Admixtures and Special Concretes

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Lecture -28

Mineral Admixtures: Types, Composition and Particle size distribution

Types of mineral admixtures:

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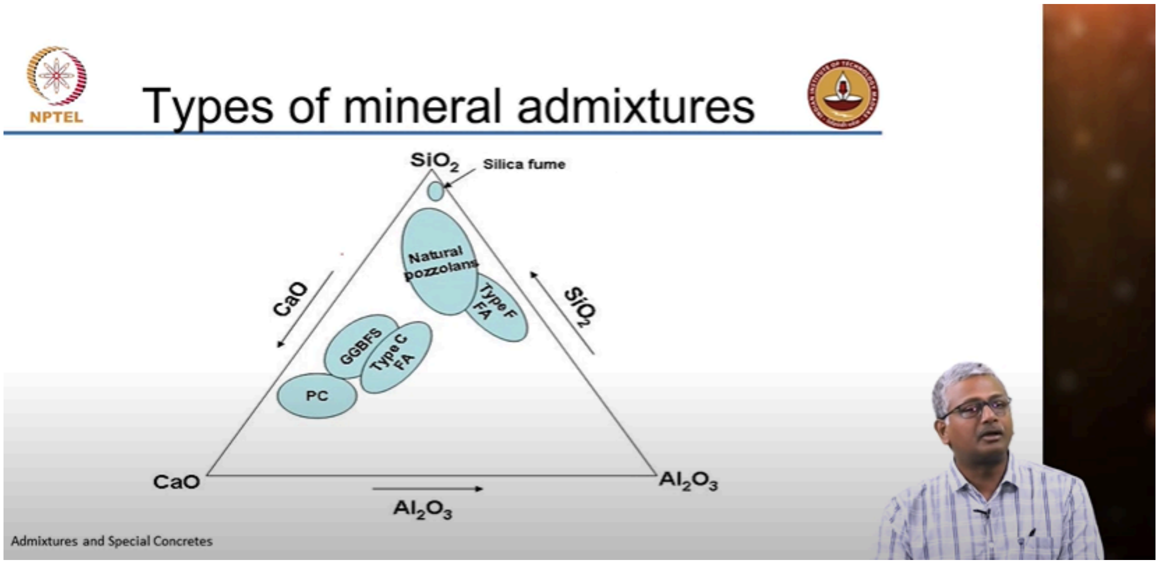

Types of mineral admixtures

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So, if you look at the typical compositions of these metal admixtures, usually cementitious materials the composition is expressed on this ternary diagram between calcium oxide, aluminum oxide and silica. Each vertex is 100% of that material. So this vertex represents 100% calcium oxide. This line represents 0% calcium oxide. This line is basically the line between silica and alumina so CaO is 0. So that means if you go along parallel lines like this the fraction of CaO decreases in the other direction or increases in this direction. So that is called the ternary diagram and usually this ternary diagram representation is used for many of the cementitious materials.

So if you look at typical Portland cement we are obviously in a lime rich condition so generally it has got more than 65% calcium oxide. It has a significant amount of silica but not as much of alumina. Typical Portland cement will be having around 65% CaO about 20% silica and only about 6 to 8% alumina.

Compared to Portland cement let us look at where the others are placed. Your ground related blast furnace slag or slag as we know it is placed in a region which is almost in the midpoint between calcium and silicon. That means it has got almost an equal amount of calcium oxide and silicon dioxide and a little bit more of alumina as compared to Portland cement.

Type C fly ash again calcium, silica. Silica may be generally more than calcium but it could probably be somewhere better in this region because the amount of calcium is less. Class C fly ash where calcium content is generally around 10 to 20% or sometimes more but not all the time. And then you have type F fly ash which is almost a pure aluminosilicate. There is no calcium in it, there is alumina and silica and not much calcium. Natural pozzolans are also mostly alumina silicates. They may or may not have any calcium but more likely they are purer forms of silica than alumina silicate.

Silica fume is almost a completely pure form of silica. You do not really have any alumina in silica fume or any calcium. It is almost 100% silica. What about metakaolin or kaolinite clay where would that be in terms of composition? Again not much or nothing of calcium so it should be somewhere here. Clay should be somewhere here.

What about limestone? Limestone will be almost all the way here unless it is called impurities. Pure limestone is all the way there. Pure limestone is all the way at the calcium oxide vertex but if it is called impurities in the form of clay or in the form of silica or quartz then obviously the position will shift.

So this is an easy way to represent the composition and this can help you track what can be the potential compound formations when it comes to all of these different materials. For instance when it is natural pozzolans or silica fumes what do you think will be the potential hydrated compound? Now alumina is almost 0 so you will get CSH.

On the other hand with clay type F fly ash you may get CASH calcium alumina silicate hydrate. Type C fly ash also may get that plus your regular CSH also may form because of the high calcium nature. Slag typically will be quite similar to your cement in terms of its hydration so you still form CSH in that case.

