**Admixtures and Special Concretes**

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**Lecture -27**

**Mineral Admixtures: Introduction**

Good morning, so today we will start off with the next part of our course on mineral admixtures. Most often we also call them as supplementary cementing materials because many of them are used as partial replacement for cement in concrete. But very often we also use fillers which may or may not have any chemical action. So because of that the general term is mineral admixtures, but the more scientifically accepted term for materials that produce additional cementing properties is supplementary cementing materials.

**Cement Hydration:**

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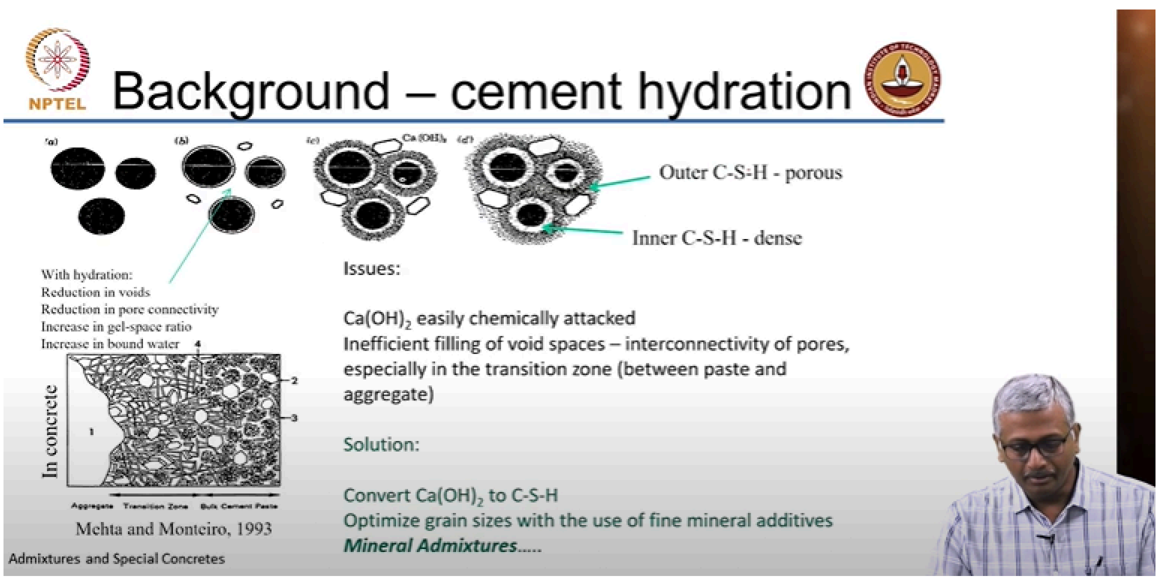


Now we talked briefly about cement hydration in the first segment of this course. The idea is that as hydration proceeds the porosity gradually fills up with the products of hydration. What are these products? Calcium hydroxide and ettringite and probably later monosulphate and other calcium aluminate hydrates. As the filling up of the porosity happens the solid phase in the system increases and the amount of void space decreases. So progressive hydration leads to decrease in the voids content. So in other words it reduces voids, reduces pore connectivity, and increases the gel to space ratio that means the volume occupied by the solids increases with respect to time. And there is also an increase in the bound water content.

What is bound water? Water that is chemically bound in the structure of the hydration products. In CSH the "H" basically is the water that is bound in the calcium silicate structure. Calcium hydroxide if you heat it up at 500°C you will remove the water that is bound within the structure of calcium hydroxide.

Now what happens in regular concrete is also an effect of the way that we mix paste and aggregate and the way that our microstructure variations happen within the system that the zone which is next to the aggregate is usually much more porous as compared to the zone that is further away from the aggregate. We call this concept the interfacial transition zone and very often this is a cause for most of the issues related to strength and durability of concrete. Incidentally it also turns out micro structurally that because of the conditions favorable for crystalline formation there is more calcium hydroxide that is seen in the zones next to the interface. Further away from the interface you see a greater distribution of CSH and other hydration products. But at the interface you see a lot more of calcium hydroxide.

