Admixtures And Special Concretes

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Lecture -42

Mineral Admixtures : Metakaolin

Ranking of binders in different durability tests:

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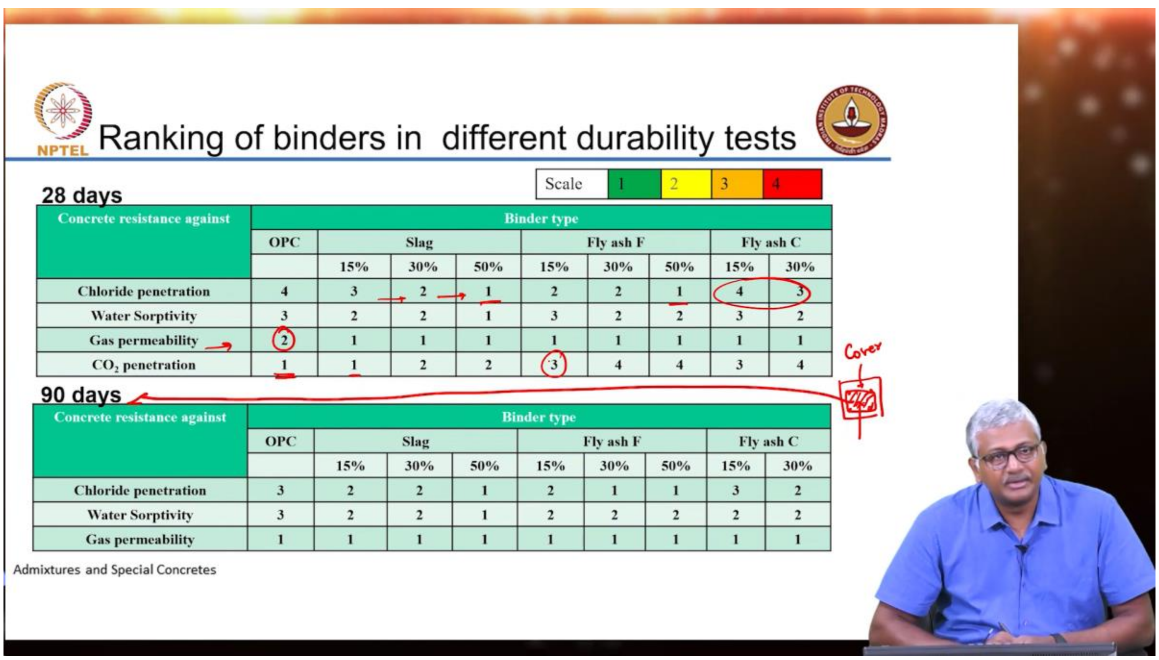

So, using this we sort of developed a matrix to rank concrete mixtures with respect to their performance and the performance was seen at 28 days, after 28 days curing and after 90 days curing. Now 90 days is obviously not something which is ever possible on the field but it does represent something of a material potential. Remember we talked about the covercrete versus heartcrete. The covercrete is here, the heartcrete is here and in heartcrete it is very difficult to visualize that the water inside will dry out at all. So in other words your long-term potential does not get depleted because water is always available in the heart of the system. So your concrete inside this zone maybe one that is subjected to 90 days curing.

So that probably reflects the quality of concrete that you have in the bulk on the inside. But covercrete obviously will be affected by the extent of curing. So at 28 days your covercrete will have definitely a lower performance as compared to if you are continuing to cure it for 90 days. So anyway what you see here is as for chloride penetration as you increase the slag content your rank is getting better.

With class C fly ash you really do not get such a big benefit in chloride penetration characteristics. So this is basically a relative rank, it is not an absolute rank but it is a relative rank. If fly ash and slag at 50% is rank 1 then that is what the rank of the other landed systems is. With gas permeability all of these mixtures were more or less good and they did better than OPC. With CO2 penetration, carbonation OPC is ranked 1 because carbonation depth is minimal in concrete with OPC.

At 15% slag does not really reduce your carbonation resistance significantly. But fly ash even at 15% may lead to a reduction in your carbonation resistance. So you have to utilize such data to then design your mixes for specific environments. So if you have to make a choice for let us say concrete to be supplied in Chennai, you will obviously go for blended cementitious systems. If you are more inland you may have to look at possibilities of blended cements which have less replacement levels.

