

## **Admixtures and Special Concretes**

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**Lecture -29**

### **Mineral Admixtures: Microstructure of SCMs and Pozzolonic reactions**

#### **Recap:**

Okay, so let us get started. So in the last class we were talking about mineral admixtures and we looked at how the use of mineral admixtures are beneficial in more ways than one. Primary idea is that you convert available calcium hydroxide into additional CSH which leads to better pore filling. And then the other aspect is that mineral additives have a much optimized grain size distribution that allows them to fill the void spaces left behind by the cement and the hydration products. So you ultimately get an impact on all three pillars of sustainability that are environmental, social and economic.

We also talked briefly about how, what is the availability of these types of materials in the different parts of the world and we saw that primarily the material that could potentially have a long term future is a supplementary cementing material and it is calcined clay. But nevertheless there will always be some options of usage of materials that are locally available like for instance silica fume or burnt shale, ricers cache. These are available in local areas and possibly they will have the best utilization when you are actually using them close to the point of their source.

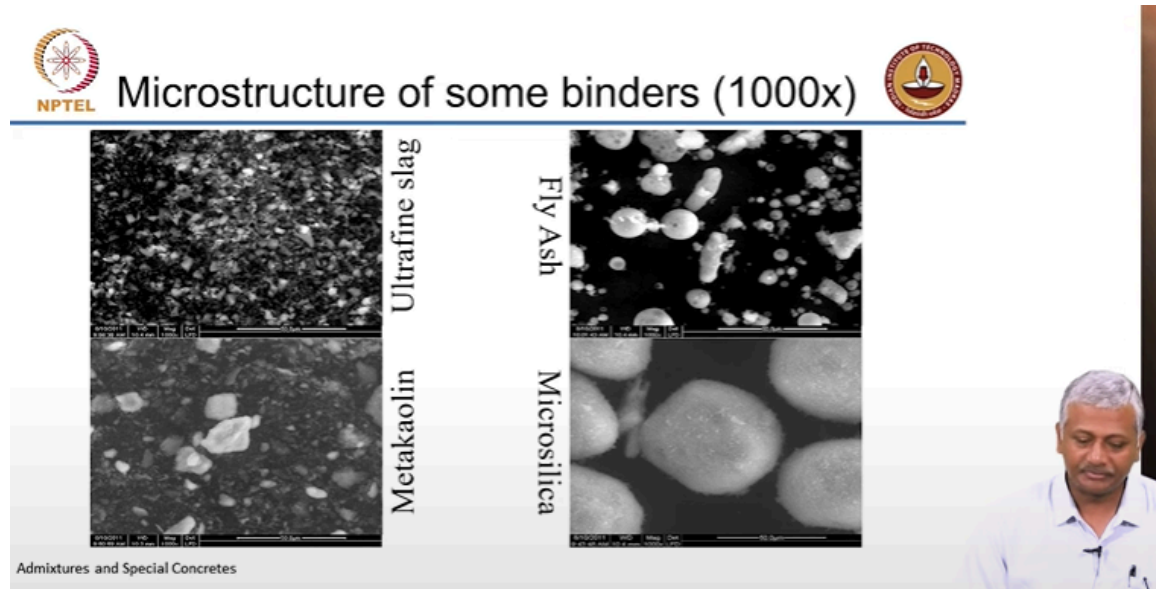
Now in terms of compositions we looked at various different representations primarily on the ternary diagram between calcium, silica and alumina and all compositions can be expressed as some mixture of these three oxides and we saw that compared to cement most of your mineral additives are rich in silica and some are rich in silica and alumina. And based on their initial chemical composition the final phases that can actually come into these systems also varies. When you have a rich alumina system instead of just forming CSH you may form calcium alumina silicate hydrate or CASH. You may also have other compounds forming depending upon the initial chemistry of your system.

So we also extended the same look from the ternary diagram on to a typical composition system and then we discussed a little bit about particle size distribution and the difficulties in obtaining the right particle size analysis primarily because we have an issue of agglomeration of some of these fine particulate materials which does not allow a clear

understanding of the particle size especially when we are looking at something like a laser diffraction we have to make sure that the particles are properly dispersed and only then we can get a clear estimate of the particle sizes.

