Advanced Concrete Technology
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Lecture - 17
Chemical Admixtures – Part 5

In the last lecture we were talking about set controlling chemicals and air entraining chemicals. Today we will have a small discussion on speciality admixtures. So very often we come across situations in concrete technology where we need certain very specific types of performance.

For instance, when we have to control the segregation of highly flowable concrete that is one instance where we need to actually come up with the slightly different methodology to design the concrete mixture. One possibility is to include more cementitious materials larger amount of fines in the system that will enable a better stability of your system The other thing is to actually include another type of chemical, which can additionally impart that attribute of improving the resistance to segregation. The other aspect could be for example we want to reduce the shrinkage of the concrete mixture. One way to do that is to obviously increase the extent of aggregate in your system; that we have discussed before that the primary component that imparts resistance to dependant deformation is the aggregate in the concrete. The more aggregate you have the better the resistance to deformation. But at the same time there are certain mixes for which you cannot do that because when you are going for higher performance concretes you need to ensure that there is sufficient cementitious content also in the system. In those cases, when we try to restrict your shrinkage it can be effectively done by a chemical which can be added to the concrete like a shrinkage reducing admixture.

These are specific chemicals that are not used on a day-to-day basis, but can have significant amount of impact on the kind of quality that you can get from different kinds of concrete.

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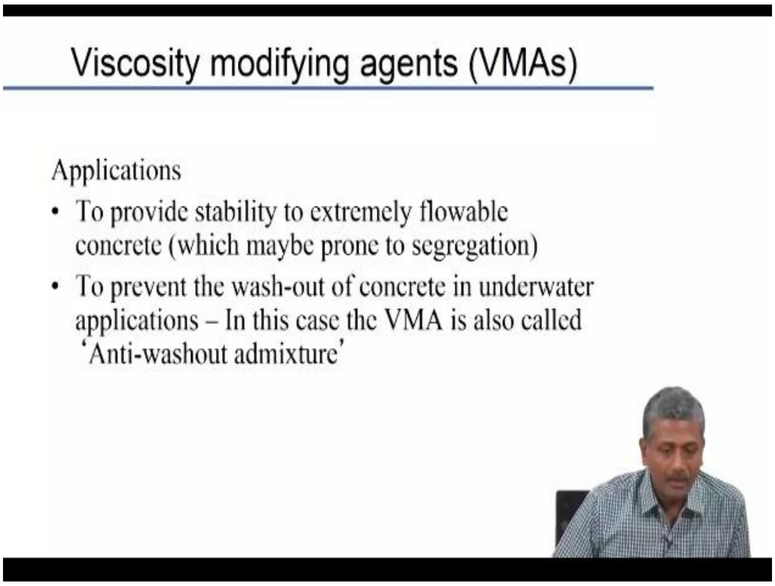

Let us start our discussion with viscosity modifying agents. The primary purpose for which we use VMAs today is to improve stability of the extremely flowable concretes like self-compacting concrete. We know very well that self-compacting concrete can compact under its own self weight. It has very high degree of flowability that is brought about by the use of superplasticizers. We also do an efficient design which gives us the best type of flowability possible. But we also know that when flowability is high there is also a danger of separation of the ingredients and that happens because our paste viscosity is not large enough to actually control the settlement of the aggregate. Now we will discuss this phenomenon in more detail when we get to the fresh concrete lecture. But in general in normal concrete we have lot of aggregate. So when you pour this concrete into a container if you have lot of aggregate, the aggregates help to keep the other aggregates from settling so that is otherwise known as lattice effect. Since you have a lot of aggregate in your system each aggregate prevents the next one from settling down.

But when you go to concretes that are more specialized which have less amount of aggregates and more cementitious paste there the chances of settlement of the aggregate are large and that needs to be avoided by ensuring that you have sufficient viscosity in the paste to eliminate or to reduce the extent of settlement of your aggregate and that is brought about by viscosity modifying agents.

In the past when VMAs were originally developed the first use of these was is anti-washout admixtures. In certain applications the concrete has to actually interact with water for example when you do a tremie concreting for pile there will be water inside the pile. So when you do the concreting water has to get displaced by the concrete and the concrete should be of such quality that the water does not mingle with the concrete and washout the concrete. So because of that you need specific cohesive ingredients to be included in your concrete. That was the first instance of using VMA like an anti-washout admixture. In the past it was also called an anti-washout admixture, but today we commonly know this as a rheology modifying additive or a viscosity modifying agent.