You cannot go with high replacement levels when you are looking at carbonation resistance.

Metakaolin:

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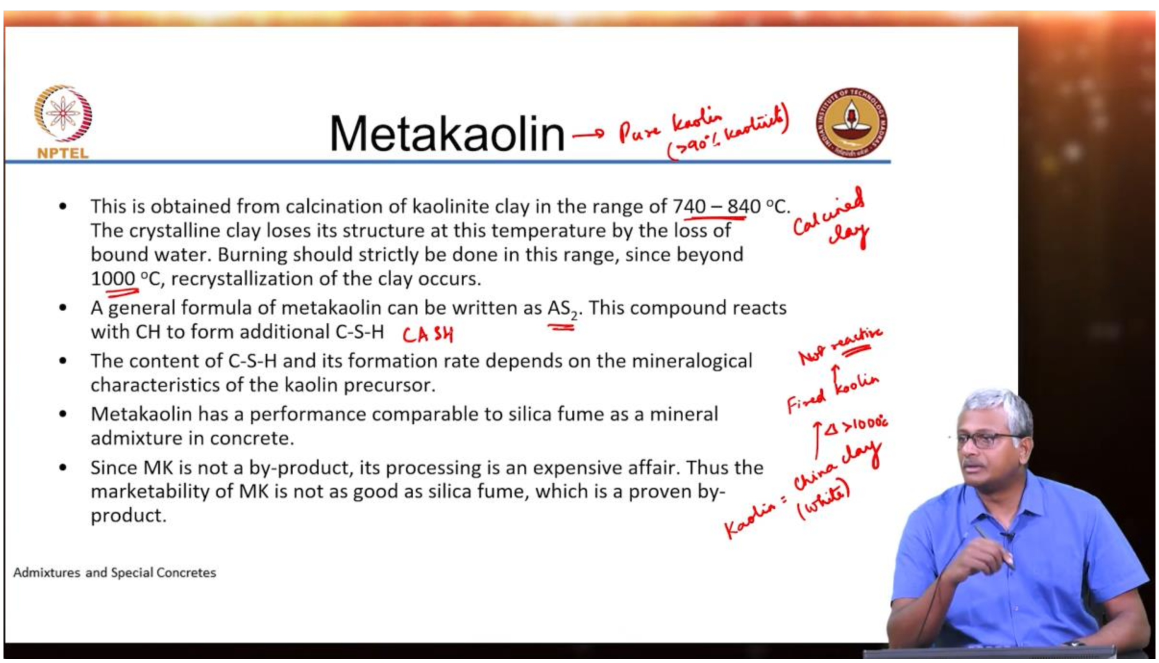

You cannot go with high replacement levels when you are looking at carbonation resistance. So let us move on from fly ash to slag to metakaolin. Metakaolin is the name given to calcined kaolinite clay, calcination of kaolinite in the range of 740 to 840 degrees Celsius. What is kaolinite also known as? What is the common term for kaolinite? Market term? It is China clay. And where do we use China clay? For ceramic, for paints, all of these are applications.

But there what you do is you take this kaolin and you heat it up to more than 1000 degrees Celsius. So it recrystallizes in forms that are very hard. Just like you do for your brick manufacture, the alumina silicate bricks are fired in the kiln for temperatures more than 1000. So you have the ceramic bond that forms in the brick and makes it hard. But if you do not fire your bricks high enough, if you are only in this range 740 to 840, you then get a reactive material.

So this 1000 degrees gives you fired kaolin which is not reactive and that forms basically your filler in the paint industry, the powder industry for your ceramics and so on. That is a high-end application. What is the color of China clay typically? White. It is typically white in color. But when it has impurities in the form of iron, in the form of quartz and other such impurities, it may not have the whitish color.

And in such instances, this white-colored clay may not be very easily available and because of which you may have lower grades of calcined clay. So any clay that is burnt at temperatures that make it active is simply called calcined clay. But metakaolin only refers to burning of pure kaolin. When you talk about calcined clay, it could be any clay that is calcined to a temperature that activates it. But metakaolin only refers to calcining of pure kaolin that means it has got more than 90% kaolinite content and, very less amount of impurities.