Now calcium hydroxide in itself is a good solid material it blocks pore spaces so it is contributing to the strength but it is also a phase that gets easily chemically attacked. In some instances the quick reaction of calcium hydroxide in a chemical attack scenario is beneficial for instance in carbonation the attack on calcium hydroxide is beneficial because it creates a barrier of calcium carbonate. But in many other instances the presence of calcium hydroxide is a deterrent to a good performance. For instance in sulphate attack or chloride attack when you have calcium hydroxide reacting you produce phases that are either soluble or weak. When chlorides attack concrete the chloride will react with calcium hydroxide to produce what? Calcium chloride and calcium chloride are highly soluble so you essentially increase the porosity of your system because calcium hydroxide is getting dissolved away. If sulphate attacks calcium hydroxide what forms? Gypsum calcium sulphate right gypsum will form as a result of calcium hydroxide interacting with sulphate and this gypsum again is much weaker as compared to your calcium hydroxide or other cementitious phases so you are slowly reducing your strength capacity of the concrete.

So essentially the presence of calcium hydroxide is good from the point of view of balancing pH from the point of view of providing some porosity that is filled up with calcium hydroxide but at the same time it may act as a deterrent when it comes to chemical attack.

So the other aspect is the void spaces are not getting filled up well enough. If the void spaces are not filled up properly then your pores are going to be interconnected and if you have interconnected pores it is going to lead to higher permeability in the system and when higher permeability is there your durability is going to be poorer. So the key to ensuring durable concrete is to ensure that the pore spaces have been sufficiently filled up. Now which is the compound in cement hydration products which can have the most efficient filling of pore spaces? CSH, because of its irregular structure, because of its sheet-like structure and very high surface area it is able to really provide extremely dense packing in your system. On the other hand calcium hydroxide, ettringite are very well defined crystals so unless they pack very tightly they will obviously leave a lot of void spaces here.

So conversion of calcium hydroxide to CSH is a phenomenon that will lead to more efficient filling up of available pore space. That is why conversion of calcium hydroxide to CSH and also the optimization of the grain size by using minerals that are not of the same fineness as cement some coarse some fine. If you mix it up with the cement there is a much more efficient packing of the entire system that happens and this is where the mineral additives become important to use in concrete. So two primary aspects one is mineral additives should have reactive silica that can convert the calcium hydroxide to CSH. Mineral additives should have an optimized grain structure or grain size distribution that can nicely fit into the gaps that are provided by the cement concrete so that you can optimize the packing of the system. Those are the two ways to look at it.

Additionally we also know very well that not all of the cement that we put in concrete will hydrate. Theoretically you need about 0.23 gram of water for hydration of 1 gram cement. That means any water to cement ratio above 0.23 should lead to complete hydration of cement, but this is not true whatever additional water that you add some of that also has to go into the gel pore spaces interlayer pore spaces of the cementitious gel hydrated cement gel. As a result not all of the water is used up for hydration and very often it is not physically possible for all the water to get to all the sites where cement is present because again when you form the hydrated structure you form a barrier to the easy entry of water or easy movement of water. So definitely it is not going to be conceivable for each and every grain of cement to get hydrated and as a result you have a condition where some cement sits there simply as a filler it is not doing anything but cement has a role as a filler.

Now that is a very stupid thing to do right, put cement in there but it is not reacting it is just acting like filler what is the point? There again your fine metal additives are providing an additional advantage by reducing the amount of cement that you put in your concrete. We know that is a justifiable cause of sustainability of the concrete and we are still filling up the pore spaces instead of using excessive cement in the system.