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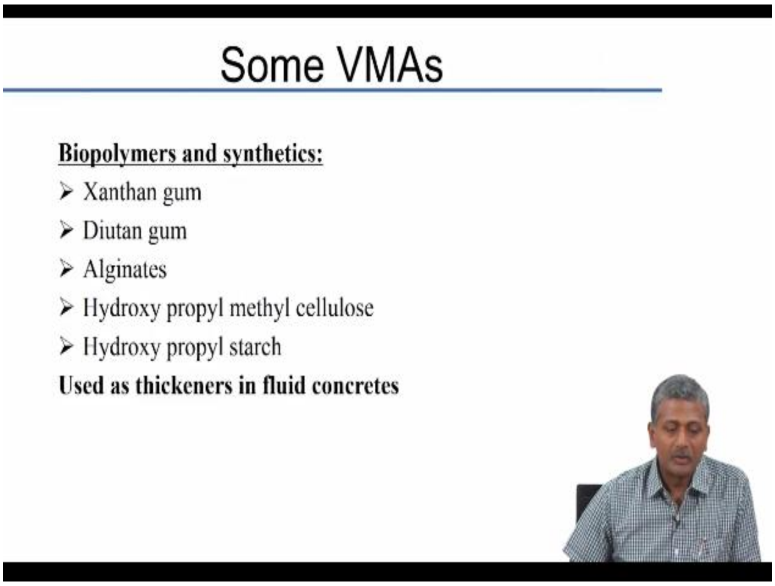

So these compounds are basically gums. The primary objective is to make the concrete cohesive. We want to prevent the interaction of concrete with the water that is in the surrounding medium, or in the case of segregation resistance we want to ensure that the concrete is cohesive enough that the aggregate does not start settling out.

So these are different types of gums, essentially water soluble polysaccharides like xanthan gum, diutan gum, alginates, hydroxypropyl methyl cellulose and hydroxypropyl starch. These are thickeners just like when we make soup we use thickeners like corn starch or corn flour.

Just like that we can add these ingredients to provide stability to the concrete essentially increasing the viscosity of the continuous phase so that the discrete particles of the aggregate have some difficulty in settling. So what is the mechanism of action?

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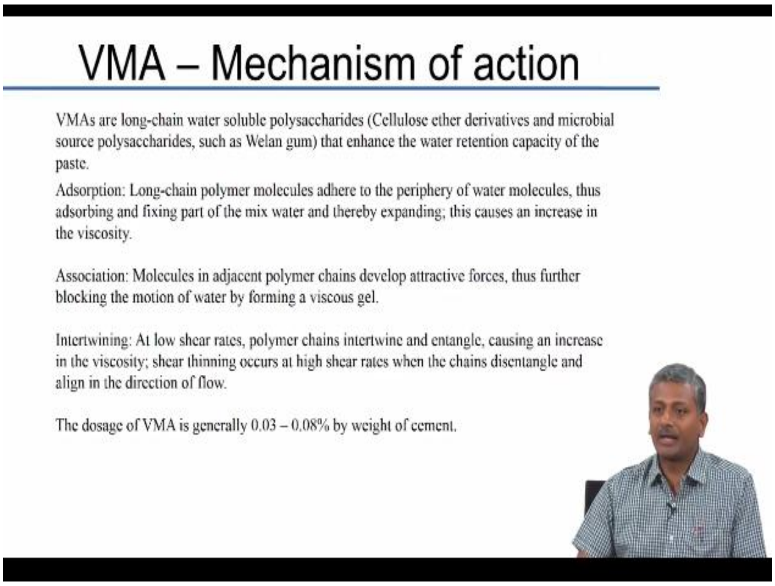


There are several theories suggested. These are polysaccharides which are water-soluble polymers and they have long chain molecules. So to look at one of the strategies of understanding the mechanism of these materials; one mechanism is intertwining. The molecules of the VMA which are long chain hydrocarbons or long chain polymers they start intertwining or they start entangling with each other. So when they are entangled they have a cohesive network built in the system, but at the same time when you start vibrating this concrete or when the concrete is flowing these entangled chains get disentangled and straighten up. When the chain straighten up there is very little resistance to the flow. In other words, when you are applying a very high shear rate like for example you are pumping the concrete for instance; you want the concrete to flow as easily as possible. So when you are pumping the concrete or when you are pouring it these molecules tend to get disentangled and align themselves in the direction of the flow. So that causes some ease with which you can actually end up flowing the concrete. But once the concrete comes to rest the chains get tangled again and lead to an increase or build up in the viscosity of your system, that prevents the aggregates from settling.