So the crystalline clay, clay is obviously crystalline, it has these platelets, alumino silicate and in kaolinite structure these are bound by water molecules in between the platelets. At that temperature, the water molecules are removed and your plates become more active. The surfaces of the plates now are reactive, they can react with calcium hydroxide to lead to a pozzolanic reaction. But if you go higher temperatures beyond 1000 degree Celsius, recrystallization of the clay will occur and it will not be reactive anymore. That is basically your fired kaolin which has lot of applications in other high end industries.

So for a China clay industry to manufacture metakaolin may not be as profitable as manufacturing the higher-end fired kaolin because it is used for more niche applications which get more profits. So there are not too many suppliers of metakaolin around the world, very few number of metakaolin suppliers are there. Now, metakaolin is obviously an alumino silicate, most clays at least kaolinite clays have alumina to silica ratio 1 is to 2, molecular ratio of 1 is to 2 and this compound reacts with your calcium hydroxide to form additional calcium silicate hydrate. Now not just CSH, it will be CASH because the significant amount of alumina present in your system. And the amount of CSH that forms and the rate at which it forms depends obviously on the kaolinite precursor, how reactive it is and so on.

When you go outside and just get some clay, it may not have only kaolinite, you may have other types of clay also present like illite or montmorillonite and things like that. Those clays have also been looked at from purposes of reactivity and they are found to be not as reactive as kaolinite. For all cementitious purposes kaolinite clays have the most reactivity. And metakaolin generally in literature it is been reported to have a performance that is comparable to silica fume as a mineral admixture in concrete. Now you can imagine that it is obtained from again a specialized industry, you need a high purity china clay to produce metakaolin, it is going to be expensive.

So the cost of metakaolin is nearly similar to the cost of silica fume. So that is something which we need to consider.

MK Reaction:

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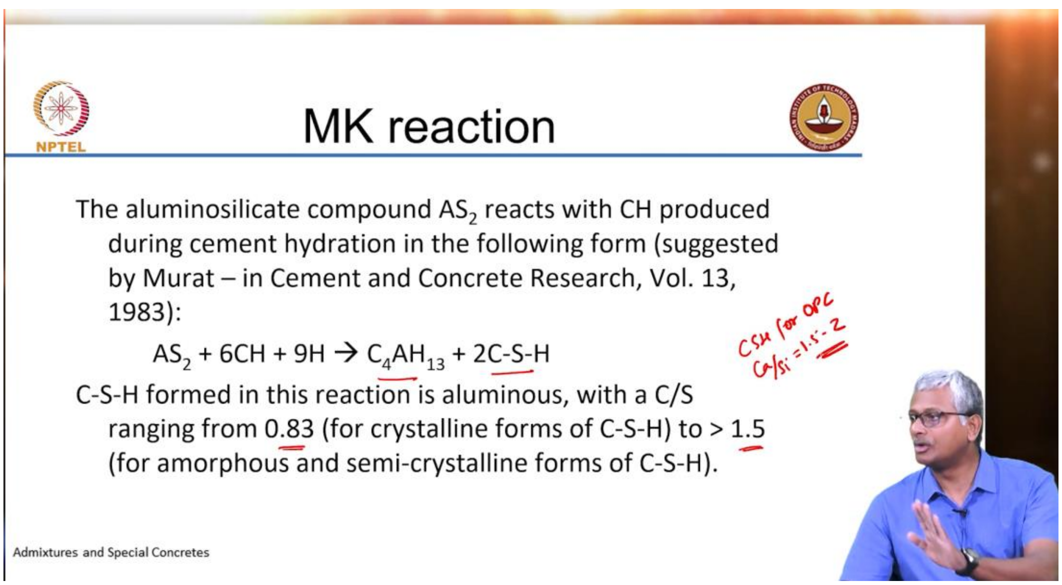

Again some ideas of a reaction are presented here, so you have calcium aluminate hydrate, calcium silicate hydrate and a mixture basically. Your calcium-to-silica ratio is lower in this case 0.832, sometimes 1.5, what about CSH for OPC? What is the calcium-to-silica ratio there? It is generally 1.5 to 2. More calcium is there in the CSH of OPC as compared to the CSH of blended cements. The more reactive the blended cement, the lower will be the calcium-to-silica ratio. More silicious the mineral additive, the lower will be the calcium-to-silica ratio.