### Microstructure:

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So moving on to one additional scheme of characterization that is typically followed with most mineral systems is microscopy and under the microscope we can actually get to see some of these structures more closely. So if you look at fly ash they have mostly these spherical or these oblong types of particles. Those are particles of silica some are spherical some are oblong and mostly what happens is since fly ash is collected from the source that is flying out after burning of the coal it also flies out with lot of gas and depending upon how the gas condenses you can actually form different shapes but I will talk about that in more detail later when we discuss about fly ash.

If you look at micro silica look at the size here you can see that these are not actual micro silica grains because micro silica is supposed to be even finer than one micron but here you are seeing grains which are very large and that is because these are condensed silica fume particles. They are agglomerates of particles of silica fume which need to be broken down sufficiently well when you do the concreting.

Metakaolin has got all of these clay particles which are irregularly shaped. Ultrafine slag of course you are breaking down slag into much finer sizes. I must say that is not a very good image that we have for you here but I will show you some more pictures later on that will make the texture much clearer. Slag has a lot of angular particles so slag will

have mostly angular particles. Calcined clay also will be mostly angular. Fly ash will have spherical particles and silica fumes of course in the condensed form it has got the spherical particles. In the finest divided form it will still be spherical but the size is so small that it increases your water demand.

Similarly compared to an angular particle a spherical particle will lead to lesser water demand. In fact, substitution of cement by good quality fly ash which has spherical particles should lead to an increase in workability. Your slump should increase when you replace cement with fly ash and indeed that is what we saw when we looked at some of the compatibility aspects of OPC and PPC along with SNF and PCE. Anyway we will come back to individual mineral admixtures a little bit later.

### X-ray diffraction:

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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 SiO<sub>2</sub> phase.

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Another scheme of characterization that is commonly followed with mineral additives is X-ray diffraction. Now X-ray diffraction is a study in which let us say this is your sample. We have a beam of X-rays that is made to interact with the sample and there is a reflected beam or a diffracted beam we call it a diffracted beam of X-rays. And of course observing most of you, you may have heard about this law in physics called Bragg's law. Bragg's law essentially says that the specific angles of incidence at which constructive interference happens will be controlled by the Bragg's equation which is

$$n\lambda = 2 d \sin \theta,$$

Where  $\theta$  is the angle of incidence and  $d$  is the inter-planar spacing.

So you have in crystal lattices you have several planes and these planes have very well set spacing between each of their planes. And this  $d$  is basically the inter-planar spacing.  $\lambda$  is the wavelength of the X-rays.  $\Lambda$  is the wavelength of the incoming X-rays. So the incoming X-rays and the outgoing X-rays are going to be the same angle  $\theta$  and essentially the diffracted beam will be constructively seen only when you have this equation defined by Bragg's law getting satisfied. So there is a lot more to that of course you have to take in a subject on characterization to really understand this phenomenon better but the idea is that for any well-defined crystal the pattern that you see in X-ray diffraction will produce all of these well set peaks. You have very clear peaks that are coming out for any well-defined crystal.

However if the material is mostly amorphous you will get a very diffuse band like this. You will not get a clear peak but you will get a diffuse band over which you see X-ray intensities on the Y-axis typically the X-ray diffraction pattern you plot the intensity of the X-ray that is collected here and twice the angle of incidence. That is typically the way that the X-ray diffraction pattern is drawn. Idea is that if you have a lot of crystalline components you will be able to see distinct peaks for each of these. However if you have mostly amorphous you will see a diffuse band.

What kind of phases do we want to see in metal additives? Crystalline or amorphous? We want to see amorphous because we want to see the presence of amorphous silica phases; only those will be reactive with your calcium hydroxide to produce the pozzolanic reaction. However there are some mineral additives as you saw which are not completely pozzolanic. They may have a significant amount of calcium also like slag for instance.