**Sustainability Impact:**

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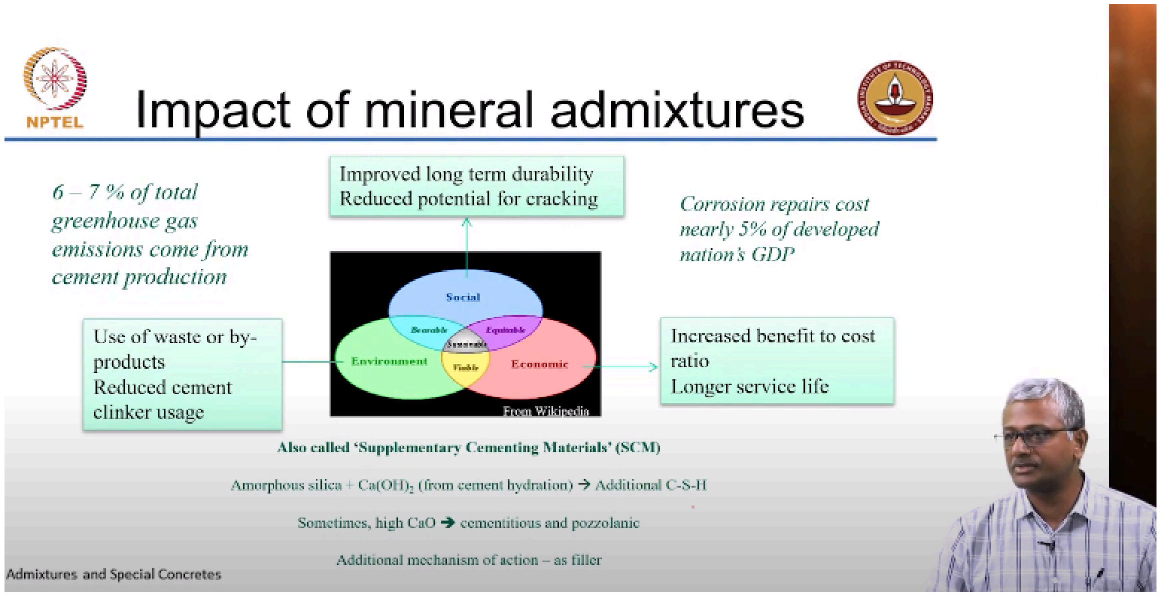


So overall if you look at the sustainability impact of middle admixtures you are hitting on all the right points with respect to the definition of sustainability. If you look at the general definition of sustainability it has to have the process or the product or the technology to satisfy what is known as a triple bottom line.

The triple bottom line of sustainability includes environmental, social and economic effects to be satisfied by the process or the technology that you choose. So environmentally obviously you are reducing cement so that is a big thing for concrete because you know that 6 to 7% of total $CO_2$ emissions are coming from cement manufacture. So less cement used in concrete means less impact of the cement in concrete.

Then of course many of these mineral additives are waste or byproducts they are coming out of other industries and are not going to find useful utilization unless you use it in very large bulk applications and construction is obviously one of the largest applications you can imagine. So you are definitely leading to a much better environmental impact when you replace cement with pozzolanic materials or with supplementary cementing materials.

Socially what produces social impact in construction? Your construction should be durable, your construction should be such that cracking and other problems are avoided. Typically the cracking which happens because of use of higher cement contents is either because of thermal effects or shrinkage. If you can restrict these cracks then socially your technology becomes a lot more acceptable. So certainly mineral additives can help you on that front.

And then obviously the benefit to cost ratio is the scoring point with respect to the environmental conditions, economic conditions that need to be satisfied. Very clearly we spend a lot of money repairing damage of concrete structures due to reinforcement corrosion and very clearly the evidence indicates that the use of mineral additives reduces the potential for corrosion and therefore the required maintenance of concrete structures subjected to corrosion also gets reduced when you use mineral admixtures. So obviously you are leading to a better service life and as a result you also get increased benefit to cost ratio. So on all three fronts related to sustainability, the use of mineral admixtures clearly scores and that is where we have to realize today that it would, I have gone on several fora saying that if you use plain cement in concrete today it is a criminal waste, criminal waste of resources and you are causing unnecessary additional $CO_2$ emissions, you are causing your concrete to have a higher embodied energy. So it is very important for us to now cut down the extent of cement that we use in our concrete.

