Admixtures and Special Concretes

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Lecture -24

Chemical Admixtures: Corrosion inhibitors, Shrinkage reducing admixtures

Service life:

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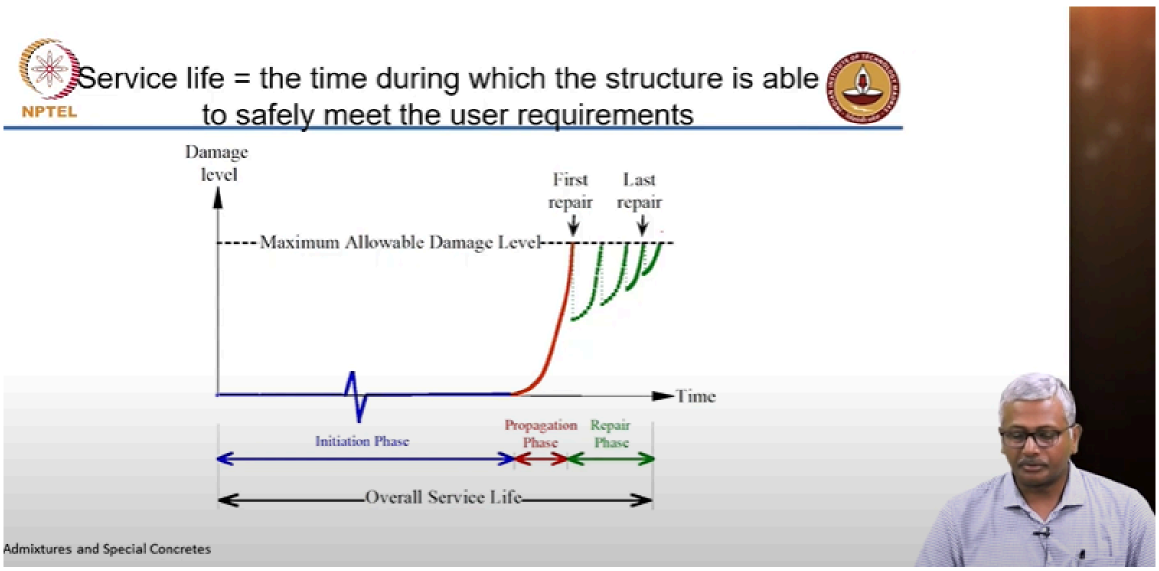

So, again just to show you a more generalized approach, so you have the initiation phase and then the propagation phase. The propagation phase initially has a less slope and then the slope increases significantly. So, if you do an inspection, timely inspection, you can then ensure that you can bring down the level of damage below what is maximum allowable in your system, repair it so that you get a fresh lease of life for your reinforced concrete structure, and extend the service life beyond. And then do periodic repair that continues to extend the service life of the structure. So, obviously it is very important in corrosion, if you are in those final stages you need to do regular maintenance, regular inspections and decide on a strategy that will further extend the service life. But what we want to look at in more detail is the initiation phase and that is where we will make the most difference when it comes to increasing the service life of the structure.

Critical Service life parameters:

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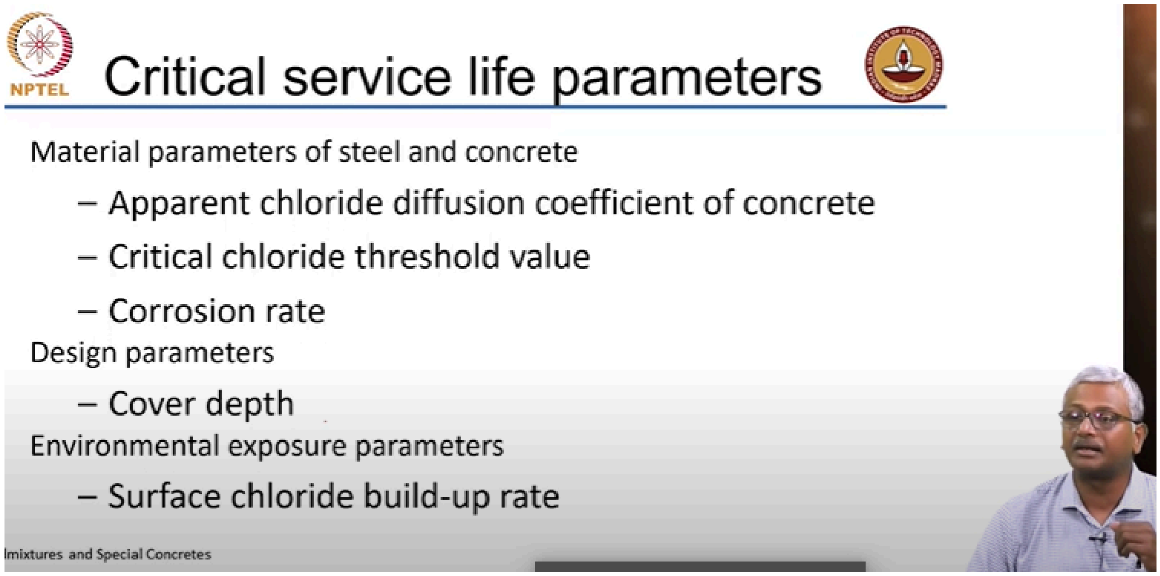

So, how do we do that? For that we need to understand what the critical service life parameters are. One is material parameters of steel and concrete, the first one being the apparent chloride diffusion coefficient of the concrete. Now what do you mean by this apparent chloride diffusion coefficient? What is the amount of chlorides by difference in concentration? Concentration outside is more than concentration inside the concrete so chlorides from outside will start diffusing into the concrete and that generally happens in saturated systems.

The other aspect is critical chloride threshold value. Now the critical chloride threshold value means at what concentration of chlorides on the steel surface will that de-passivation happen? At what concentration will this layer start getting broken down? So, that is the critical chloride threshold. What do you think it will depend on? Intuitively what will it depend on? Depends on what?

Depending on the properties of concrete, steel the chloride threshold will depend on steel. Interestingly enough research has been done to show that also on type of cement. This chloride threshold not only depends on the steel type it also depends on the type of cement.

The other is obviously the corrosion rate. The corrosion rate obviously will again depend on the properties of the steel and the concrete around it.

Then we have design parameters that are the cover depth because cover depth will determine how long it takes for the chloride or carbon dioxide to reach the level of the reinforcing steel and surface chloride build up in the environment to which the concrete is exposed. So if the concrete is exposed to seawater this build up is much faster. Chlorides are building up to a very high concentration of the surface. But if you are in a ground water condition and the water table keeps fluctuating the buildup of chloride will take a longer period of time. So all of these things are going to affect the service life of the structure. Service life again in most cases we are defining as the end of the initiation phase because we do not want to allow corrosion to happen and then say that okay I am happy with the certain level of deterioration. That is not going to be the case. When you adopt a conservative approach it will always be the end of the initiation phase as taken as the end of service level. Now where all of these things really make a difference is in the material selection process. So you need to select your materials appropriately to ensure that you are extending that initiation phase after understanding how all of these characteristics are making a difference to the service life.

Corrosion Inhibitors:

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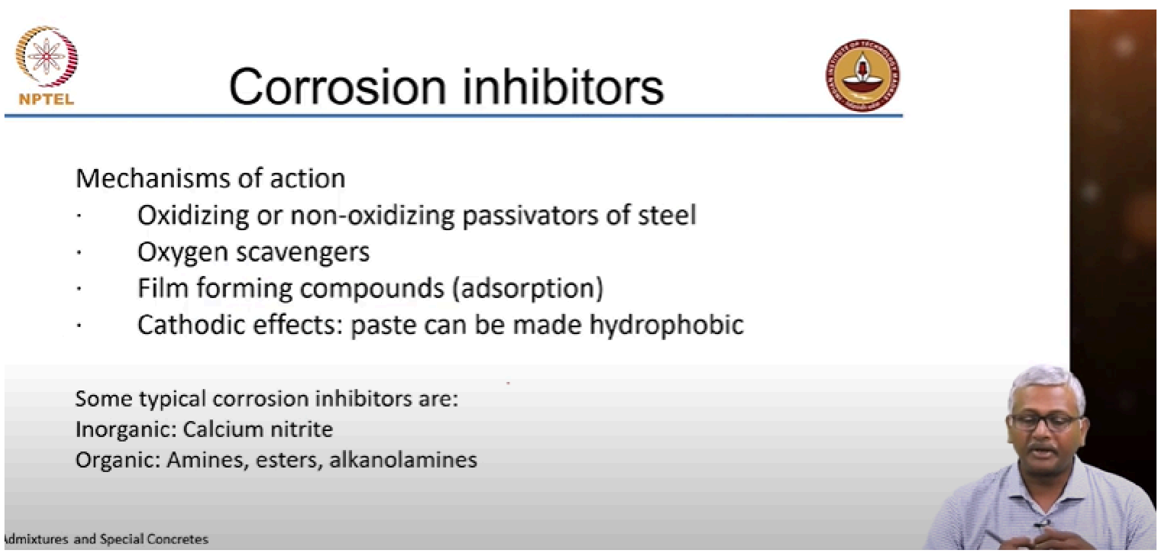

So here what we want to do is enhance the corrosion resistance by utilizing corrosion inhibitors. You can always utilize different types of steel, corrosion resistant steel, stainless steel but the problem there is you are enhancing the cost of your structure significantly unless you are going for a monumental structure where you want the structure to be definitely free of any corrosion damage for 500 years or 1000 years in such cases it is justifiable to go with stainless steel. But for your regular residential construction or for a bridge construction stainless steel may be just pushing things a bit too far because the cost of stainless steel is going to be extremely high as compared to your regular reinforcing steel. So it is cheaper to treat the concrete rather than treating the steel.

There are also other approaches you may have seen epoxy coating of steel bars that is another approach. Now that has to be done very carefully and very well otherwise you are creating more problems than you are trying to solve and any plastic or polymer coating on the steel will also reduce the bond with the concrete. Those numbers are very clearly shown in several research studies and actual practice. They have seen sudden failures of fusion bonded epoxy coated rebars primarily by pull out. So because of this people realize that oftentimes protecting the steel by using higher quality concrete is a much cheaper and much more viable option. One way to do this is obviously to reduce the water to cement ratio of the concrete. You can reduce the water to cement ratio of the concrete but if you want a strength of M35 you are not going to simply keep reducing water to cement ratio because your strength may get exceeded even twice or thrice if you really want to protect the steel from corrosion at that level of strength. You have to design the concrete for its particular application. So you cannot keep on reducing water to cement ratio because your strength requirement may be simply too low as compared to what you are realistically getting for providing corrosion resistance.

Let us say you want an M35. What is the water cement ratio of M35 concrete? Maybe about 0.45 or so but at 0.45 it is possible that you may not get the required corrosion resistance so let us say you decrease it to 0.35 but what will happen to your strength now? It will go up to M60. You do not need 60 MPa where you needed M35 concrete. So you have to make a justifiable decision to not really keep on reducing water to cement ratio because it is going to change the grade of your concrete, cost is going to go up, whatever.

So when you have to work at a particular grade the choice is to start using admixtures like corrosion inhibitors which could act with different mechanisms. One is they can increase the passivation of the steel, they can strengthen the passivating layer that forms on the steel surface. The other can be oxygen scavengers, what do you mean by that? They eat up the oxygen, they do not allow the oxygen to get to the steel surface as we saw earlier oxygen is needed for the cathodic reaction diagram. So if the cathodic reaction can be suppressed by removing oxygen then you can have a control of the corrosion process. You can also have compounds that form a film in the steel surface. In addition to the passive film you have an additional film forming on the steel surface that makes steel more stable for a longer period of time and then systems that make the paste hydrophobic can also work because again moisture can be required, you can reduce the moisture in the system.