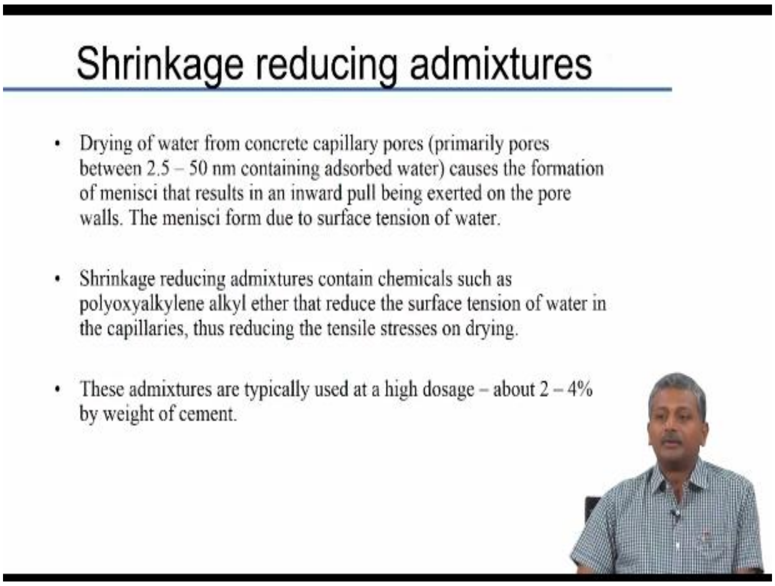
There are other mechanisms also suggested such as adsorption in the cement particles sometimes, but more commonly, it is the association of the water molecules. What essentially is done is these molecules in the polymer chains develop attractive forces and trap the water inside forming a viscous gel, causing the motion of water to be blocked. So the concrete will become less workable. Superplasticizer were freeing up the water and causing more workability. So if a gum is used in the system and it starts blocking the water from mingling easily then obviously it is going to reduce the workability of your system.

Secondly if there is also the adsorption mode of action,i.e, adsorption of the VMA molecules on the water molecules occurs this will lead to an expansion of the VMA molecule. This causes an increase in the viscosity. But with the same kind of mechanism these VMA molecules can as well get adsorbed on the cement particles. So they will have a competition with the superplasticizer to adsorb on the cement particles. So that is why they can again interfere with the action of the superplasticizer if their mode of action is based on adsorption.

So for the most part what we have is these polymers which are active ingredients in VMAs tend to have the mechanism of action in which they actually do this intertwining sort of mechanism. At low shear rates you have entanglement of the chains, but at high shear rates when you are trying to push the concrete they start getting disentangled and align themselves in the direction of the flow.

So that is the reason why flowing concrete does not give too much resistance to the flow but once the concrete comes to rest it builds up an internal structure or an internal viscosity buildup which leads to a reduction in the potential of segregation. So that is basically the principle of action of viscosity modifying agents and generally we add very little amount of these, about 0.03 to 0.08% by weight of cement.

These cause extremely bad side effects if you use them in very large dosages. One of them is the reduction in your workability of the concrete. The other could be retardation of the concrete setting. These could retard significantly your concrete setting these are polysaccharide, so it is like a sugar. So this is also going to cause retardation in a long term. So you have to be, be extremely careful when we use very high dosage of superplasticizer and along with that we also use a VMA, we may end up retarding the concrete system significantly and very often such concretes may not set for 3-7 days' even. **(Refer Slide Time: 09:46)**



The other speciality admixture is the shrinkage reducing admixture. Shrinkage happens because there is free water present in the concrete which has to dry out if there is drying conditions surrounding the concrete. When this water starts drying out from small pores it leads to a very high capillary pressure in the pores and that capillary pressure is what causes shrinkage related cracks.

If you have very high capillary pressures your movement of water within the capillaries can result in shrinkage related cracking. To avoid that what if you come across a scenario where you make it easily for the water dry out. In other words, you lower the surface tension of the water so that when the water tries to dry out of this capillary pore you also reduce the capillary pressure.

As in the capillary pressure equation, it depends a lot in the surface tension of the liquid in the capillary. If you bring down the surface tension the capillary tension also comes down. Lower capillary tension implies lesser shrinkage related cracking, okay. So again essentially what the SRAs or shrinkage reducing admixtures are doing is that they are lowering the surface tension.

So just to look at a pore on the surface of the concrete; suppose there is water inside the pore and when this water tries to dry out, water forms a meniscus inside the pore. It forms more and more of a convex meniscus as it starts drying out and because of that it is trying to pull the pore walls in. In other words, the paste that is in that region is now being subjected to tension. So that causes appearance of a crack there. So that is basically related to shrinkage related cracking.