Unfortunately in many of the uncontrolled construction projects like when you have probably seen your neighbors or your parents build their residences, you would have seen these trucks dump the material on the ground, they cover up the road, does not matter whose construction it is, nobody seems to bother that general traffic has to pass on the road, they will put it on the road. In any case what you see there happening is there is only cement, sand and stone, nobody uses any other material because they do not know. Luckily today in such projects you can only get Portland pozzolan cement, so you are getting automatically a fly ash based cement. So without their knowing they are actually using cement that has fly ash. If you had left the choice to them they would say no, no, no I do not want any waste in the cement.

So today the policy has been dictated such that the trade users, that is the people who do common construction, have to only get Portland pozzolan cement, they cannot buy ordinary Portland cement. OPC is only available for infrastructure usage in our country and that is a very big step towards reducing the cement clinker usage in concrete. So the primary reaction we have already talked about in our overview of cement chemistry is that the amorphous silica from the middle additive when it has amorphous silica combines with the calcium hydroxide from cement hydration to form additional CSH and as we just discussed before additional CSH is better from the perspective of blocking porosity. Sometimes your mineral additive may also contain some calcium oxide, so it may have a cementitious effect also that means the source of calcium and silicon is coming directly from the mineral additive itself like slag for instance. So slag can produce CSH without the need for combination with calcium hydroxide because there is sufficient calcium provided by the slag itself.

Of course the additional mechanism of action is also as a filler, it can act as a filler and produce a concrete that is denser or more compact. Now very often people confuse this increasing density of concrete. Now we are not increasing density in a numerical sense, we are not changing the density of concrete from 2.4 to 2.8 or something like that, that is high density concrete, that is totally different, and you cannot achieve that by replacing cement with mineral additives.

How do you obtain high density concrete? You have to change the aggregate because aggregate is basically 75 to 80% of your mass in concrete, if you change the aggregate to a high density aggregate automatically you change the mass of the concrete or density of the concrete. When we say increase in density just means increase in the packing of your system, that is all, improvement in packing, reduction in voids in your system because all this is happening in the paste, which is only one fraction, so you are not changing the density significantly.

**Sources:**

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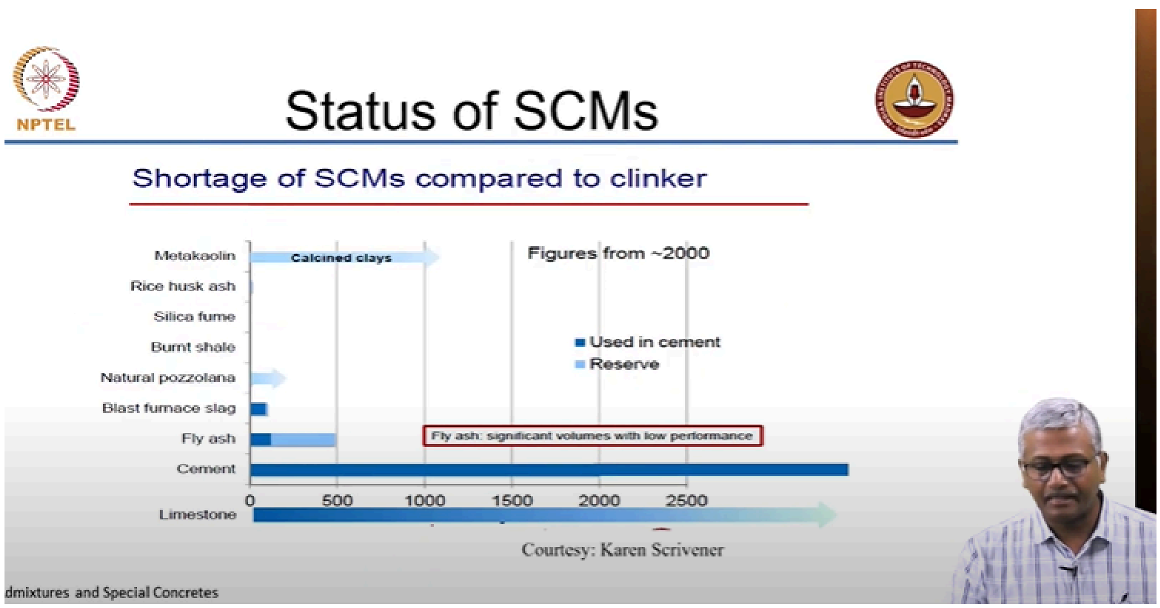