So inhibitors could be anodic which primarily act on the anodic reaction or cathodic or sometimes some inhibitors can be both anodic and cathodic we call them as bipolar inhibitors. That means they work on both anode and cathode. Most of these organic inhibitors are exhibiting bipolar kind of characteristics where they are very effective as they control both anodic and cathodic sites. Now interestingly here one of the common corrosion inhibitors that was used extensively earlier before people started working a lot more with bipolar is this calcium nitrite. Calcium nitrite is an anodic inhibitor and because it is inorganic and it is calcium nitrite it is very cheap. Where did you see calcium nitrite previously? What type of admixture accelerator? Calcium nitrite, calcium nitrate they are both accelerators also. So calcium nitrite could be a useful anodic inhibitor but the bipolar inhibitors are by and large more effective like amines or esters or alkaline amines. These are organic but these are more expensive as compared to calcium nitrite.

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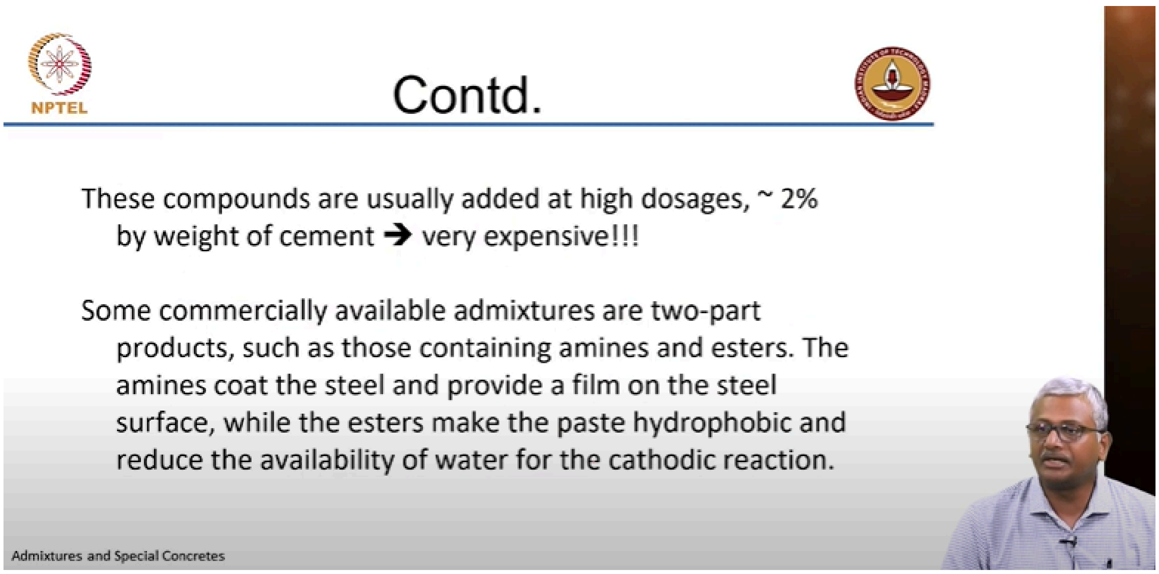

Now generally you need high doses because again you have a very large surface area of the reinforcement is going to be quite extensive around the concrete. So to ensure that these are reaching that level you need to have a large dosage of these mixtures to be used for 2% or more is used by weight of cement. So it makes the concrete quite expensive. So however the cost of protecting reinforcement from corrosion from this approach is going to be much lower than the cost of adopting alternative steel types. Alternative steel is a lot more expensive as compared to protecting concrete.

So again these amines and esters sometimes are available as 2 part systems which contribute both to the anodic and cathodic effects.