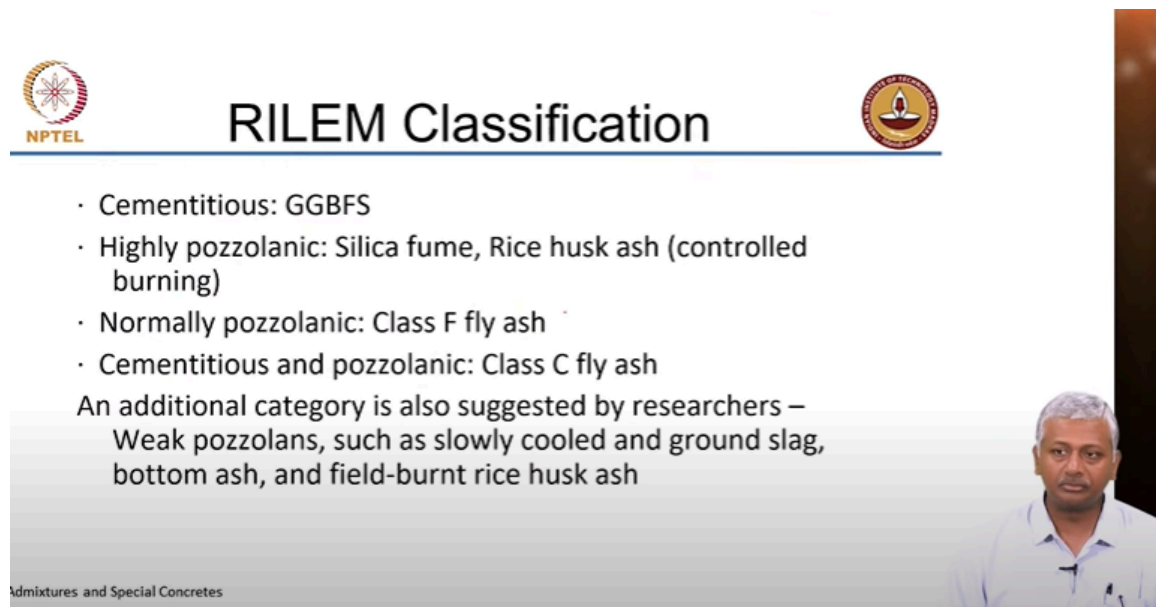
Now when you have a calcium bearing system what will happen is this diffuse band or this amorphous band is seen to be shifted to the right. See this is high calcium fly ash you have this diffuse band shifted to the right whereas in plain silica bearing phases or plain amorphous silica bearing phases like type F fly ash or low calcium fly ash this band is seen at a slightly different location.

Now this last pattern is from Santorin earth. Santorin earth is essentially volcanic ash found in the island of Santorini in Greece and that also has very good pozzolanic properties. Here again you see the glassy phase is fairly diffuse but it has got a significant bit of crystalline components also. You can detect some quartz and feldspar as crystalline materials within the mixture of this Santorin earth. So what you have to look for is if you have a silica rich band it will happen somewhere around this 20 to 25°C. A silica rich band will be usually between 20 and 25°C. If you have a calcium silicate bearing system like a slag or a type C fly ash or a high calcium fly ash you will probably see it around 28 to 35°C. The shift in the X-ray diffraction pattern of the amorphous band that you will see if you have a low calcium system or a high calcium system.

What you essentially need to look for is that you have a majority of amorphous phases present in your system. Now there are complicated ways in which you can quantify all of these phases and get a clear extract of what is amorphous, what is crystalline in your system. But just by looking at it you can clearly see that for ground granulated blast furnace slag do you see any crystalline peaks? You don't see any crystalline peaks. It is almost 100% amorphous. For high calcium fly ash we do see some crystalline peaks. For type F fly ash or low calcium we again see some crystalline peaks. For Santorin earth also you see some crystalline peaks. All you need to do is understand how much is actually reactive. Further there are several ways in which you can adjust the reactivity of these systems and that is what we will take a look at today.

### Classification:

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The slide features the NPTEL logo on the left and the RILEM logo on the right. The title "RILEM Classification" is centered at the top. Below the title, a bulleted list categorizes materials based on their reactivity. An additional category is noted below the list. A portrait of a man in a light blue shirt is visible in the bottom right corner of the slide area.