Now one has to be very careful about what are the potential sources of materials that can be used as cement replacement, it has to be clearly something that is available in very large tonnages for a long period of time. If you discover some new material but there is only one deposit in a very finite area that does not really come up as a good solution for a long term usage for cement replacement. So you have to evaluate these sources very carefully, this is data from some time ago but it still is quite valid, obviously limestone is available aplenty.

Only problem with limestone is that the cement grade limestone, that is the high purity limestone is available in a much lesser quantity and in many instances the limestone deposits that may be available may also be within forest reserves. In India it is estimated that out of all the limestone that is available nearly 80 to 85% is in forest reserves which cannot be mined and from the limestone that is getting mined only a small fraction of that is available as cement quality limestone.

So generally high purity means calcium oxide content of greater than 44%, high purity limestone means CaO content should be greater than 44%. In some instances you get even purer forms, in some instances you get less pure forms so as long as both these forms are available in your mine you can mix the two and get it to 44 and above. But what if you are only getting low grade limestone, you are not going to be able to use it directly for cement manufacture.

So limestone as a raw material for cement manufacture may be getting lesser and lesser in quantity as we move forward. I mean people have several sorts of numbers but estimations say that if we produce only OPC today, only OPC no blended cement. If you only produce OPC today the stock of limestone reserves will only last us 40 to 50 years, that is it, after that no concrete. But luckily we have shifted to alternative cements so we can reduce the amount of limestone usage to produce the cement. But anyway limestone is available so as long as limestone is available obviously cement is available but compared to cement if you look at the quantities of the raw materials that are available as supplementary materials, fly ash is available a plenty, there is a lot of fly ash available.

But a lot of this fly ash is not of the right quality, the significant volumes are available but much of that is actually low quality. So today a lot of research effort in major universities around the world is about how we can reclaim the fly ash of poorer quality and process it to make it high enough quality. You may have seen in thermal power plants they collect fly ash but they also have this bottom ash which does not fly out, I will talk about that. Lot of the fly ash is basically getting dumped in ponds next to the thermal power plant because you cannot dispose of it in a solid form, it is a very fine material, it will start flying off so you have to mix it with water and dump the slurry in a pond. Now these fly ash is from the ponds they may have some heavy metals which will slowly seep into the groundwater and that is something which can cause contamination of the groundwater and that is an unacceptable thing.

So again one has to be very careful about how to utilize this fly ash that has already been dumped, how can we reclaim it and make some useful utilization out of it. So fly ash is definitely available, it will be with us as long as thermal power plants are a reality. How much of India's power is given by thermal power? 60% of India's power comes from burning coal. There are several countries around the world which have cut that down significantly realizing that that is a big source of atmospheric pollution. You are cutting down the thermal power plants, they have started going to other power streams.

Of course India is investing largely into unconventional means of power also like solar and wind. We have really done very well in terms of actually increasing our capacity there but because we are developing at such a fast rate we cannot do away with our thermal power plants. They will be there for a long time to come. Even if there is a coal shortage we will import coal and still produce power using these plants. So the power demand is going to be so high in India because we are nowhere near the power consumption of many of the developed countries.