Anodic v/s Bipolar inhibitors:

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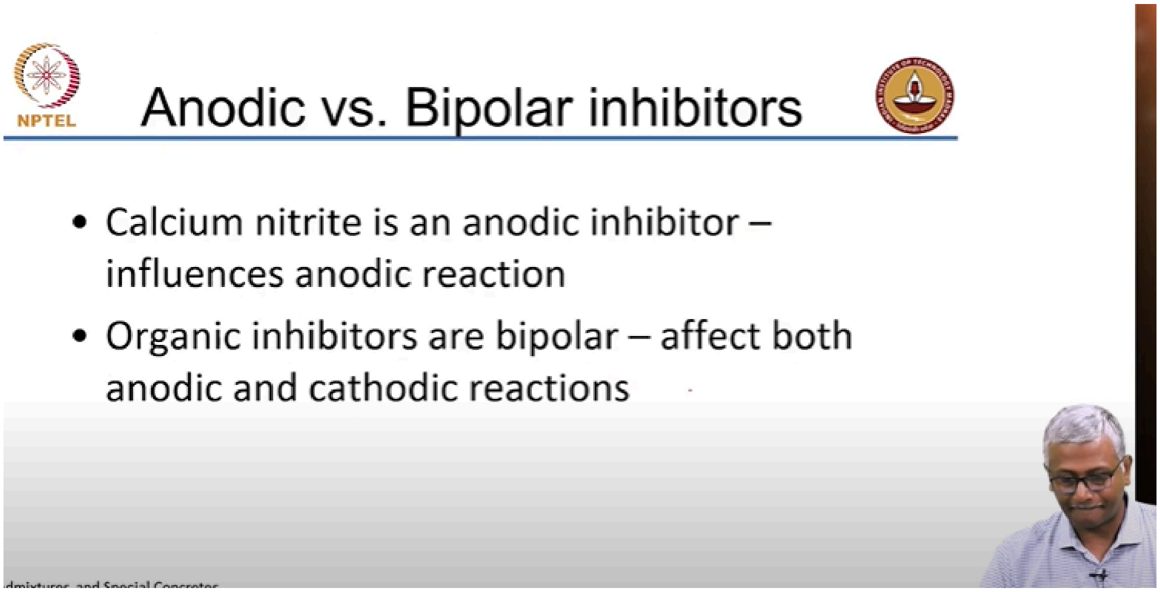

Effects of inhibitors:

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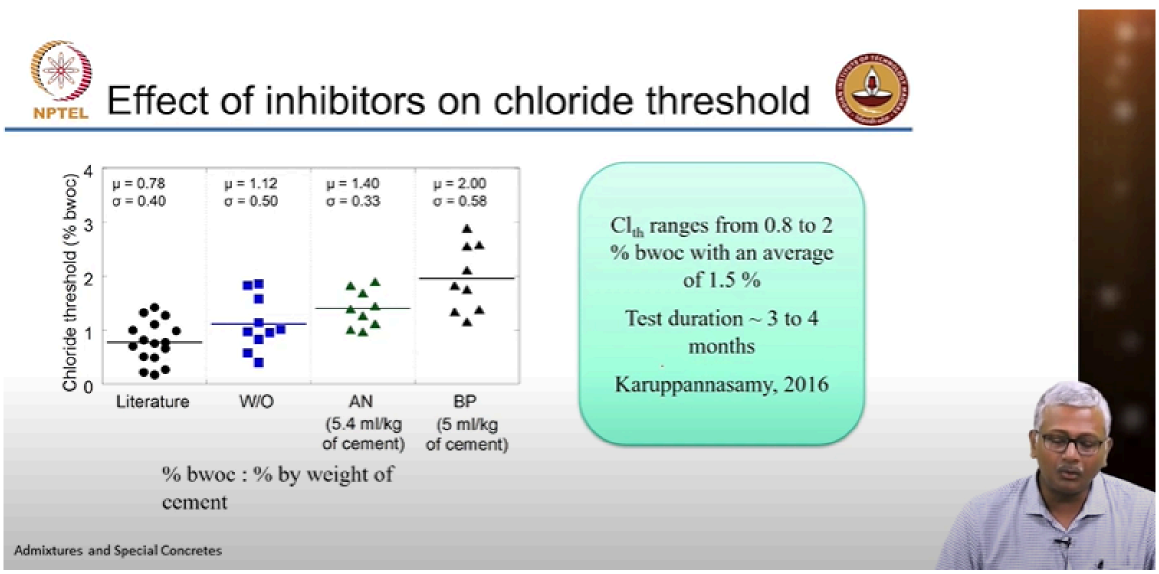

