

Advanced Concrete Technology
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Lecture - 18
Mineral Admixtures – Part 1

Good morning every one, we will get started with topic on mineral admixtures in today's class. Some of you may be hearing the term supplementary cementing materials also instead of mineral admixtures so depends on where you are in the world you can probably hear the term mineral admixture or supplementary cementing material, and these are in sections 8.5 and 8.6 in the textbook.

Now what I want to do in this chapter is take a look at the different categories of mineral additives which are added to the concrete which provide unique characteristics to the concrete and at the same time try to reduce the extent of cement clinker usage to produce the concrete. So we have been talking about clinker usage being a major problem as far as the energy emissions and carbon dioxide emissions are concerned.

So there is a worldwide push obviously to recognize those materials which can be used as additives that can reduce the extent of cement consumption inside concrete. Of course we are not making concrete a non-Portland concrete we still rely on the Portland cement as a main binding material but we are simply augmenting the amount of cement in the concrete with the help of supplementary cementing materials.

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Background – cement hydration

With hydration:
Reduction in voids
Reduction in pore connectivity
Increase in gel space ratio
Increase in bound water

Issues:
Ca(OH)₂ easily chemically attacked
Inefficient filling of void spaces – interconnectivity of pores, especially in the transition zone (between paste and aggregate)

Solution:
Convert Ca(OH)₂ to C-S-H
Optimize grain sizes with the use of fine mineral additives
Mineral Admixtures.....

In concrete
Aggregate Transition Zone Bulk Cement Paste
Mehta and Monteiro, 1993

So again just to briefly rekindle the background on cement hydration. We talked about the fact that with progressive hydration the space in between the cement particles starts getting filled up with the hydration products like your calcium silicate hydrate, calcium hydroxide, AF_T and AF_M phases and you ultimately result in a situation which develops the microstructure of the concrete.

The cement paste microstructure itself develops with different types of CSH products. We have the inner CSH and the outer CSH and there is greater porosity in the outer CSH, but with more and more hydration much of this porosity keeps getting filled up and you ultimately lead to a reduction in the inter connectivity of the pores also. So in the long term you get a durable system because your pores are highly discrete and not interconnected.

And that depends on the extent of hydration that is happening in the system. So some of the issues which we see in typical cement chemistry or concrete with cement is that you are forming phases like calcium hydroxide which although nicely crystalline occupying some volume in the cement paste microstructure and contributing to the strength they are phases that can easily get attacked by chemicals.

For examples your chlorides and sulphates and so on will tend to first attack the calcium hydroxide, and there is also an inefficient filling of void spaces especially when you look at the scenario in concrete where you have aggregates apart from the paste and because of influence of mixing, because of the influence of the kind of products that can actually form spaces around the aggregate you ultimately end up with the zone around the aggregate.

Which we otherwise term as interfacial transition zone, which has very different characteristics as compared to the bulk paste which is away from the interfacial transition zone.


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Impact of Mineral admixtures

6-7% of total greenhouse gas emissions come from cement production

Use of waste or by-products
Reduced cement clinker usage

Improved long term durability
Reduced potential for cracking



Also called 'Supplementary Cementing Materials' (SCM)


Amorphous silica + Ca(OH)₂ (from cement hydration) → Additional C-S-H

Sometimes, high CaO → cementitious and pozzolanic

Additional mechanism of action – as filler

Corrosion repairs cost nearly 5% of developed nation's GDP

Increased benefit to cost ratio
Longer service life



So this leads us to a system that is probably reflecting the fact that the pore spaces are not getting appropriately filled. So if you have fine filler materials or fine supplementary cementing materials you can now start occupying the space which is around the aggregate trying to fill up the interfacial transition zone and densifying the ITZ. So when you densify the ITZ you are going to make concrete more and more homogenous.

And probably that may lead to an increase in your strength and durability characteristics. So there is inefficient filling of void spaces which causes interconnectivity of the pores and this is primarily stark as far as the transition zone is concerned. So the solution is you can try and convert your calcium hydroxide to useful calcium silicate which we know is semi-crystalline material.

It occupies a very large volume because it has good space filling ability, thanks to its large surface area as opposed to calcium hydroxide. So you start filling up more space and that reduces the extent of porosity that you have in the system. Further it blocks off the pores and reduces interconnectivity of the pore space also.

And the other aspect is when you have fine minerals which you can add in the system they can start blocking the pores especially in the ITZ and lead to a much more densified ITZ. So the solution which looks at both these issues being tackled at once is the use of mineral admixtures

or supplementary cementing materials. We already talked about mineral admixtures to some extent when we talked about special cements.

We talked about blended cements where we had Portland pozzolan cement, Portland slag cement, where slag and fly ash are essentially used as the blending materials which have a pozzolanic reaction. They react with the calcium hydroxide in the system to convert that to CSH and because of the fine particle sizes they tend to optimize the particle size distribution of the cementitious materials that leads to a more efficient filling up of the pore space.

So now everybody talks about sustainability, but what you have to understand is when sustainability is looked at for a particular process or a particular material it has to satisfy 3 aspects, the social aspect, the environmental aspect and the economic aspect. In other words, we call this as a triple bottom line. Again you can do a search on Wikipedia, you will get several different hints that tell you about what this triple bottom line actually means.