So when this happens, if you reduce your surface tension of the water you load capillary pressure and that leads to a reduction in the overall shrinkage that happens and the kind of compounds that are typically used are again organic chemicals like alkyl ether, or sometimes even a polyethylene glycol could be used as a shrinkage reducing admixture. Today the superplasticizer molecules with PCE can be suitably altered that the side chains can actually have an inclusion of the shrinkage reducing element also. For example, polyethylene glycol is often found in side-chains of superplasticizer molecules that are based on the modern technology of PCE. So there you can have a dual component of super-plasticizing effect as well as shrinkage reducing effect. So modern chemicals can be suitably altered to bring in all these effects together. These chemicals which are used as SRAs are typically very expensive because they also have to be used at high dosage as they need to spread across the entire volume of your concrete.

So you need to use them at very high dosage for them to be effective and as a result they increase the cost of your concrete significantly. So if you have to use these speciality chemicals in concrete you have to have sufficient justification that you are not been able to do it with other conventional techniques. VMAs are not very expensive. VMAs can be easily found for a low cost, but SRAs are significantly expensive.

SRA dosages are in terms of the liquid; however, but when I talked about the VMA dosage it is in terms of the solid. It is because most VMAs are available in terms of solid formulations of the gums which could be stabilized by making them into liquid solutions also. Construction chemical industry basically want to sell all their products as liquid so that onsite there are no difficulties in dispersing the chemical. If you have to disperse a small amount of powder inside your concrete it is going to be quite difficult, but if you have to disperse a liquid all you have to do is mix it with the mix water and it can get dispersed quite easily. So VMAs also although here I am talking about the dosage in terms of the solid VMAs also are available as liquid solutions from most of the construction chemical manufacturers.

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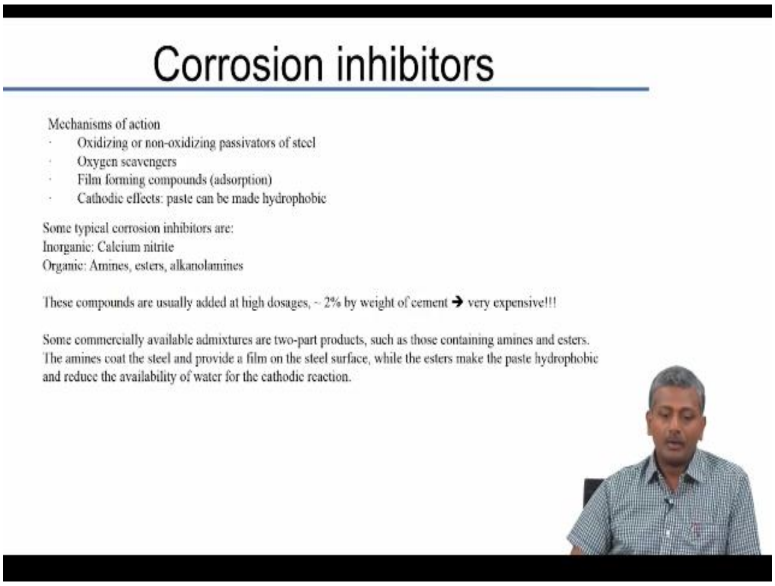

Tthe other class of speciality chemicals are corrosion inhibitors. We will deal with the problem of corrosion in more detail then we actually come to the durability chapter, but I just wanted to give you an idea that we can include chemicals in concrete to bring about some resistance to corrosion of the reinforcing steel. Reinforcing steel is protected in the alkaline environment of the concrete and anything that causes a destabilization of the alkaline environment around the steel will lead to corrosion. Corrosion inhibitors are again chemicals that are added to the concrete so that they can create mechanisms that are more protective for the steel as opposed to what is there is ordinary concrete. So what are these mechanism of action? One is they can passivate the steel. In other words, they can interact with the iron on the surface of the steel and create some sort of a film or passivating film that can protect the steel from corrosion. Alternatively, these compounds can even adsorb to the surface and simply lead to the formation of a film that makes it difficult for the interaction, which leads to corrosion.

The other sort of methodologies by which you can have these compounds acting is ‘oxygen scavengers’. In other words they tie-up the oxygen that enters the system and for corrosion process, oxygen and moisture are both required to be sustained.

So if you are able to eat up either one or both of them, for example you can also make the paste hydrophobic or waterproof that prevents the entry of water into the system. So if both oxygen and water are not available in your system, corrosion reactions may not be able to propagate further. So many of these chemicals that are used can have one or more of these types of effect.

The types of chemicals that are used inorganic chemicals the most popular one is calcium nitrite. We also saw this calcium nitrite earlier as an accelerator. Calcium nitrite is also a very effective corrosion inhibitor, okay and the organic chemical include amines and alkanolamines and these can be more effective than your inorganic inhibitor which is calcium nitrite.

