiler, the ash along with the flue gas the smaller particles of ash which are very light fly out and those are collected using electrostatic precipitators.

How does the electrostatic precipitator work? It introduces a charge to the particle and the particle basically gets attracted to the plates of the electrostatic precipitator and then once a charge diminishes the particles just fall and are collected in specific fields. So that is the idea of an electrostatic precipitator: you charge the fly ash particles and then collect them in the opposite poles. Now there is some ash which is coarser in nature and does not fly out. That is why we call it bottom ash which is collected at the bottom of the boiler. Now this ash may not exhibit high reactivity because it is not fine enough but some of this ash may be of sufficiently good hardness to work as aggregate because it is not reactive; it could be processed as an aggregate also. But again we have to be careful that it is not reactive because if it is used as aggregate then it may lead to alkali silica reaction in case there is some reactivity exhibited by the silica in the fly ash.

As I said a lot of the fly ash is getting dumped in ponds as slurry but increasingly we have had a lot of utilization of the fly ash that is collected from the ESP's and thermal power plants. Generally the cement companies have the first access to utilization of the fly ash that is why usually the good quality fly ash is taken by the cement companies. Of course when you are using fly ash in a blended cement you are essentially controlling the quality of the blended cement that you thus get because of which the composition is more or less uniform you do not have too much variability between batches. But when you use fly ash directly in the concrete you are collecting the fly ash directly from thermal power plants you may or may not have processed it further because of which the quality of fly ash can be variable and introduce all kinds of variabilities in your concrete itself. So we have to ensure that fly ash has less variability in order to have a consistent performance in concrete.

Electrostatic Precipitator:

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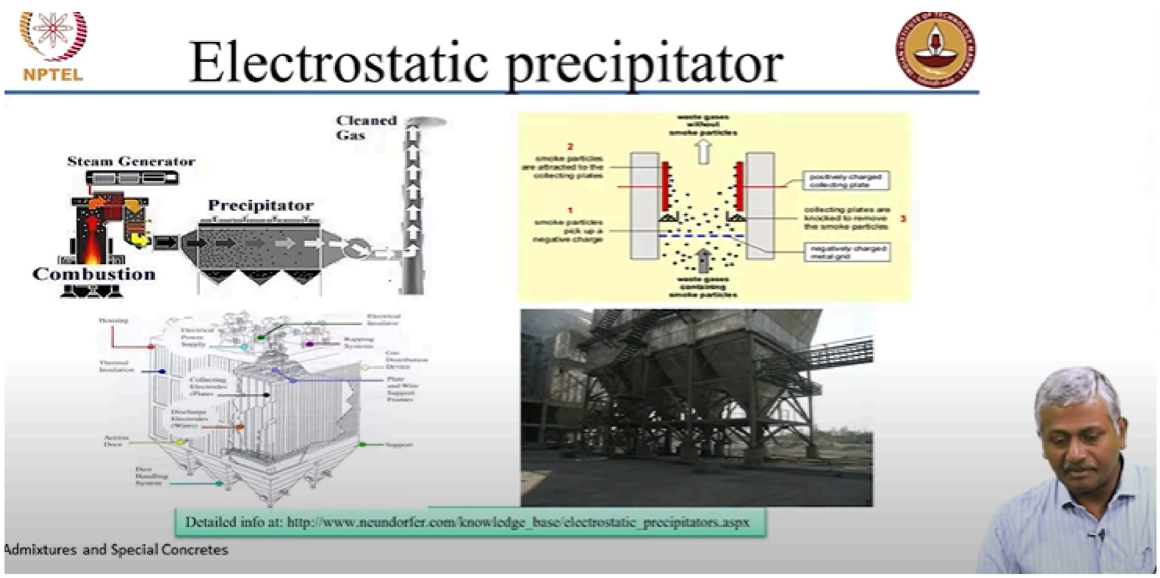