So let us look at it from that perspective and see whether the use of mineral admixtures make sense or not. So from the environmental perspective most mineral admixtures or supplementary materials are byproducts or even waste products from other processes. So instead of dumping them we are trying to utilize them. So that is obviously an important environmental constraint that we are satisfying.

The other aspect is we are reducing cement clinker usage and because you know that 6-7% of total CO₂ emissions are because of cement clinker usage and that is a big service in that direction. Now social perspective is a little bit difficult to understand, but if you look at it from the point of view of the fact that you are producing more durable concretes, you are producing concretes that are going to be crack free for most of their service lives right that is a positive social impact that you can consider for the mineral admixtures.

So improve long term durability and reduced potential for cracking. Of course I am telling you all this even before we actually got into the mechanisms by which the durability parameters are improved when fly ash or slag are used as mineral admixtures, but we will talk about that in due course. Then finally as far as economic aspects are concerned how does the use of mineral additives save money?

First of all, of course reducing cement usage means you are obviously saving some money to make the concrete, but apart from that primarily you get improved benefit to cost ratio because you are reducing the cost of the initial concrete but you are prolonging the life of your concrete structure. So you get better benefit to cost ratio and you also get longer service life as a result of using mineral additives if you use them in the correct fashion.

So much of what we discussed about the sustainability impact can only be realised if you are using mineral admixtures in the correct fashion and what is that correct fashion we will see it as we progress along with the study of different types of mineral admixtures. So again I am just repeating myself with these mineral admixtures also called supplementary cementing materials.

And supplementary materials are the ones which usually give you amorphous silica which reacts with calcium hydroxide from cement hydration and leads to the formation of additional CSH. In some cases, the mineral additives may also have lime content, which makes them cementitious along with pozzolanic. So if you have reactive silica as well as lime present in your system you might have some cementitious and pozzolanic characteristics.

And of course additionally many of these can also function as filler. Just to take a look at it from different perspective let us see I design a concrete with only cement. Let us say I have a concrete mixture of M40, I use about 400 kilograms of cement, 400 kg/cubic meter cement and maybe I use a water cement ratio of 0.42 or something like that.

Okay now you know that theoretically with 0.42 water cement ratio you can actually end up hydrating each and every grain of cement. We discussed this earlier when we calculated the hydrated cement paste structure that with 0.42 water cement ratio you will have enough bound water to react with all the cement and enough water to actually fill in all the porosity that is present between the gel.

However practically with 0.42 water cement ratio it may not be possible for you to actually react all your cement why is that practically what is the difficulty there, yeah, you will lose some water from the mix anyway because of drying out of the water, what else, some aggregate may actually absorb the water. So effectively you have less water cement ratio present in your system what else will happen.

Again please remember hydrated cement paste, once the structure starts forming the water has to diffuse through the hydrated barrier to reach the unhydrated cement products. So when that happens there is only a limit up to which this can happen. You cannot continue to have continuous diffusion of the water.

At some stage this process is likely to stop. In other words, what I am trying to say is out of the 400 kilograms of cement that you have added to this mix your hydration may actually end up completely stopping by the time 250 to 300 kilograms has hydrated, that means the remainder of the cement will likely remain unhydrated for the entire service life.

If your structure is standing for 50-60 years, at the end of 60 years if you take a sample of concrete from inside the structure and try to look at the microscopic image, you will still see white unhydrated cement particles in the system and that is because it is not physically possible to hydrate everything unless the particles are really small. We know that cement has a range of particle sizes starting from 150 microns to about 1 micron.

If you are close to 1 micron obviously it is more than likely that all your cement particles will get hydrated, but the larger the particle size, the lesser the potential for complete hydration. So in other words much of the cement is just sitting there as a filler. In this case, probably close to 100 kilograms of cement that you add in this system is simply sitting as a filler.

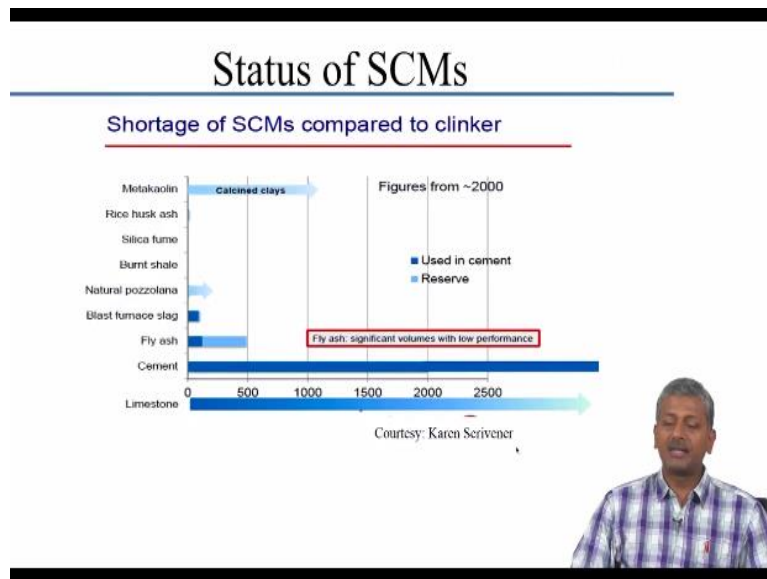
So there if you start supplementing that cement by replacing it partly and putting in a material that actually functions more as a filler it makes sense environmentally as well as economical. So you can save cement in large fashion by reducing the impact, the amount of cement that is present in the concrete for obtaining a particular characteristic. So again we are certain that we do not need all of the cement to hydrate.