When you go deeper in to the study of corrosion inhibitors you will find that they are of 2 types anodic or bipolar. Anodic means inhibitors that are trying to prevent the anodic reaction. So in anodic corrosion there is a corrosion or oxidation of the steel which is basically iron oxidising to Fe^{2+} giving away 2 electrons. So the anodic inhibitors are the ones which are trying to suppress this reaction from happening.

But the bipolar, these are the ones which are going to be more effective because they are going to be suppressing the anodic reaction at the same time they will have these effects of scavenging the oxygen and preventing the moisture access to the steel site. That means they are active both on the anodic and cathodic sites.

So that is why the bipolar inhibitors, which are more the organic inhibitors, are a lot more effective than the inorganic inhibitors. But calcium nitrite is much cheaper than any of the other inhibitors that is why it is quite popular to be used as a corrosion inhibitor.

Now very often when we go to these construction chemical manufactures website they also talk about something called a migrating inhibitor. So far we have been talking about chemical admixtures, that means these inhibitors are added to the concrete mixture directly, but you can also have a different class of chemicals called migrating inhibitors. How these function is that even in concrete there is already in place, concrete that is hardened, what these chemical manufactures claim is that you can actually spray or brush the chemical on the surface of your concrete and they will migrate to the sites of the reinforcing steel and lead to a protection by one or more of these mechanisms.

There are mixed opinions about whether these are actually effective or not, but all the data that you get from construction chemical manufactures always say that these are really effective. That sounds almost like science fiction mostly that you have these chemicals applied in the surface they get to the steel level and then start protecting the steel, but some data seems to show that that does indeed happen.

But some other data tends to show that there is nothing substantial that can be gained out of this. Interestingly in our construction projects people have started hearing about corrosion inhibitors and often times you get specifications when the real intension is to use a admixture that means something that needs to be added to the concrete but the specification is based on migrating inhibitor.

That is, the contractor is going to be using a corrosion inhibiting admixture that means the person is going to actually mix this inhibitor into the concrete, but the specification says that you have to test the properties of a migrating inhibitor. This I have come across nearly 4 or 5 times. People have come to us with this question that how do we test this now. But we go back to them and ask them okay how is it that you are using this material, they say that no we are mixing it with the concrete then why are you testing this migrating inhibitor. You should be testing properties of the corrosion resistance brought about by admixed concrete but unfortunately the lack of standards in test methods makes it very difficult for us to implement these regulations in practice.

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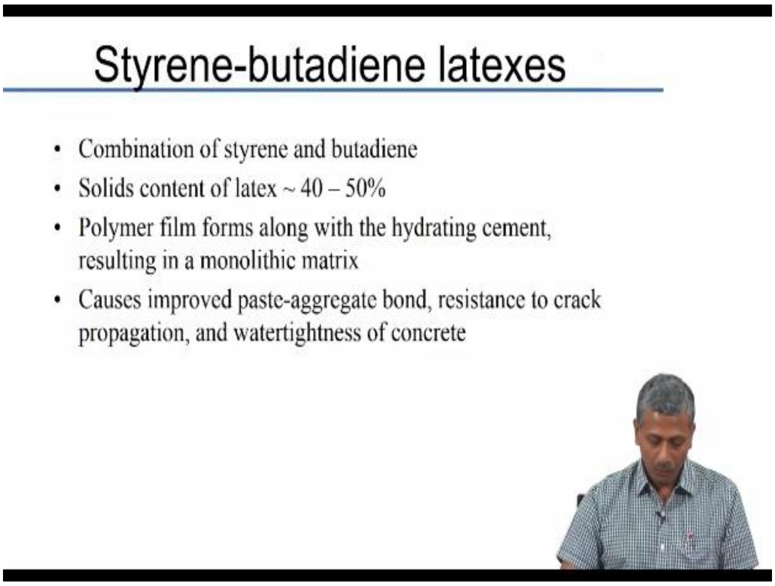

One common ingredient that is used as an admixture especially in repair mortars is latex. Latex is essentially a suspension of styrene-butadiene and water. Styrene-butadiene is nothing but rubber, and you prepare a suspension or an emulsion of these in water and typically, these have about 40-50% solids, okay. So what happens is when you have this material mixed fresh it is a monomeric material. When you put this into concrete along with the hydration of cement that leads to the formation of hydration products the latex also polymerizes. It makes itself into a polymer film and the rubber is that it will give more flexibility to the system. So essentially what the latex ends up doing is provides the concrete, the resistance to cracking.