So again just to reinforce calcium nitrite is an anodic inhibitor that influences the anodic reaction organic inhibitors are generally bipolar which affect both anodic and cathodic reactions. So let us look at some studies that were done at IITM by one of our previous PhD students who looked at how these inhibitors are affecting the chloride threshold values. We talked earlier that the chloride threshold will depend on the type of steel it will also depend on the type of cement. Interestingly the presence of the inhibitor further affects the value of the chloride threshold. The chloride concentration at which corrosion starts is affected by the presence of the corrosion inhibitor. So now without any inhibitor you are seeing a chloride threshold value of about 1% bwoc.

About 1% for comparison purposes about 1% bwoc. This is data from literature which showed about 0.78 as the mean value. When an anodic inhibitor was used at 5.4 ml/kg. 5.4 ml/kg is how much? 5.4 ml approximately 5.4 gm/kg. So if you think about per 100 kg you are talking about 540 gm per 100 kg. So 0.54% is not really very high in this case. So at this level they were able to bring up the average chloride threshold value to 1.4. The bipolar inhibitor further took it up to 2. That means you need more chloride now to cause corrosion. Obviously that means your initiation phase is going to get extended when you use these corrosion inhibitors.

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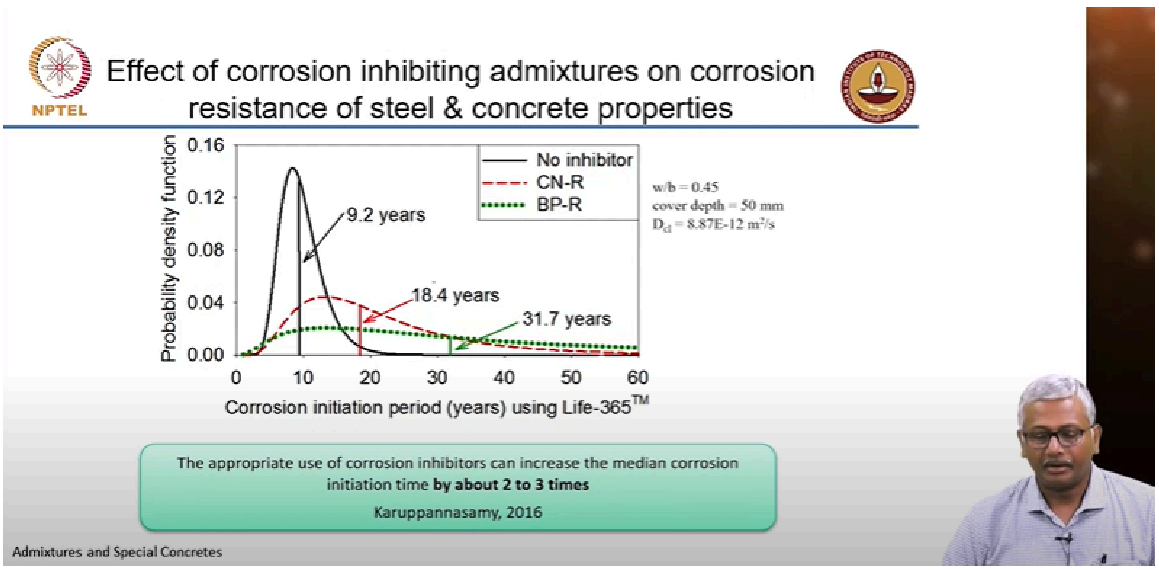

Now there are models available that can actually look at the service life of the structure using these inputs whether what kind of water cement ratio you are using, what is the cover depth of your system, what is the property of the concrete in terms of chloride diffusion coefficient. So in such cases the same study by Dr.J.H. Chandran saw that when you use corrosion inhibitors calcium nitrite and bipolar inhibitor, the service life which was 9.2 years without any corrosion inhibitor was enhanced to 18.4 years for the corrosion concrete with calcium nitrite corrosion inhibitor and to 31.7 years for the concrete with bipolar corrosion inhibitor. So again the model can obviously have some error in its prediction but the mechanism is quite simple to understand. It is just that you are having these additional chemicals that enhance the resistance to anodic or cathodic reactions or both and that leads to the formation of better corrosion resistance in the system.