Some cement functions as filler, so why not replace that cement with a supplementary mineral additive. From that perspective it should be okay even if I replace the cement with a nonreactive mineral additive, is that correct. To some extent I can probably get the same performance if I replace cement with a nonreactive mineral additive like for example I can replace it with quartz powder.

I have put in quartz powder at the same size of cement or even finer, I will probably get good particle size distribution of the entire system better filling up of the porosity, but I may not get any reactivity from quartz powder. What we will see later is that when there is reactivity in addition to the filler effect you produce a much better microstructure of the concrete.

If you only rely on filler effect from the inert materials that are added, you may not get the correct level of strength and durability that you can get with reactive mineral additives.

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Having said that we also have to look at what is the status of materials that are available as potential supplementary cementing materials. So we know very well that cement obviously is derived from limestone so as long as limestone is available large quantity of cement continue to be available.

What is the current production of cement, current production capacity of the cement around the world, what is the extent of cement that can be produced? About 4000 million tonnes, 4000 million tons of cement can be produced today with the capacity of all the plants put together, out of which nearly 1300 million tons are produced in China. India produces about 300 million tons of cement, that is the second largest producer.

Now compared to the quantity of cement that is produced, the quantity of the mineral admixtures that are likely to make an impact need to be compared. So for example if you look at fly ash, worldwide fly ash availability, this was figures from 2000 probably now it is a little

bit different because in some sections of the world thermal power plants have been shut down. In some places like in India we continue to rely on thermal power.

And probably the likely usage of thermal power is going to stay for a long time. However sooner or later we will also start realizing the kind of pollution that is getting caused by these plants and rely more on alternative technologies, but for now fly ash is definitely here to stay for at least the next 20-30 years without any question. So fly ashes, they are available up to about 500 million tons.

Now the issue is that much of the fly ash that is available is unusable and you only have a small part of that which is usable. Okay in India, for example, it is about 200 million tons of fly ash that is available in India, but maybe only about 100 million tons is actually utilized for cement production. For construction material usage for example.

Slag on the other hand, the availability itself is limited because again slag depends on the iron and steel manufacturing industry, you cannot obviously have more than a certain limit to that because again you need to mine natural resources, the iron ore and process that to make the iron as a result the kind of slag or quantity of slag that you can get is going to be limited as opposed to fly ash.

Natural pozzolana you see that there is only an arrow there that indicates that we are not sure how much is actually available. Because natural pozzolana is the material that comes out as volcanic ash from volcanic explosions or volcanic eruptions. The ash that comes out cools very suddenly and develops an amorphous structure which makes natural pozzolanas from volcanic ash also useful substitute for cement.

The only problem is the geological events associated with volcanoes are spread over millions of years. So very often the ash deposition due to a volcanic eruption can get laid on by other materials like clay or other overburden which often completely eliminates them from the earth's crust. So you may have to actually go deep down to extract your pozzolanic volcanic ash that was deposited because of volcanic eruption.

Just recently, there was a research project in Anna University where they were trying to investigate the deposits of volcanic ash that were produced by volcanic eruption in Indonesia

75,000 years ago. Okay this was volcanic eruption in Indonesia and the ash you know very well because of the prevailing winds and the currents they get carried in the atmosphere. I do not know how many of you were aware a few years ago or even last year we had a major flight disruption over Europe because of some active volcanos in the Iceland area.

Okay the volcanic eruption basically fuses out the ash. The ash that is very light forms a cloud and because of that the airplane visibility is reduced. So for a long time they had to cancel lot of flights because of the ash. So this ash slowly but surely will go and settle somewhere and get collected. So this Indonesian volcano that erupted 75,000 years ago spewed out lot of ash.

And some of this ash moved towards India and some of it settled in several locations in India. So there are geological events that are probably well recorded. Okay so what this team from Anna University did? The geology team, they went and investigated where this ash deposit was. They found a place in Andhra Pradesh where they could actually get this ash deposit, but it was under about 4-5 meters of over burden.

So they had to reach that level and extract that ash. We estimated the pozzolanic characteristics of this ash and found it to be quite useful, but the problem is how much of such ash is available around the world? we do not know. So until we actually have a proper record of all geological events like volcanoes we will not be able to actually track the extent of material that is actually available.

So that is why this arrow does not show a typical end right, there is no end to that arrow because we do not know exactly how much quantity is available. Burnt shale, silica fume they do not even show up in this map because the quantities are so small that they are insignificant as oppose to the extent of limestone or clinker that is available in this.

Rice husk ash, very limited, probably because the kind of rice husk ash that we need for pozzolanic replacement of cement is the high quality rise husk ash, which requires very controlled type of burning. You know that India produces lot of rice. We produce lot of rice and there is lot of rice husk production. Rice husk has a good calorific value, they burn it, they use it as a fuel, and this burning finally leaves behind the ash, which is very rich in silica.

The problem is if you do not do this burning in a controlled environment you may end up getting a very weak pozzolan. You do not get a material that is reactive. In much of the cases in India the farmers who collect the rice husk have very random sort of a burning environment. They do not really control that burning well enough. So you cannot produce good quality rice husk in large quantity that is why the quantity is still limited here.