Therefore, when you apply a repair mortar or a patching mortar on the surface of concrete, you expect this patching mortar to have some flexibility because the concrete will undergo deformations when it is shrinking or expanding. Therefore, if the layer that you apply on the top is very rigid and, if the base concrete starts expanding or contracting, the layer that is applied on top will crack.

So very often when polymeric formulations like latexes are used inside these repair mortars it gives them the flexibility to undertake or to sustain the movements that are there in the base concrete. Latex also improves the paste-aggregate bond and water tightness of the concrete because of which latex modified concrete for a long time has been used as overlay material for bridge decks that are exposed to chloride bearing environments. The concrete that we prepare with this is called latex modified concrete or polymer modified concrete, which means it is a regular concrete in which you have used some modifying polymer, okay.

And most of the time the polymer modification that you do in concrete is essentially the application of latex in the concrete. What does the term polymer concrete mean? There are some polymers which are embedded into cracks for instance like poly methyl methacrylate you can embed that into cracks. But you are not mixing it with your regular concrete ingredients; there is no cement in that system. So polymer concrete is the concrete in which the cement itself is the polymer. The monomer is mixed with the aggregate and it polymerizes in place. So that is basically a polymer concrete. You have seen that there are some flooring systems that are put on top of regular flooring systems to provide extra degree of stability and hardness of the floor. These flooring are typically not done with cement, they are done with some material called epoxy. So epoxy is mixed with aggregate and simply laid on the surface that provides a very high degree of resistance to damage because of falling objects and accidental hits and so on and so forth. So polymer concrete is where no cement is there, but polymer modified concrete is regular concrete where polymer has been used as an ingredient in the system.

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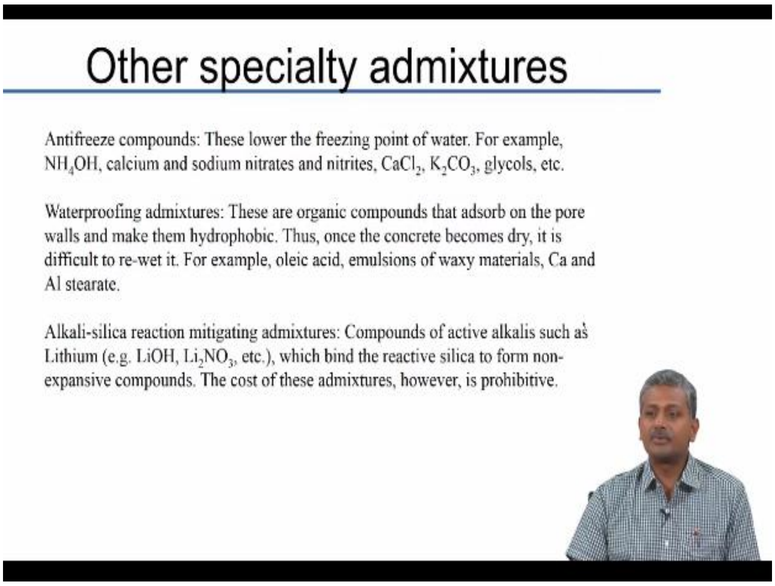

Finally to end this chapter, some other speciality admixtures can also be used like anti-freeze compounds. When you are doing construction in extremely cold climates, you can add specific chemicals that will help sustain the reaction of the cement with water. Typically, for temperatures less than -10°C there is no reaction between cement and water. Therefore, you add chemicals, which are essentially these ammonium hydroxide, calcium and sodium nitrate and nitrites, calcium chloride, potassium carbonate, glycol and so on and so forth.

What do you intend to do with that? When you add these chemicals, there will be no freezing of water because of which you will maintain the reactivity of the cement water system. So they are basically freezing point depressants. All these chemicals will depress the freezing point and prevent the freezing of water that enables the interaction of water and cement.

About water proofing admixtures I have presented only 4 lines, but actually there are people who can conduct an entire course, talk to you about different types of water proofing treatments that can be there in the construction industry. However, as admixtures were are still talking about only those chemicals that are added into the concrete, but there is a whole lot of water proofing treatments that are much beyond the scope of even admixtures.

There are water proofing systems that can be applied on the surface of the concrete or as layers between the concrete and so on and so forth. You have learned about some of these in your detailing for example when you design the flooring of any building you will also have a layer called damp proof course. There are also specific designs of the water proofing for the roofing that we do. We do these weathering courses and we include the damp proof course or water-proofing course on top of the terrace. All these are specialized systems that require the understanding of several different types of polymeric systems that are in practice today. We are not going to be looking at that. I just wanted to give an example of water proofing chemicals, which can be added to the concrete.