Some results for metakaolin:

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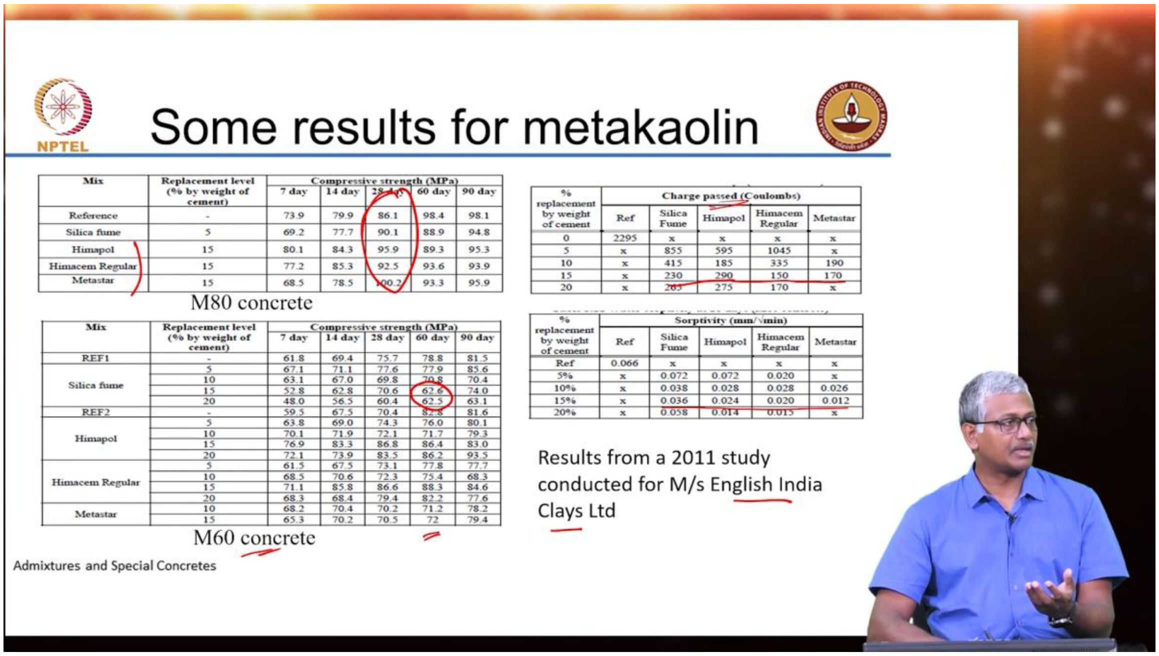

This is some work that we have done for a company called English India Clays in Trivandrum. Of course, they have not been producing material for some time now. So they were actually producing, in those days they were producing metakaolin for the Middle East market. In India they were not able to sell as much because market still favored silica fume, metakaolin was not able to get in in a large way. So we did the study to show them or show the result that you can get comparable performance with metakaolin.

So they produced different grades of metakaolin which we compared with silica fume in terms of strength gain. So here you can see that we did M80 concrete, 28 days strengths are well in excess of 80, so it satisfies the strength requirement definitely. And we also of course tested the charge passed in the rapid chloride penetration test. You can clearly see that when you use higher amounts of metakaolin, the result is quite similar to what you get with silica fume, it is not much different. So you do get the reduction in ionic conductivity as well as an overall reduction in the permeability when metakaolin is used as a replacement of cement.

So again similar water sorptivity result you can clearly see that there is an even better performance as compared to silica fume at the same percentage replacement level. And these were M60 concrete, again you can see that 60 days strengths were significantly higher than what was required with large amounts of silica fume, the strength was actually going down and this could have been because the particles are not really getting very active and may be starting to form more agglomerates and really not leading to a good hydration. You do not see that problem with metakaolin. If you remember the structure of metakaolin, I showed you highly angular particles but very fine particles, so they will also increase the water demand. Any fine particle would increase water demand, so you need a superplasticizer to appropriately compensate for that.