One thing that is available in large quantity is calcined clay, of course not calcined clay, I should say clay that is available in a large quantity. You have to burn it to make it calcined clay, and that is a good mineral additive like metakaolin for example. Kaolin burnt at some temperature that makes it more reactive. Just like what happens inside the cement kiln, the clay that is added in the cement kiln, at about 700 degree Celsius it gets activated.

And becomes available to react with the calcium oxide that are generated from decarbonation of limestone. So similarly these clays which are calcined or burnt at specific temperatures can actually show some reactivity as a pozzolan and again in the case of calcined clays also there is no end to this because there are several deposits of clay all around the world. Clays you know are formed by natural weathering of existing rocks.

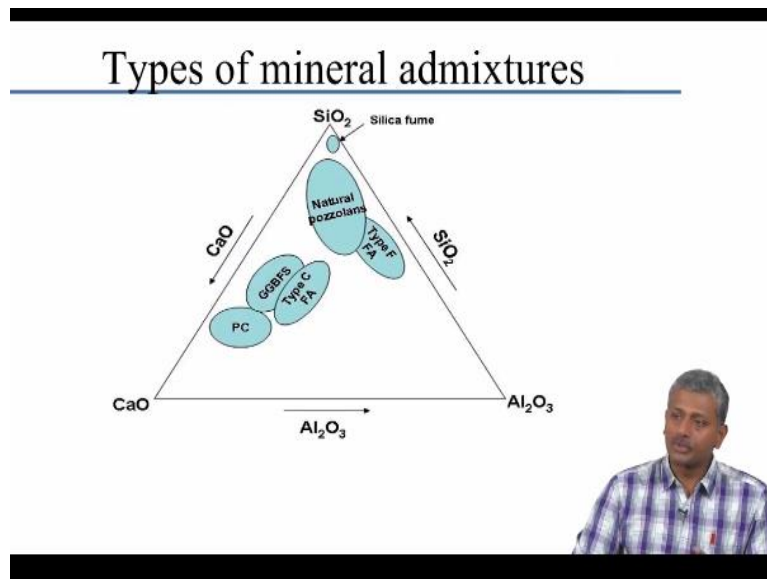
And because of the weathering you can produce different types of clay species, kaolinitic clays are most important with respect to pozzolanic replacement, but again these are the current levels of mineral additives that you can find around the world. You can find that fly ash for instance although we say lot of fly ash is available in India you may find that there are sections of the country where you do not get any fly ash.

For example, if you go to the North East there are very few thermal power plants there. So there is no possibility for them to get fly ash quite easily for construction. So if you are in the vicinity of a thermal power plant you are okay, because you can always get fly ash, but if you do not have a thermal power plant if you are relying on other sources of electricity like hydel power and things like that obviously your fly ash resource is going to be extremely limited.

So again in construction the economy is obviously driven by the availability. If materials are available locally that would be the most appropriate to use for your particular concrete. So in general you have to look at it from a perspective of a global usage of materials and a local

usage of materials. I will give more examples on this as we go towards the end of this chapter and look at some alternative sources that can be made use of but in very local environments.

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So the most common types of mineral admixtures are plotted here in terms of the ternary diagram that we were familiar with earlier when we talked about cement. The calcium oxide, aluminum oxide and silica ternary diagram. So the vertex represents the point which is pure calcium oxide in this case or pure SiO₂ or pure Al₂O₃ in this case. So if you look at cement we are located in a region that is rich in lime or rich in calcium oxide.

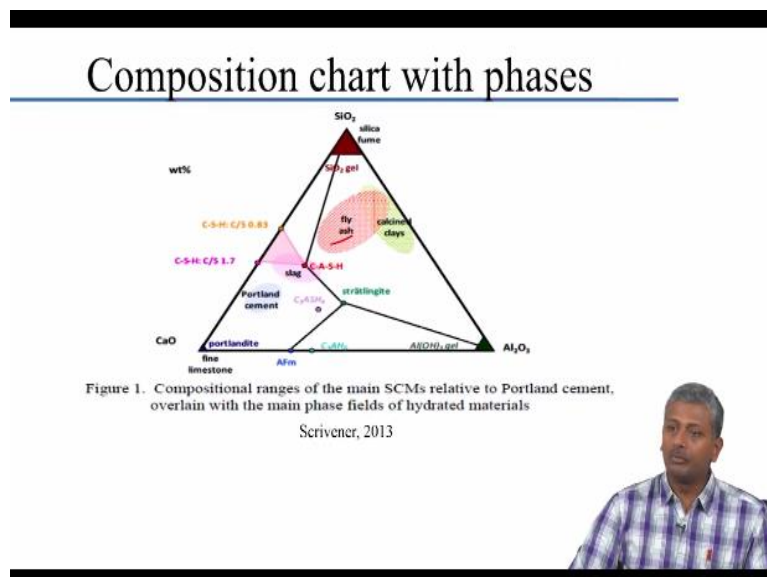
If you look at silica fume, again we look at how silica fume is actually obtained but silica fume is a very high purity silica, it has got almost 95-96% SiO₂ in some cases probably there are some which have slightly less than 90% also, but for the most part you have almost a pure SiO₂ that is available as silica fume. Type F fly ash is the material that is having very little of calcium oxide but mostly it is silica and alumina.