There is essentially organic compound that are adsorbing on the pore walls and making them hydrophobic, for example, wax. If I do a wax treatment on a table, and if I pour water on it, water will not stick to the table anymore; it will roll off because the wax essentially makes the water non-wetting. It makes the surface non-wetting.

So these chemicals adsorb in the pore walls and prevent the entry of water because the water cannot enter a hydrophobic sort of a pore. So, once the concrete becomes dry you cannot rewet it again. External water will not be getting absorbed into the concrete. So the kind of chemicals that are used are oleic acid, emulsions of waxy materials, calcium and aluminum stearate and so on.

So these are water proofing admixtures that are added to the concrete. One thing which I have not mentioned here which may become quite popular when you guys practice is the crystalline water proofing admixtures. As per the claims of the construction chemical manufactures, these crystalline water proofing admixtures are those which are added to the concrete and whenever they come across a void or a pore or a space where growth can happen they start growing into much larger crystals and that sort of ends up blocking the pore. Sounds like science fiction again right? Xypex, penetron several of these chemicals are available in the market, which claim that they can form these large crystals inside pores or even if there are cracks in the concrete these chemicals apparently can occupy the cracks and start forming large crystals which blocks the pores and cracks. Of course, if you are causing blockage of your pores and cracks you are going to be improving your water tightness of the concrete. You are making your concrete waterproof.

But, is the expansion large enough that it can crack the concrete? typically not. I have not seen examples of it cracking the concrete. However, we have also not yet seen proof of it actually being effective in concrete as far as our lab studies are concerned. As far as the literature supplied by the construction chemical manufacture is concerned it all shows excellent performance of these chemicals but when we have tried to use these in our concretes we have not really seen the same kind of effect as what is being claimed in the literature. So we probably have to arrive at the correct mode of testing which can actually bring out the performance of these chemicals. So I hope you understand the distinction between the watertight system and water proof system. A watertight system is one, which can prevent the entry of water but will fail when there is water pressure. So if there is only some absorption of water because of capillary suction and things like that, a watertight material can prevent that from happening. But a waterproof material on the other hand will be able to actually prevent entry of water even if there is substantial hydraulic pressure. So for example in the case of water gushing into a structure, if you have a water proofing material in your concrete it will prevent the entry of this water completely even if there is pressure maintained on top.

For the most part when we do engineering of concrete structures we engineer the structure in such a way that, if there is going to be likely high water pressure we provide a channel for this water to flow through. That does not mean you make your concrete porous and allow the water to come through the concrete because then it will be a danger for your reinforcement also.

You provide channels or provide alternative path for the water to achieve through the concrete system or you prevent completely the entry by providing an alternative flow out region. The issue is if you do not do this and only rely on the performance of these crystalline water proofers you are probably not going to be seeing the kind of effectiveness that you want.

One example of this is that in Chennai Airport, they were building the utility tunnel just outside those airport terminal buildings, which are 1 km away. So they had to connect all the electric and all the other supply lines of these new terminal buildings through a utility tunnel that came out right in front of the buildings.

This utility tunnel was built with concrete which was of M30 or M35. These had a chemical called ‘Penetron’ in it. Because the contractors thought they were using a water proofing chemical in the concrete they sort of avoided the other systems which are important to keep water penetration in place like the use of water bars for instance. And because of that what happened is when there was the 2015 flood, a lot of water actually started gushing in into the utility tunnel. The problem there is now utility tunnel is carrying many electric cables and things like that, if lot of water gets in then you obviously have a problem.

So water was actually seeping in through the concrete because there was no other alternative for the water to flow which was provided in this tunnel. Because they thought, it was a waterproof concrete, water was simply not come in through the concrete, but you cannot stop flow of water; it will try to find a path wherever there is weakness.

So it was actually gushing through the concrete and they tried to plug the concrete by putting grout into the concrete. Now the problem is grout you can apply any pressure that you want but grout can only go if there is a cavity or a void present for it to go. If the concrete does not have cavities or voids grout will not go anywhere. So again grouting did not show to be quite effective and so on.

So ultimately, they realized their folly in that they were not doing good engineering practice they were trying to think that the use of a good quality material or an additive which imparts that good quality in the system was enough to actually bring about the water proofing nature. But the same thing happened even before during the construction of the terminal buildings also. So they were building a retaining wall, which was the wall of the basement here.

This basement retaining wall obviously has to be extremely crack free otherwise water will simply seep in and so on. So when they build the retaining wall they started seeing that after about 3 or 4 days there were regularly spaced vertical cracks that were coming in the system. What is the first thing that you can think of when there is regularly spaced vertical cracks in the system? Shrinkage!