What about limestone? Limestone may not produce anything unless of course there is alumina available which is available with cement. So limestone plus your calcium aluminate. What is calcium aluminate in cement? What types of calcium aluminate are present? Tricalcium aluminate and tetra calcium aluminoferrite of course the ferrite phase does not react much at all so tricalcium aluminate in the presence of calcium hydroxide will give what is called mono carbo aluminate. That is only if the limestone is reactive and that is something we will talk about later when limestone reacts it can also exhibit certain characteristics that are useful with respect to filling up of cementitious microstructure. The ternary diagram essentially helps us understand where different phases may be or different types of chemical compositions may be present.

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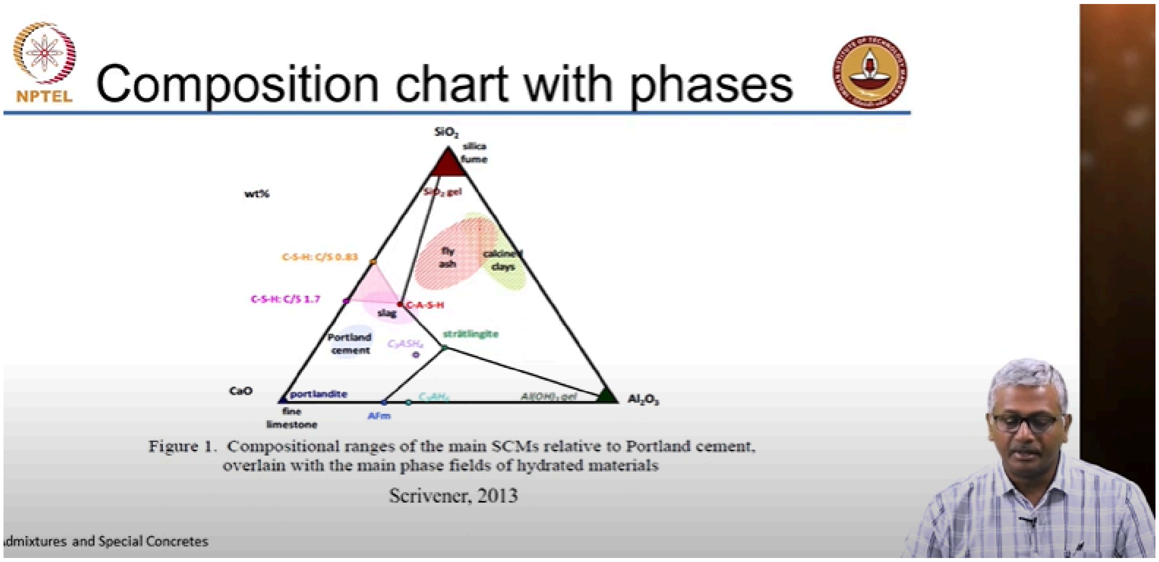

Composition chart with phases

Figure 1. Compositional ranges of the main SCMs relative to Portland cement, overlain with the main phase fields of hydrated materials

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As I said again the type of hydration products will also help or will also be dictated by the original composition of your cementitious systems. So what will happen with Portland cement is you will produce a CSH with a higher calcium silica ratio. With slag you may have a range of calcium silica ratios that can form and because of the alumina content you may also form the CASH calcium aluminosilicate hydrate phases.

Strathlingite is one such phase which is a pure crystalline phase which forms when calcium aluminosilicate hydrate of a certain perfect stoichiometry forms. Now whenever we represent something like CSH or CASH that means it is not a perfect crystal it is like a gel. But when we give a name like strathlingite, ettringite, portlandite these are all your perfect crystalline compounds.

What is portlandite? Calcium hydroxide. The crystal form of calcium hydroxide is also called portlandite. Now of course the pure alumina part is called aluminum hydroxide gel and that aluminum hydroxide may form in some instances when you have a very highly alumina rich system. So these are the different compounds that may form. So for instance this calcium aluminate hydrate or C_3AH_6 is usually one of the phases that forms when cement hydrates in the absence of gypsum. If gypsum is not there this compound actually ends up forming in your system. So again the way that your distribution of hydrated phases happens is in consonance with the initial chemical composition of your system and that is only obvious.