Natural pozzolans are again your volcanic ashes that are mainly rich in silica and may not have much of calcium oxide and aluminium oxide. Where is clay going to be? Yeah it will be probably somewhere around near Type F fly ash. Clays are aluminosilicates, but mostly they have silica more than alumina, for example kaolinite has 2 silicas to an alumina, approximately, so you essentially have a system which is richer in silica and lesser in alumina probably almost 0 as far as CaO is concerned, so these are clays.

Type C fly ash which is the high calcium fly ash is more towards the center of this ternary diagram whereas slag is even richer in calcium oxide content as opposed to type C fly ash. So if you look at your mineral admixtures from this ternary diagram perspective you can know what type of things to expect from them. For example, from type C fly ash and from slag apart from the pozzolanic characteristics that is reaction of the reactive silica with the lime you may also expect some cementitious characteristics.

That means because of the high calcium oxide content, you will probably start seeing some cementitious reactions also taking place in these systems. Whereas for natural pozzolans, for type F fly ash and for silica fume what you will essentially end up with this pozzolanic type of reactions which are possible with these kind of binders.

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So when these materials react with water they will produce different types of phases. So the silica based, the materials rich in silica will end up producing something like a silica gel. Now issue is in a system that is rich in lime for example lime contributed from the cement hydration the silica gel and lime together will form CSH obviously. We are forming CSH, but since there is more silica available, the type of CSH that you end up forming will be lower in your calcium to silicon ratio.

On the other hand, with Portland cement the type of silica gel or type of calcium silicate hydrate gel that you form has a calcium to silica ratio which is closer to about 1.7 or 1.8. So this is actually the same ternary phase diagram where it has been, I mean populated with the kind of

hydrated phases that can actually form in the system. Again obviously for a pure calcium oxide you will end up forming Portlandite or calcium hydroxide.

Portlandite is same as calcium hydroxide, is the name of the crystal of calcium hydroxide. For the calcium alumina phases the type of phases that you will end up forming stably are C_3AH_6 which is one of the calcium aluminate hydrates that forms in the system you may also form AF_M or aluminum hydroxide gel if you have a system which is very rich in alumina.

On the other hand, if you have materials like slag, you may form phases that are calcium aluminate silicate hydrate, CASH and there is a very specific phase which exactly represents the certain formula of CSH called stratlingite, that can also be formed in systems that have alumina and silica in addition to your lime contribution from the cement. So you often find these phases with all your mineral admixtures.

Which are rich in alumina also. All mineral admixture rich in alumina will end up giving you the calcium aluminate silicate hydrate phases and specifically stratlingite. For example, if you use a calcined clay it gives you lot of alumina and silica so you will end up forming CASH. So you are forming CASH inside the concrete.

There are other phases also that can form in these systems but again ultimately because of the semi-crystalline or loosely amorphous nature of these materials you do not have an exact stoichiometry, you often give very approximate compositions that is why we say CSH or CASH depending upon the type of mineral admixtures that you have. So if you have a mineral admixture pure, rich in silica and having very little alumina you will form CSH which has a low calcium to silica ratio.

If you have alumina rich mineral admixtures you will end up forming these kind of compounds which are having aluminate and silicate in the CSH structure, and of course if you have alumina rich mineral admixture you will end up forming aluminate phases or CAH phases or calcium aluminate hydrate phases or in the case of extremely high levels of alumina in the system you will probably form aluminum hydroxide gel.

So this picture just tells you what are the compositional ranges of the main supplementary materials relative to Portland cement and what can you get in terms of the hydrated phases once this system reacts with water.

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Typical compositions

% by mass	PC	GGBFS	F-FA	C-FA	SF
SiO ₂	21	35	50	35	90
Al ₂ O ₃	5	8	25	20	2
Fe ₂ O 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



So typical compositions are presented in this table, you know very well Portland cement is having a majority of calcium oxide probably close to about 2/3rd of cement is calcium oxide and you have silicon dioxide, probably lesser of aluminium oxide and some iron oxide. As far as slag is concerned you get an almost equal formulation of calcium and silica in slag. On the other hand, with type F fly ash which is a low calcium fly ash.

Type F fly ash or low calcium fly ash you have very rich silica but almost 0 calcium oxide content, you may have significantly large amount of alumina in the system and probably also a large amount of iron oxide. As far as high calcium fly ash is concerned, type C fly ash. Any idea where we get this type C fly ash from close by to Chennai? We get it from Neyveli. What type of coal is used in Neyveli? Lignite.