- 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

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Now to classify these systems based on their reactivity, RILEM which is an international organization which looks at the research and industrial application of various types of concrete materials. It describes the mineral additives or supplementary materials as cementitious when you have let us say slag because slag does not need calcium hydroxide as we will discuss later. It can react on its own with water with some activation.

Highly pozzolanic materials include silica fume and rice husk ash which is produced from controlled burning. Again I will talk about these distinctions between controlled burning and variable burning or uncontrolled burning later on. The idea is that you have systems that are of high purity silica that is why you get highly pozzolanic behavior from these systems. Normally pozzolanic is something like class F fly ash. Comparatively in

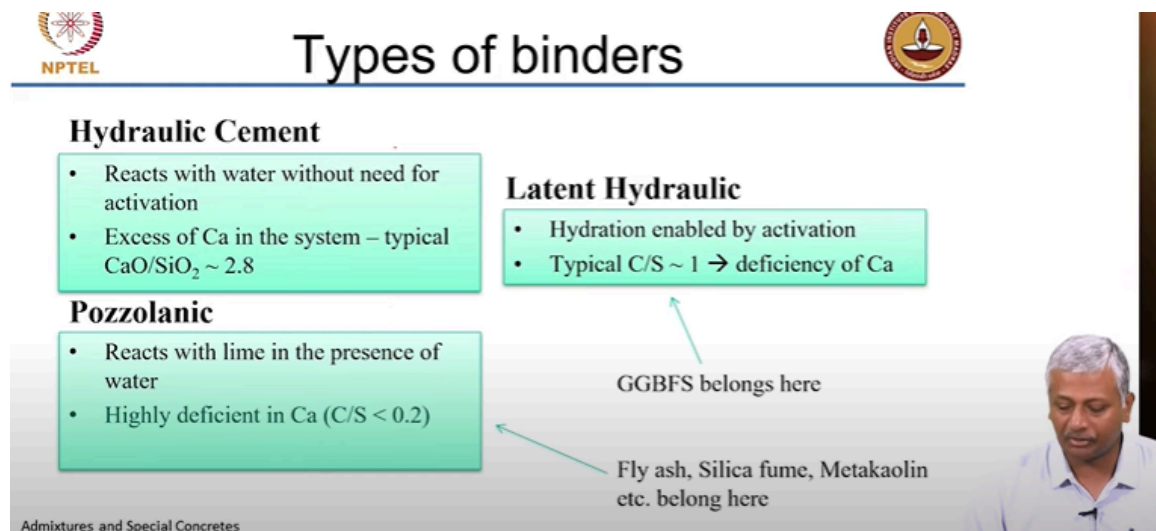
terms of composition the highly pozzolanic material has silica content of the order of nearly 90%.

Whereas when you talk about normally pozzolanic systems we have around 50 to 60%. Cementitious and pozzolanic which can exhibit both cementitious properties and pozzolanic properties because you have sufficient calcium present; it is like class C fly ash or high calcium fly ash. High calcium fly ash is not the same as slag. Slag can react on its own with water but high calcium fly ash would still need a sufficient amount of lime in the system, calcium hydroxide in the system to really undergo the reaction. There are other fairly unreactive materials also which can be called as weak pozzolans or weakly pozzolanic materials such as slowly cooled and ground slag. Again we will see the distinction later. Bottom ash that means the part of the ash that does not fly out and field burnt or uncontrolled burnt rice husk ash. Again we will see these later. The idea is that you classify them based on their reactivity.

A highly pozzolanic material will react very fast. Normally pozzolanic material will be a little bit slow. A weakly pozzolanic material will take forever and perhaps not even react in the way that we wanted to react.

### Types of binders:

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So just to give you a better assessment of the composition, we have hydraulic cement which is your normal ordinary Portland cement. Why do we call it hydraulic cement? What is the reason we call it hydraulic cement? Why do we call cement as hydraulic cement? It can react with water but under what circumstances? Why do we call it hydraulic?