Typical compositions:

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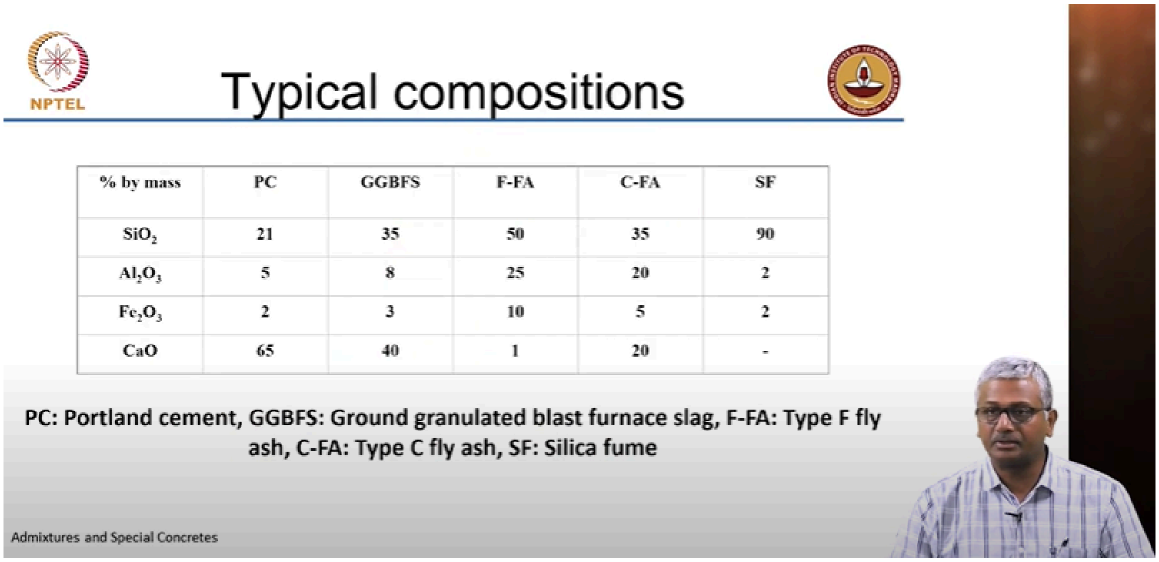

Typical compositions

% by mass	PC	GGBFS	F-FA	C-FA	SF
SiO_2	21	35	50	35	90
Al_2O_3	5	8	25	20	2
Fe_2O_3	2	3	10	5	2
CaO	65	40	1	20	-

PC: Portland cement, GGBFS: Ground granulated blast furnace slag, F-FA: Type F fly ash, C-FA: Type C fly ash, SF: Silica fume

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Again just the same typical compositions are presented in terms of actual numbers. So as I said in slag your silica and calcium oxide content are nearly equal. Your alumina content is generally more than cement. But generally your fly ash will have an even greater alumina content. 25 is probably very high, close to 15 would be the right level.

Calcium content in type F fly ash which is also called low calcium fly ash that is usually 0 or less than 5% typically. Type C fly ash will have a calcium content of at least 20 % or 10 to 20% or more.

Silica fumes as I said pure silica 90% or more, higher purity silica are also available but mostly it will be around 90% purity.

What about calcium clay? If I put on the same table CO will be close to 0 let us say 1 or 2%. Iron may be significant, maybe up to 5 to 10 % possible.

I am not saying it is always going to be there. But between silica and alumina generally there will be for kaolinite clay, kaolinite clay there will be almost two times the silica as there is alumina for kaolinite clay. So let us say out of the remaining 55 % will be silica and about 25 % may be alumina, something like that. Let us say 50 to 55%. So it is a silico aluminate or aluminosilicate depending on which way you call it. Mostly we call it aluminosilicate.

Particle Size Distribution:

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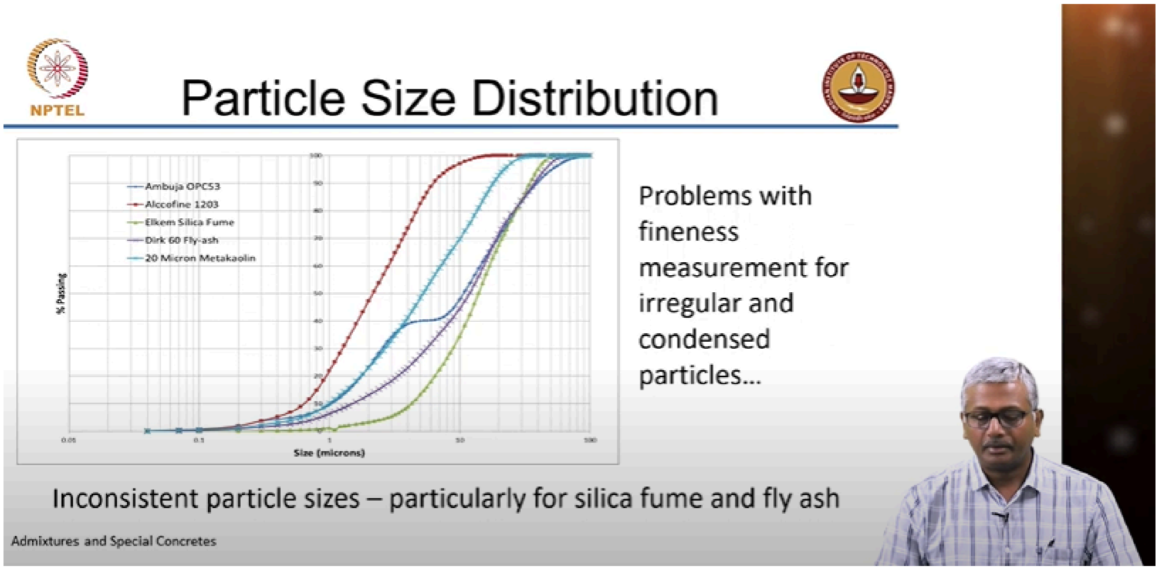