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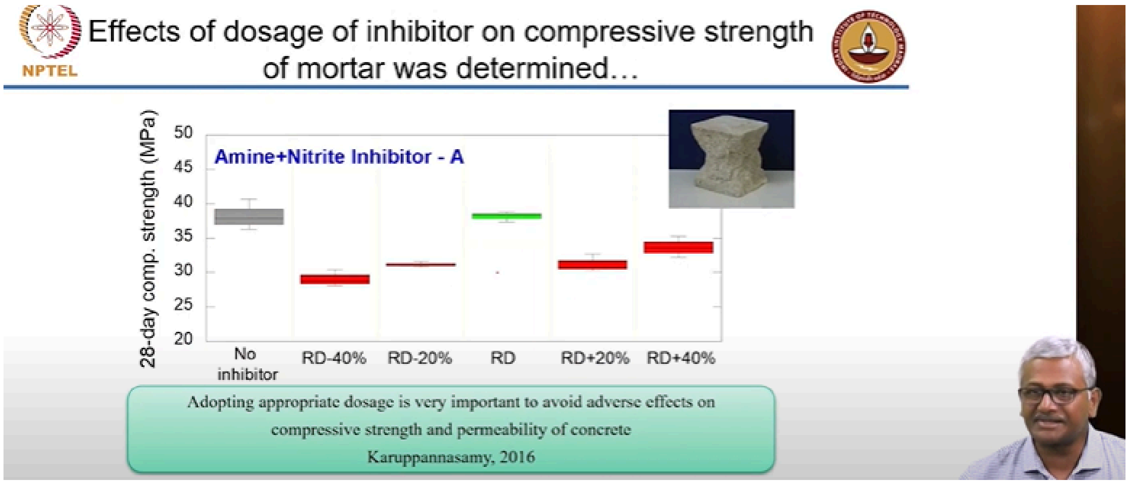

Now interestingly it does not just stop there like any drug there are side effects. So corrosion inhibitors have side effects in terms of strength. So you see here without any inhibitor you have a certain level of strength but when you have the correct dosage of the inhibitor added you are not seeing much difference in the strength but any overdose or underdose you seem to have some effects in the strength. So you have to also look at what are the side effects that can actually happen if you are not at the right level of the dosage. So if you look at the manufacturer's data sheet they need to ascertain that the admixture in its recommended dosage levels should not adversely affect any of the properties of concrete. But here we are seeing that this is quite surprising that even at lower dosages it is actually reducing strength. That high dosage reduction in strength may be attributable to some mechanism or the other but why is it happening the other way around also. So one has to be careful about how these systems are assessed in terms of their impact on other structural properties.

Shrinkage reducing admixtures:

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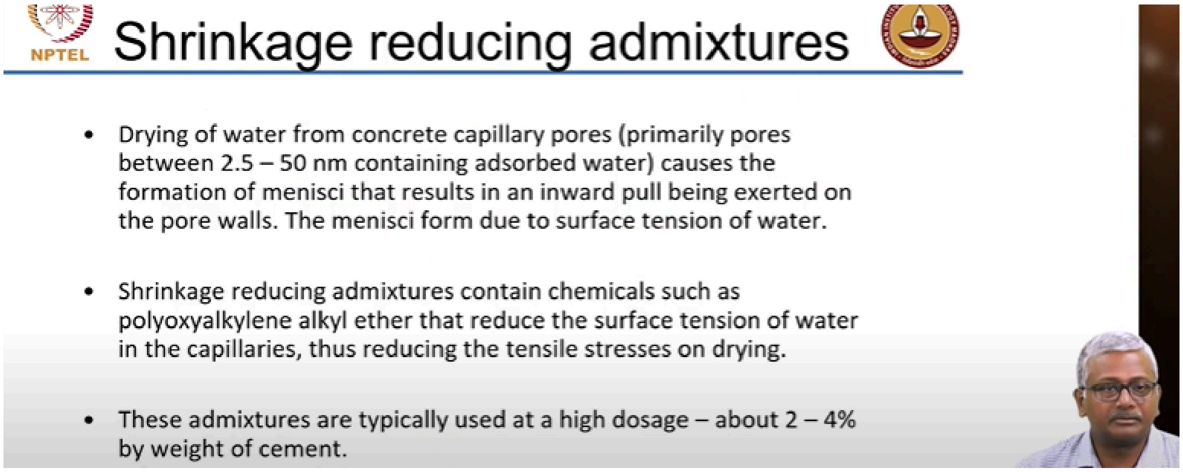

We often have other problems apart from durability in the long term service of the structure. One problem obviously is shrinkage. Shrinkage can happen very early during the life cycle of the concrete. As soon as you place it you may get what is called plastic shrinkage. In the long term we get drying of water from the system that causes drying shrinkage. There are additives that you can add to the concrete mixture to reduce the level of shrinkage and these additives are typically called shrinkage reducers or shrinkage reducing admixtures. Now if you imagine concrete has porosity on the surface, I am just drawing an exaggerated view of porosity.

Let us say that is a pore on the surface and let us say the pore is partially saturated and has got water inside. Now you put this concrete in a drying environment, what is going to happen? If I draw a bigger view of the porosity, let us say this was the meniscus of water that was there in this pore. As drying happens what is going to happen? This meniscus is going to get a lot more convex or rather not convex, concave but you are going to increase the angle of the meniscus because drying is happening leading to the water getting evaporated and because of this there is pressure on the pore walls. There is going to be pressure on the pore walls which is trying to put the walls in tension or the concrete surrounding the pore is now getting put in tension. So when tension happens it is likely to get cracking in the concrete which is subjected to tension.

So shrinkage effectively leads to a condition where drying of moisture from your concrete is leading to strains in your system and these strains are likely to cause cracking if there is any restraint. If this concrete is free to move there is no problem but no concrete is free to move unless you are in zero gravity. In zero gravity if concrete is drying it is not going to crack but there is always something or the other preventing concrete from moving that restraint causes cracking. So shrinkage reducing admixtures do not change anything; what they simply do is they affect the surface tension of the water that is there in the pores.

So they reduce the surface tension. So when you reduce surface tension the capillary pressure associated with this drying reduces. All you are doing is reducing surface tension in the water so you are reducing the capillary pressure. This extent of pressure that is felt because of the drying of water from these capillaries is getting reduced. So that is how shrinkage reduces typically act and that will reduce the tensile stresses that are generated on drying. So again several organic chemicals are used, even propylene glycol that is a very good shrinkage reducer. Your polycarboxylic ether which is a good water reducer is also a good shrinkage reducer. Your air retraining systems could also reduce shrinkage because they are also going to lower the surface tension of water. But you cannot use air entrainers in the quantities required for shrinkage reduction because that will lower your strength significantly.

What do you think will happen if I use shrinkage reducers to the strength? Will it get affected? Should the strength be affected? In the quantities that I use shrinkage reducers may actually affect the strength because again lowering surface tension means promoting bubble formation. During mixing more bubbles may form and more porosity may get introduced in your concrete and lead to loss of strength. Because you have to use very high levels of dosage about 2 to 4%. That is why you cannot use your regular high range water reducers like PCE's as shrinkage reducers because at that dosage it will cause complete separation of your concrete. It will make it so fluid that your water will totally separate out. But in the dosage that it is there it is still acting as a good shrinkage reducer.