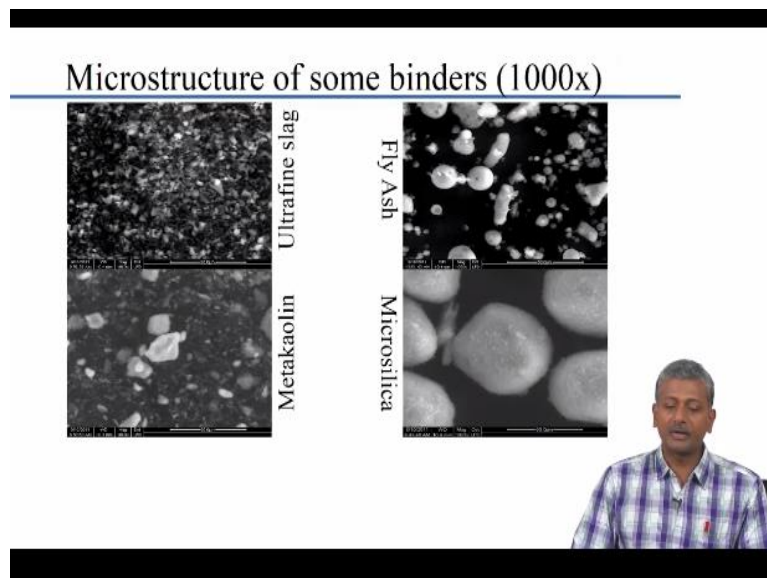
Lignite is an impure coal that has a large proportion of these clayey impurities which can give you a high calcium fly ash, so it is about 20% of calcium oxide, lesser amount of silica probably the same alumina as type F fly ash and probably the same iron oxide or slightly lesser than type F fly ash. Silica fume on the other hand is high purity silica that is 90% and you are getting a product that is mostly SiO₂.

You do not have much of the other ingredients present. Now based on the ternary diagram that I showed you previously let us try to work out what we will have with clay or calcined clay. You would approximately get about close to 55% of silica and about 40% of alumina with some minor constituents which are iron oxide and so on maybe 5% iron oxide. These are just approximate compositions.

Calcined clay will have mostly silica 55% and about 40% alumina with almost 0 calcium oxide content in the system. Now of course calcium oxide maybe present as an impurity in the clay. For example, if you have limestone as an impurity in the clay, if you burn the clay it will give you some calcium oxide, but for the most part the clay will contain silica and alumina in the system.

Rice husk ash, what about rice husk ash, it will be the same as silica fume. Rice husk ash will also have a very high purity silica which will be almost similar composition as the silica fume. Later I will explain also that we can burn the sugarcane bagasse to form what is called bagasse ash and that bagasse ash is somewhere close to fly ash, sugarcane bagasse ash, SCBA. I will come to that at the end of the chapter when we are discussing special type of mineral admixtures okay.

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So just some microstructure given here for different types of binders. So here you have metakaolin you can see the angular particles of the metakaolin here. You can see also slag, again this is ultra-fine slag, so it has been ground very fine, you can see that this entire size is

about 50 microns. So these particles are all probably 5 microns or smaller. You can see the angular particles again for the slag.

And as far as fly ash is concerned mostly you will get the spherical particles and you may also get these oblong particles that you see here. Micro silica is presenting a very interesting feature here. This size is 50 microns that means these particles are 50 microns across, but you all know that micro silica or silica fume is a material that is extremely fine. We talk about fineness which is 10 times or maybe even 50 times finer than cement.

So what is happening here, why the particles looking so big? These are agglomerated particles because silica fume as a powder, which is collected in industry where it is collected from, is very difficult to handle because of its extremely small size and low specific gravity. So for that what people do is make it into a densified or compacted form and when you densify it the particle size becomes close to 20 to 50 microns.

Because of which you see very large particle sizes. Now you can easily understand practical difficulties of using silica fume, what would that be? If I use these particles in concrete what do I need to do? I cannot grind it, it has to get dispersed or these particles have to get broken down into the fine silica fume particles, how will that happen? Superplasticizers obviously needed, then mixing.

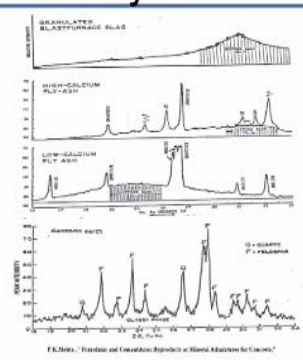
The effect of aggregate impacting the silica fume particles, so that will cause these particles which are compacted to disperse into the very fine particles that are going to be quite useful as a pozzolanic material. Otherwise what will end up happening is these silica particles which are large in size, will just be unreactive and occupy the microstructure and maybe some may even end up being sites for alkali-silica reactivity.

That is an interesting thought although nobody has proved it, people do suspect that if the silica fume particles are not broken down to release the extremely fine particles the large agglomerates of silica fumes may act as reactive aggregate because what is reactive aggregate contain. It contains reactive silica. Now we will discuss later why the reactive silica from mineral admixture does not cause alkaline aggregate reactivity.

Because alkalis can also react with the reactive silica in mineral admixtures, why does it only react with reactive silica from the aggregate, so there is obviously some size effect that is coming into play. When mineral admixtures, which are finely divided particles, they are able to actually capture the alkalis without leading to an expansive reaction that we will see later, we will see the mechanism of that little bit later.


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X-ray diffraction studies



The cementitious materials such as slag and Type C fly ash have a broad peak in the range 28 – 34 ° 2θ, while for siliceous materials such as Type F fly ash, this broad peak is shifted towards 24 – 26 ° 2θ.

The highly pozzolanic materials, such as Santorin earth which is shown in the figure, do not have a clearly broad peak, but show some background radiation corresponding to the glassy SiO₂ phase.



Now very often we use other techniques also to try and understand the characteristics of these mineral admixtures, one is X-ray diffraction. So those of you who have visited the cement plant saw that they were using something called X-ray fluorescence, in a X-ray fluorescence experiment if this is your sample you are subjecting the sample to X-ray radiation.