Particle Size Distribution

Problems with fineness measurement for irregular and condensed particles...

Inconsistent particle sizes – particularly for silica fume and fly ash

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Now one of the important things that you need to characterize whenever you get a mineral additive is the particle size distribution and it is very important to see how these compounds are distributed with respect to the particle sizes of your principal binding material that is cement. So this is only one of the examples. It is not the only particle size that is possible but just one of the examples from one of the research projects that we have done.

So you see here the cement is somewhere here. The blue line is that of cement. So OPC 53 is represented there in terms of the particle size distribution. Compared to OPC this is a processed fly ash. DERC 60 fly ash is a processed fly ash. I will talk about this later when we discuss fly ash in general. Processed fly ash, so it is actually something which is made as a specific product and sold in the market. It is not the fly ash that is directly collected from the thermal plant but it is processed. And then we have this blue line which is your metakaolin calcined clay.

As you can see it is much finer than cement and here this is ultrafine slag. So slag that has been ground to much finer sizes and that is again much finer even compared to the metakaolin. It is also important to specify the method by which the measurement is done. Now when very fine powders are there you can measure the fineness in several ways.

In cement what do we do? We can do a sieving test. Sieving through 90µm or a 45µm sieve but that does not give us the particle size distribution. It only tells us a bulk fineness or sometimes we do the Blain's air permeability test. That again gives us a value of the fineness in square meters per kilogram. It still does not give us a particle size distribution.

To get the particle size distribution you have to adopt various strategies. For soils we use something like a sedimentation test. Many of the initial tests that we use for cementitious materials also were like sedimentation tests.

So you prepare a suspension and then observe the sedimentation by passing light through the suspension. When the system is having all the particles suspended then light will not be able to pass but slowly with time as more and more particles settle your light passage will change. So the turbidity test, we used to call it Wagner turbidity meter test but the problem with that is again the accuracy is quite limited. So because of that we have to shift to more accurate techniques.

The one which is used for this diagram is the laser particle size distribution. As the name implies we use a laser so we put a stream of particles at high velocity travelling through air and there is a laser that strikes on to this stream. So this laser depending upon the size of the particle will produce different diffraction patterns. If the particle is too large the laser will simply strike and then reflect back but if the particles are small, smaller and smaller it will produce more and more diffraction patterns. So analyzing the diffraction pattern you can then look at what is the range of particle sizes that the system will exhibit and this is obviously not done manually. It is all done with the help of the instrument and the software that controls this hardly takes about 5 minutes to get the entire particle size analysis done using a laser. So laser particle size analysis is quite useful. Only problem is you need to suspend your material uniformly. If your material has a tendency to form flocs, if it sticks together then you will have a problem in getting the actual particle distribution. So when you deal with finer materials like Metakaolin that may actually end up happening that you are forming very thick flocs or groups of these particles together.

With silica fumes you see this green curve. We expect silica fume to be much finer but here it is coming out to be coarser than even the fly ash. There is a reason why that happens. Silica fume is not sold in terms of a fine powder, silica fume is sold as condensed silica. We usually sell them as condensed particles. So particles of silica fumes are usually condensed together by application of pressure and this condensed silica fume essentially has a size which is comparable or even larger than fly ash particles.

Now what does this mean? When you put this in concrete how will you get the individual silica particles out? You have to mix thoroughly, the aggregates will tend to break these conglomerates of silica particles. Further you need to have a super plasticizer. Without a super plasticizer your silica fume will not be effectively dispersed. Again it will form a floc. So prolonged mixing, we have talked about mixing effects before, prolonged mixing and addition of a super plasticizer is absolutely essential when silica fumes are used.

So in this case you are seeing a much coarser particle size only because it is directly tested as a condensed material. That is the most difficult part about doing laser diffraction on condensed silica fumes. There is no way to accurately disperse or get the individual fine particles of silica out for a test of this nature. We have tried all kinds of things but it simply does not work. We tried to mix it with sand and sieve out the sand. It produced a lot of difficulties to actually extract the small silica grains out without the action of the mixing that is given by the aggregates. So this and several other difficulties with measurements is something that we will discuss in the subsequent lectures.