So we are going to be a power hungry nation for a long time. Now because of that thermal power is going to be there so fly ash is definitely going to be there in India. In countries like the US, fly ash availability is already becoming a problem because many thermal power plants are shut down and the US is blessed with several different types of natural resources. They have gas, they have other forms of power for instance they have lots of reserves obviously of oil so they can actually even burn oil and make power. So for them it is not really a big deal because the country is so vast and they have to support a population that is one third of our country, actually now one fourth of our country. The size of the US is nearly 7 times the size of India area wise and the population is one fourth. So they have 28 times the advantage of India.

So anyway, what I wanted to say is that you are facing a very different situation in these places. Now blast furnace slag is obviously available wherever steel is getting manufactured and this blast furnace slag the quantities are obviously going to be limited as compared to that of fly ash. Steel manufacture produces slag approximately. I think if I am getting my number right about 1 ton of processing of steel of actual steel that you get in the end produces an equivalent amount of slag as a material. So 1 ton of slag from 1 ton of steel. Now that slag has very good use immediately in construction as a replacement material for cement and we will see that it is used in much larger replacement levels also but there are only limited quantities available. Natural pozzolana, volcanic ash, siliceous volcanic ash that is where the term pozzolana basically is from where?  It is from a place called Pozzoli in Italy. So they use the ash from the eruption of Mount Etna. That was a long time back they used the ash as an ingredient in lime water and found that it enhances the properties of lime water. That was the first known use of pozzolana and then of course the Greeks also did a lot of work with pozzolanic additives, ash and stuff like that and from there on of course it spread significantly and the name itself pozzolana basically comes from Pozzoli in Italy.

Now natural pozzolana is available everywhere. The only thing is we do not know where it is available.  Why? Because these are geological events, eruption of volcanoes I do not know if you are familiar with some of the later eruptions that happened in the last decade. What happens is the ash is very light so depending on the nature of the winds the ash can form clouds and get carried to a distance which is far away from the volcano and ultimately this ash basically comes in deposits on the ground and geologically these events may happen in gaps of several tens of thousands of years. So the ash deposit may be lying underneath a major overburden over which people have been living for centuries now. So something like this was also found from a location in Andhra Pradesh where we found the ash that has been deposited from the eruption of a volcano in Indonesia long time back 75,000 years ago this eruption has happened and carried the ash all the way up to India and we have this ash deposited and I think they were doing some of the mining in the region that they discovered this material and ultimately when we evaluated this material it had very good pozzolanic properties. It is a volcanic ash, volcanic ash is almost 100% amorphous silica so you can imagine it has got to have very good pozzolanic characteristics and so this pozzolanic material is available but we do not know where it is available.

Burnt shale again this is one way if you have shale deposits you can actually when you burn them to produce burnt shale is also used for production of power and burnt shale can also be a good source of silica but then the quantities are very small. Silica fume again is obtained from manufacture of or production of silicon metal from ferrous silicon alloys and the silica fume again is collected in quantities that are not large enough to really make a major difference. Rice is cash processing. You remove the husk and burn the husk because it gives you a lot of energy but then the ash that remains has very interesting pozzolanic characteristics because of the silica that is present in it and that ash can also be used as cement replacement material. But all of these are present in extremely small quantities and not really utilisable to a very large extent.

One thing that is possibly available is clay. Again we need to have a clear estimate of how much clay is actually available in the earth's crust and where all it is available in a form that can produce material that is reactive and realisable as a cement replacement. So what we need to do is obviously we cannot use clays directly in concrete because what would clays do directly in concrete? Some clays are of the swelling type obviously you cannot put too much swelling material in your system. Kaolinity clays are not necessarily the swelling type but still putting a soft material like a clay in your system is not really going to help a lot. If you can calcine it you release the alumina and the silica and these become available for pozzolanic reaction and then you produce calcium aluminosilicate hydrate which has excellent characteristics as a pore filling CSH phase which can lead to much improved performance. So again metakaolin or calcined kaolinite clay have a very large potential for utilisation as supplementary cementing material and this is something that a lot of the people in the world are now working on different types of calcined clays because you can always not get kaolinite clays all the time. So sometimes you have to work with mixed sources of clays and that may affect the kind of performance that you get out of these clay systems. .