So, you can see here of course the layout of the electrostatic precipitator and this is the actual picture from a thermal power plant where you have the boiler and then you have the set of electrostatic precipitators where the fly ash is collected then at the bottom. Now what happens here is that based on the fineness of the fly ash it can either travel less distance or more distance as it flies out. The coarser particles, the finer particles essentially will get charged very easily. At the same time the coarsest particles do not get charged very easily so they do not get separated at the same instant they get separated at different instances. So these individual stacks into which we collect the fly ashes they are called fields. There are different fields in which you collect the fly ash so the fineness of the fly ash may vary in different fields. So there again you are not guaranteed if you are collecting a fly ash from the thermal power plant directly to make use in concrete you have to be careful about which field you are collecting it from because otherwise you may get significant variation in the particle size or you need to be consistent in the field that you collect from because every time if you collect from a different field you get inconsistencies or if the thermal power plants is going to store this in a silo collecting from all the fields and then transporting it to the silo then you get a mixture of all fields.

Uses of Fly ash:

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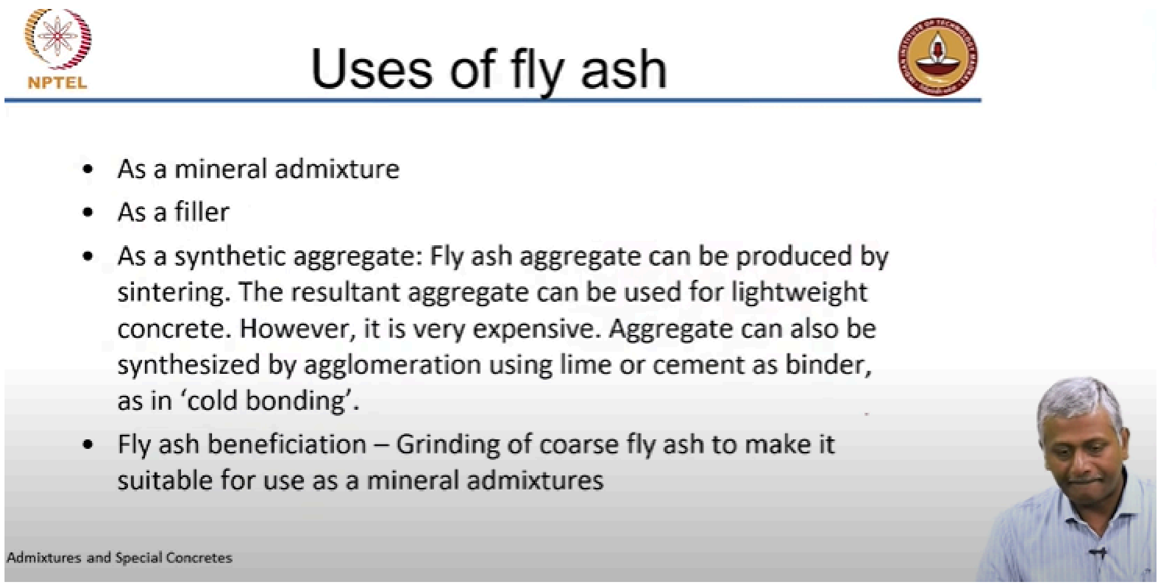

Nevertheless one has to be aware of where this fly ash is getting collected. Now fly ash as I said we use it as a mineral additive, we could also use it as a filler. Fly ash can also be used as synthetic aggregate. There is significant research that shows pelletization of fly ash that means making aggregate size pellets from fusing the fly ash particles together and then sintering at high temperatures or bonding it through means of hydration. For instance in type C fly ash there may be sufficient calcium in the system so that the hydration can actually bond these pellets together. So you can form pelletized fly ash particles which are good as aggregate.

So sintering can be done for type F fly ash typically the fusion is done by sintering just like you do for bricks and type C fly ash we do with cold bonding where we rely on the hydration of the fly ash itself to actually lend to the hardness improvement of the pellet and finally we produce the pelletized aggregate. The bottom ash as I said is not reactive. You can take it and grind it finer and cause it to beneficiate the fly ash that means you are harnessing the reactivity from the fly ash by grinding it fine. Obviously you need to justify the cost and the performance that you are likely to get out of the system.