It can continue reactions and get hard even under water. That is the idea of calling it hydraulic even under water even in wet conditions.

You can continue this reaction and cement will ultimately get hard. That is why we call it hydraulic cement. Conventional characteristics are when your material is directly reactive with water and it is a condition where even presence of additional water pressure around the system is not going to alter this reaction significantly. In fact of course we know that the presence of external water helps in the continuous hydration of the cement. There is no need for activation. It can react on its own and we know that cement reacts fairly rapidly. This is happening because there is a lot of calcium in the system. Typical calcium to silica ratio is around 2.8. So a fairly high calcium to silica ratio.

Then you have the latent hydraulic systems that means hydraulicity is there in the material but it cannot be brought out unless you do some activation like your slag, ground granulated blast furnace slag where calcium is not very high. It is deficient in calcium. Calcium silica ratio is typically around 1 and the hydration is enabled by activation. You need some sort of an activator to get this hydration going otherwise it does not happen.

Then you have a pozzolanic system which cannot react with water on its own. It reacts with lime that is calcium hydroxide in the presence of water and these systems are highly deficient in calcium. Only about 0.2 calcium to silica ratio or maybe even less. So your aluminosilicate based systems are all belonging here that is fly ash, silica fume, metakaolin and other aluminosilicate admixtures. Your rice husk ash, sugarcane bagasse ash all of those will be pozzolanic and not latent hydraulic.

### **Pozzolans:**

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## Pozzolans





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



So again just to go over this definition again I showed you this in our overview of cement chemistry also. So pozzolans are essentially siliceous or aluminous materials which by themselves do not have any cementitious properties but in the presence of lime and when they are finely divided when they are not coarse when they are finely divided or fine grained they can react to form cementitious compounds in the presence of moisture.

Essentially what compounds are formed is calcium silicate hydrate or calcium aluminosilicate hydrate CASH or sometimes if it is a very alumina bearing material you can also form calcium aluminate hydrate directly instead of CASH you can also form CAH.


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## Pozzolanic reaction

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

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So reaction obviously consumes lime and we discussed that it is pore refining. Why is it pore refining? Why does it refine your porosity or make the porosity smaller? Because of formation of additional CSH you have a better space filling characteristic as compared to the crystalline calcium hydroxide the amorphous gel like CSH is able to fill up the space better.

It also refines the interface. If you look at our definition of the interfacial transition zone you will be able to realize why the use of mineral admixtures refine the interface. Why should mineral admixtures refine the interface of your system? Interface means interfacial transition zone between paste and aggregate. Why is it refining? Generally in the interface you see more calcium hydroxide being present so your mineral additives can produce more CSH in the interfaces and refine the interfaces. Generally of course you have a filler effect where the finely divided mineral additives can go and occupy the void spaces that are prevalent in the transition zone. This reaction is slow as compared to the



reaction of cement the reaction of a pozzolan is much slower and that leads to lower heat of hydration and that is why for any application where we want less heat of hydration replacement of cement by fly ash is the right choice because it can lower the heat development significantly and this is also accelerated in the presence of alkalis and gypsum. So if you put in significantly high amounts of alkalis and gypsum in your system this reaction will happen fast. Of course when cement is mixed along with the pozzolan the alkalis and gypsum also come from the cement. So higher alkali content in cement will also promote the pozzolanic reaction. If you do some literature search you will find this compound called FALG which is fly ash lime gypsum and this is being used to also produce some eco brick building blocks basically. Why? Because fly ash obviously can react with the lime but on its own it will take forever to react with the lime so you have additional gypsum in your system that enables this reaction to proceed at a significantly fast rate. Not as fast as cement but still at fast enough rates to produce a good quality binding material in a reasonably short period of time.

So FALG is used a lot for producing bricks and blocks. The strength is not as good as cement bearing systems however for bricks and blocks you may be able to produce the right quality necessary for usage in construction. So alkalis and gypsum are generally contributed from the cement and those will lead to an enhancement of this reaction, quicker reaction. So cement that is higher in alkalis will lead to a faster pozzolanic reaction also.