Metakaolin as high-performance mineral additive:

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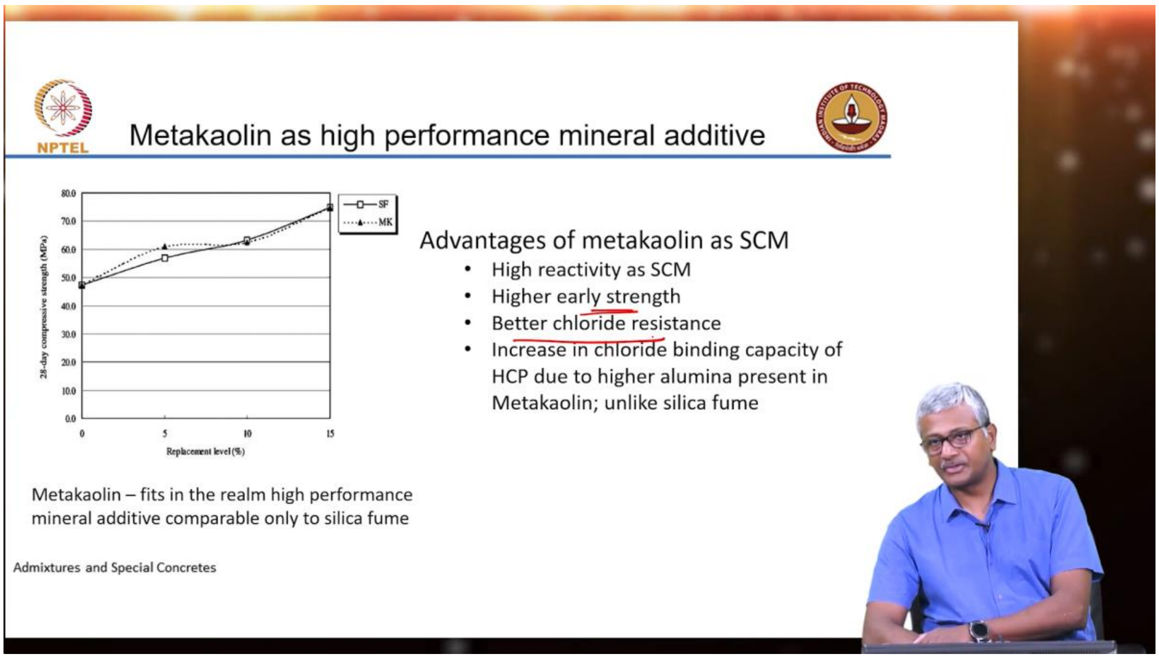

Again this is result from another paper where it shows clearly that your metakaolin replacement with silica and is comparable with silica fume in terms of your performance in compression. But other advantages could also be there, you get high early strength because of the extremely good reactivity of metakaolin, you get better chloride resistance as compared to silica fume. I mean RCPT is giving you the same result but chloride diffusion tests have shown that metakaolin may actually get you even better performance than silica fume. Why? Again because of the active alumina that is getting contributed, this alumina phases can bind the chlorides in addition to lowering your permeability. So, permeability is getting lower no problem but your binding of chlorides also is high.

Finely ground limestone as additive:

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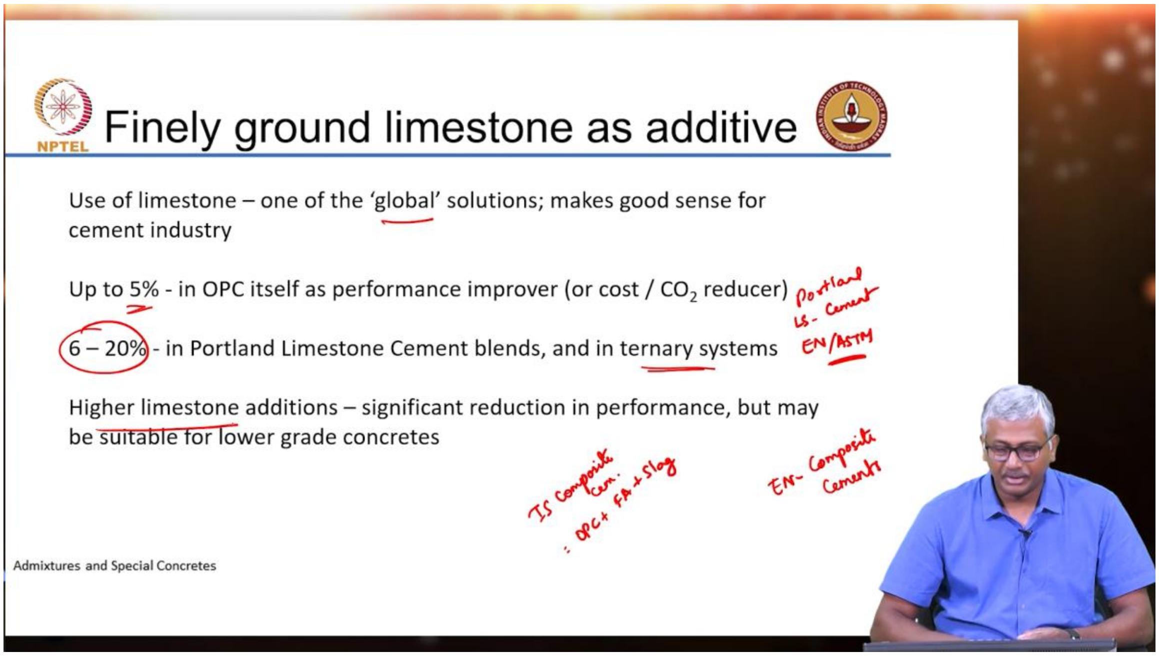

Now the next segment that we will discuss about is on the combination of limestone and calcined clay to replace cement and this has a very good potential to be a new generation mineral additive. But even before that let us just consider the case of plain limestone itself as an additive. Now limestone in most cases is available obviously wherever cement is available because cement manufacture cannot happen without limestone so that is why it is known as one of the global solutions for cement replacement. It is globally available, wherever cement is available limestone will be available. I mean for any country that manufactures cement it also has limestone and generally if you look at any cement standards up to 5% of limestone is anyway allowed in OPC itself as a performance improver up to 5%.

So you do not need any permissions to put limestone in up to 5%. But if you go to the EN standards or the ASTM standards they have standards for what is called Portland limestone cement. In such cases you are allowed 6 to 20% replacement of the cement clinker by limestone. Now what happens is you are lowering the extent of calcium carbonate added in your system that gets burnt. In cement manufacture this calcium carbonate is getting burnt so it is evolving CO2.

But when you add limestone into the system just during grinding you are not burning it, you are just grinding it with the cement clinker. So now you have calcium carbonate in your system where it is not being calcined to remove CO2. So what you are doing is essentially reducing the net CO2 impact of your cement when you move from plain

Portland cement to Portland limestone cement. In fact in all these countries specially North America, Portland limestone cement is the cement of choice these days. People use Portland limestone cement wherever they are expected to use Portland, pure Portland cement.

So instead of pure Portland cement people have shifted to Portland limestone cement because of the CO2 benefits that it gives you. You can also use limestone in these percentages in ternary systems. Ternary system means cement is replaced by limestone plus another additive like what we are going to be talking about limestone and calcined clay, sometimes limestone and slag sometimes limestone and fly ash. EN has a range of cements which they call as composite cements. In IS codes also we have a composite cement.

What is the IS composite cement? It is basically OPC plus fly ash plus slag. The composite cement described by IS standards is OPC, fly ash and slag. No other mineral additives are allowed in this combination. But now there is a new standard coming out for LC3 or limestone calcium clay cement where it will also be included as one of the composite cements but we will talk about that later. Now if you go higher than 20% you are basically reducing the amount of reactive species available in your cement.

So you are going to get significant reduction in performance because your hydration of cement is not going to happen much but nevertheless for concretes that are low grade like your residential construction that use 20-25 MPa concrete. In such concretes it is still possible to make concrete which has very high levels of limestone replacement. So we will talk about that briefly later on.