So X-rays you know are very high energy rays so what X-rays end up doing is they start interacting with the elements present in the sample like calcium, silicon and so on, and because of the high energy the electrons which are present in the shells of the elements can get dislodged. So when that happens there is some electronic transitions that take place within the atom of these elements like calcium, silicon and all that.

That generates additional x-rays so in other words this incoming X-ray is of a particular material or a particular wavelength what goes out are several X-rays for example X-rays for calcium, X-rays for silicon and so on. X-rays that are characteristic of calcium, characteristic of silicon and so on. So the detector simply captures all these X-rays and estimates how much of silicon is present, how much of calcium is present and so on.

So that is X-rays fluorescence, in X-rays diffraction what happens is, this X-rays that comes in interacts with the crystalline planes of your material and simply gets reflected. Now based on the type of planes that are there in the crystalline species that make up your material, the reflection can take place at different angles and based on the angle at which the reflection takes place we can actually qualify the type of mineralogical phase that is getting observed.

So if it is a very fine crystal, you will actually get a peak like this, for example you see here these peaks are marked as F or Q. F is feldspar and Q is quartz. So for perfectly crystalline materials you will get actually a peak exhibited when you plot the intensity of the X-rays that are getting received against the angle at which you are getting these X-rays.

So here for example the angle is represented as 2θ , so if I mark this as θ , you are representing this in terms of an axis which is 2θ . Now what if the material does not have crystalline components, you will actually get some sort of a diffuse band or a hump which is not exactly a crystalline peak but an amorphous hump. So again you see these diffuse bands or humps that are visible here.

This last case is Santorin earth, Santorini Island in Greece where a pozzolanic ash is actually formed, this hump is actually noticed or a glassy phase, which is written here, and that is basically your amorphous material that is in the background, it does not produce very distinct crystalline peaks. All the crystalline materials will be producing peaks. For example, when you look at slag you have absolutely no peak at all.

You only get this amorphous band that is there, you do not get any peak at all because there is nothing crystalline in slag, all particles are amorphous, as a result you only get this amorphous hump. In the case of fly ash, you get this amorphous band. If you have a type C fly ash you get an amorphous band, in the region that you get for slag, if you have type F fly ash you get a lower angle, the same of amorphous hump is obtained.

But you also see some peaks that are associated with fly ash. Some crystalline materials are still present in fly ash. So fly ash is not entirely amorphous, some part of it maybe crystalline. Whereas slag is almost entirely amorphous because of the kind of processing that we do. How is slag prepared? By taking the molten slag and rapidly quenching it. We just dip it entirely in water.

So when you do rapid quenching you form an amorphous material, but all the other materials like fly ash, they are getting cooled in the air, and as a result only some particles are amorphous, the other particles maybe crystalline in this material. So what will happen as a result of that? What about reactivity? It will reduce. If you have crystalline components in your system, the reactivity will not be as good as having an amorphous material.

So for slag we get very good reactivity, with fly ash we can get limited reactivity based upon the kind of material that you collect. So you will obviously get a mixture of amorphous and crystalline components. So the silica that we looked at in this table here 50% silica, not all of it is amorphous, some of it may be present in the form of mineral such as quartz for instance.

Or mullite, mullite is basically again aluminosilicate, so these minerals are forming because of different temperatures existing in different parts of your boiler, and these ashes that are getting carried out can have a mixture of amorphous and crystalline species.

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RILEM Classification

- Cementitious: GGBFS
- Highly pozzolanic: Silica fume, Rice husk ash (controlled burning)
- Normally pozzolanic: Class F fly ash
- Cementitious and pozzolanic: Class C fly ash

An additional category is also suggested by researchers –
Weak pozzolans, such as slowly cooled and ground slag, bottom ash, and field-burnt rice husk ash



So RILEM which is an international organisation similar to American Concrete Institute has done a classification of different types of mineral additives for example cementitious mineral additive are the ones which can react with water on their own, but this reaction may take a substantially long period of time so slag or ground granulated blast furnace slag. Please remember whenever slag is mentioned as a cement replacement we are essentially talking about ground granulated blast furnace slag.

There are different forms of slag available from iron and steel manufacturing industry. There are furnaces which are apart from the blast furnace also that are used for purifying the iron when it comes out, removal of carbon happens and you get purified iron to extract the iron as a metal. So in different stages you may get others slags also coming out, in copper industry there is copper slag that comes out.

But that cannot be used as a cement replacement because it has got very different characteristics. The type of material that is qualified to be used as cement replacement is the blast furnace slag and it has to be obtained in a granulated form by quenching and grinding it to cement fineness, that is why it is called ground granulated blast furnace slag.

Now silica fumes and rice husk ash which have lot of silica in them, lot of amorphous silica in them are classified as highly pozzolanic systems that means they can rapidly react with the lime. Then you have normally pozzolanic systems like class F fly ash which still has substantial amount of silica, but is not as fast reacting as silica fume or rice husk ash. Then you have class C fly ash which has some cementitious characteristics that is why it is called cementitious and pozzolanic.