And for shrinkage obviously if you do not provide with additional steel in the horizontal direction, the cracking is going to be substantially large and that’s indeed what happened in this case and without providing joints and without providing adequate steel to take care of the shrinkage cracking they provided a very long wall.

But the client was simply not willing to accept this fact and all they were doing is blaming the contractor that they had used slag based concrete. I mean what kind of a reasoning is that?

Because they are used to only ordinary Portland cement concrete. So when we started explaining this to them they were only of the opinion that this cracking happened because the same ingredients as regular concrete was not used.

We used slag in the system, so the contractor had to go through a lot of convincing. So they tried to get us in. From our side also we had 2 of us actually going and inspecting these cracks and telling them exactly what had happened. But the report was thrown out because they were not willing to accept the mistake on the part of the designer. So in real, there are many forces that play. Very often you do not get the correct solution in the field.

Finally, alkali-silica reaction mitigating admixtures are those chemicals that mitigate alkali-silica reaction or reduce the effect of alkali-silica reaction. In the aggregate chapter we talked about different types of aggregate that can react with alkalis to result in an expansive formation of a gel in the system that causes cracking in the concrete.

So what these alkali-silica reaction mitigating admixtures do is that they reduce the expansion caused by the gel formation. Here essentially what you are doing is choosing compounds that are lithium based, lithium hydroxide or lithium nitrate. So lithium occupies the position in the periodic table in the same column as sodium and potassium. It is a much lighter material and it is much more reactive as compared to sodium or potassium. So before your reactive silica combines with sodium or potassium the lithium based chemicals are able to react with the reactive silica and bind them into a non-expansive gel.

That creates reduction in the overall expansion that happens with reactive aggregate. But lithium based compounds are prohibitively expensive and again you need to use a lot of them to actually make possible resistance to alkali-silica reaction. You will see later in our next chapter when we talk about mineral admixtures that simply replacing cement with the fly ash or a slag or a silica fume would be a good enough way to actually reduce expansion caused by alkali-silica reaction.

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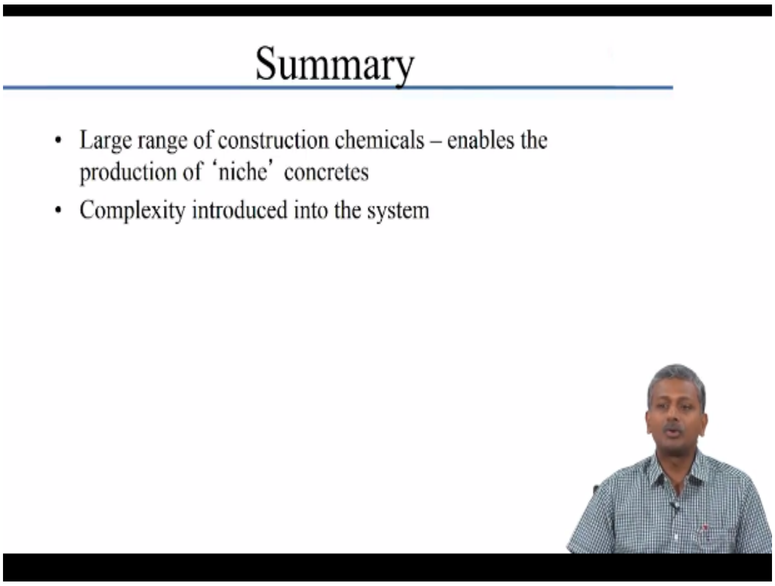

So in summary we have talked about a lot of different types of construction chemicals. It is important because these days we have to deal with construction projects where many concoctions of different types of chemicals are used. Combinations of more than 2 or 3 types of chemicals maybe there is the same concrete for instance.

For instance, if you are designing concrete for the North Atlantic region which is subjected to problems like freezing and thawing, you have issues of demand of high workability and so on so because of this you will often have a combination of different kinds of compounds. For example, you will have the superplasticizer, you will have an air entraining agent. You will probably even have viscosity modifier if you have a flowing concrete for example.

So depending up on the need of concrete you can actually come up with a requirement for different types of construction chemicals. Please remember that every time that you add a new ingredient to your concrete you are making it all that more complicated. The only way around trying to sort out these issues that can arise because of complexity is by experimentation or testing. So again we come back to the same old principles that without doing your trial mixes in the field or in the lab you cannot really get any information whether the given combination of materials will work or not.

So what we have learned in this chapter will enable us to make the right selection with respect to the type of materials that we would like to use for given situations. But whether the situation or the kind of demands of concrete in that particular situation will be met or not you can only get that by proper testing of the concrete mixes.