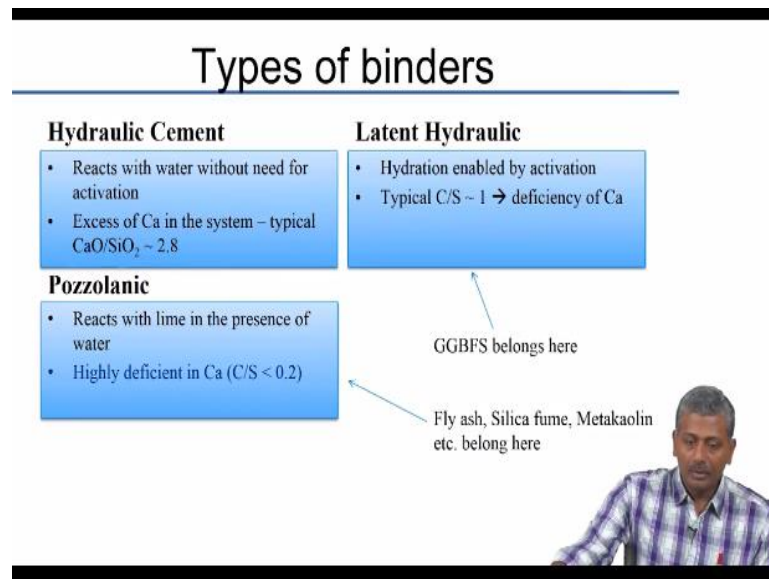
And then you have weak pozzolans which includes slowly cooled and ground slag for example if you take slag and do not quench it, if you air cool it and grind it, it may not end up being very reactive, it may be better as a filler. In fact people tend to use air cooled slag as an aggregate. You can actually crush it into aggregate sizes, it forms a nice hard material and can be used as an aggregate.

And you can also use bottom ash, what is bottom ash? When you are burning coal in the boiler the ash that is light gets carried away by the gas that's the fly ash, the ash that is heavy simply settles at the bottom that is called bottom ash. This bottom ash is not very reactive because particle sizes are not small, secondly it is probably consisting of ingredients that are more crystalline as a result it is not very reactive.

And then you have field burnt rice husk ash like what we have available plenty in India where people are burning it without any controlled environment. What do you imply by controlled environment of burning? Controlling the rate of temperature increase and decrease and the

amount of time that the material spends inside the furnace. So that has to be controlled quite well for the rice husk ash to end up being reactive.

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So we will wind up today's lecture with this understanding of the different types of binders that exist in the cementitious systems. So of course we know very well about hydraulic cement which is plain Portland cement, it reacts with water without the need for any activation. So hydraulic cement can react with water without any activator and essentially we have an excess of calcium present in the system.

Typical calcium oxide to silica ratio is almost up to 3. We have more than 60% CaO and about 20-21% of silica. So calcium oxide to silicon dioxide ratio in cement is close to 3. Now when we come to latent hydraulic binders, what do you mean by the term latent? Latent means there is something within the system which can come out but it need some prodding to come out.

So latent hydraulic implies that the hydration of these types of materials can be enabled by activation. In other words, slag can react on its own with water, but to have any degree of control over the rate of this reactively it needs to be activated and what causes this activation we will see that later, but for now I can tell you that it is essentially the alkalis and the sulphates that are contributed from the cement.

And of course the calcium hydroxide that is getting formed because of cement hydration. So in the presence of alkalis, slag can activate and hydrate on its own with reaction with water. So you may have heard of this term called alkali-activated slag, which is a different type of binder,

it is not the one which we intend by making or replacing cement with slag. Alkali activated slag means you only have slag as a binder and use an alkali to activate it.

In some sense we can call it like a geopolymer, geopolymer system. Right in the geopolymer system you have an alkaline solution and you have an inorganic aluminosilicate. Now slag is an inorganic aluminosilicate, you can always use an alkali like an alkali sodium hydroxide or sodium silicate to interact with the slag, but what you end up doing is not geopolymerization in this case you end up hydrating the slag.

That is why when slag is used and you use an alkaline solution to activate it, it is called AAS or alkali activated slag whereas if fly ash or clay is used and you use an alkaline solution to activate it, it is called geopolymer. It is not correct to call a slag system as a geopolymer because geopolymer means you are leading to polymerization of the aluminosilicate chains.

In slag hydration you are not causing that, you are only causing the slag system to react. The calcium and silica in the system will react and what kind of compounds will be formed? CSH, ettringite, aluminium hydroxide and so on because there is substantial amount of alumina also in the system. So here the calcium to silica ratio is close to 1. So there is deficiency of calcium because of which the reactivity is constrained and can only be brought out by activation with the alkali or sulphate.

In a pozzolanic system the compound cannot react on its own with water because there is severely deficient system in calcium. Calcium to silica ratio is less than 0.2 and some cases there is no calcium availability at all. So here you need substantial amount of lime to hydrate these systems, to react these systems. So pozzolanic system will need lime which is getting supplied by the hydration of your cement.

Latent hydraulic may work without supplying additional lime also, but supply of additional lime will actually help push that reaction further, because activation can be caused by alkalis or sulphates, you do not need extra lime for that. So your slag obviously belongs to this system whereas fly ash, silica fume, metakaolin are the pozzolanic systems.

What about class C fly ash? It will exhibit both, because it has got some calcium which may cause it to have a latent hydraulic kind of a characteristic, but it also has a large amount of

silica which may cause it to have a pozzolanic characteristics. So you get a mixture of two different types of interactions when you have type C fly ash. Any questions at this stage? Okay we will stop with that for today.