Admixtures and Special Concretes

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Lecture 16 - Chemical Admixtures: Set controllers – Retarders

So, what we learnt in the previous part was classification of common set controllers mechanism of action and finally we talked a little bit about accelerating admixtures for regular concrete and shotcrete.

Retarding Chemicals:

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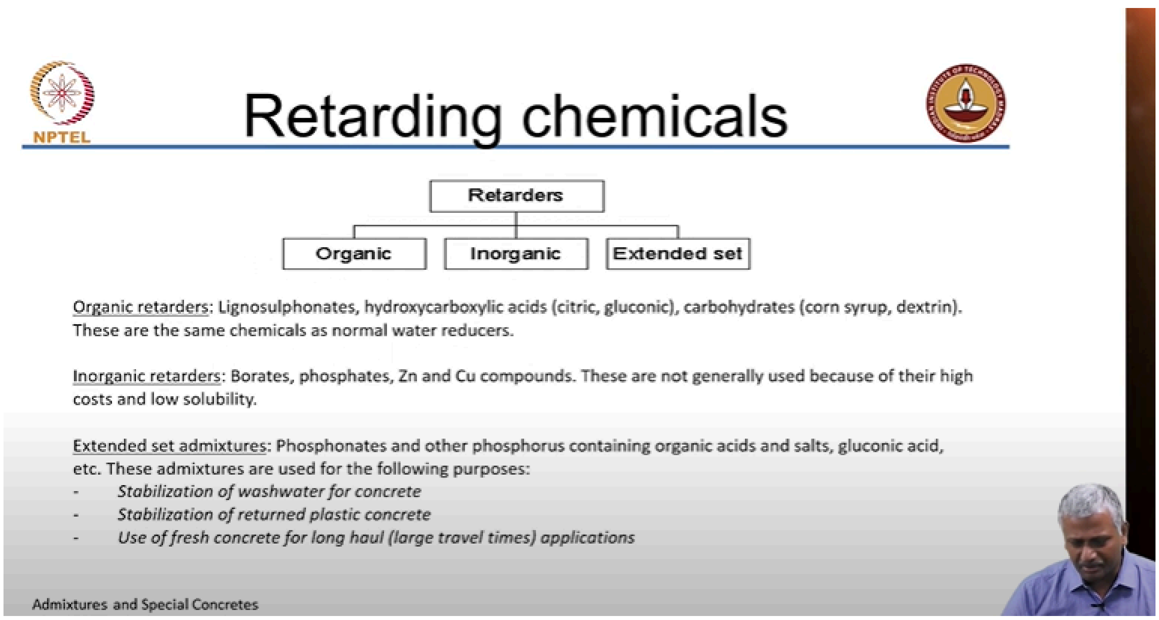

In this section which is a shortened section we will talk about retarding chemicals because retarding chemicals are functioning in a similar way as your super plasticizers or they are actually effective or super plasticizers can also function as effective retarders. So, retarders are typically classified as organic or inorganic. Organic retarders of course include the same chemicals that are used as normal water reducers: your lignosulphonate, hydroxyl carboxylic acid, carbohydrates these are all regular retarders and fairly inexpensive, for instance sugar or corn syrup these are all excellent retarders. So, I talked about this earlier that the truck driver keeps some sugar available to ensure that the concrete does not set in the truck when it is rejected from site and goes back. There are also more expensive formulations of retarders like borates, phosphate, zinc and copper compounds. Again, cost is high, solubility is not very high. So, you cannot make solutions that are as strong as the organic retarders that are typically used and the advantage here obviously is that you get a dual effect you get not just retardation, but you also get slump retention or initial workability. In some instances you want to really extend the workability for a very long time. So, that is where you want to use phosphonates and phosphorus containing organic acids and salts, sometimes gluconic acid.

These admixtures can be used for several reasons. I have put three reasons there, one is stabilization of wash water for concrete. This was an interesting application. What happens is after the concrete truck delivers the concrete it comes back to the concrete plant. It needs to be washed out. All the concrete inside has to be washed out, but this is a high pH material concrete has a pH of 13. So, you cannot let that wash water come and mix with your groundwater. Well, in an ideal situation you should not do that, but we do that all the time. So, this example I came across in Switzerland, when I used to work for SICA because SICA is based in Switzerland. So, I went there for a couple of weeks for training. So, I saw that they were collecting all their wash water in these large plastic drums and adding this extended set admixture into this water. So, what that did was it prevented the setting of the cement completely for several days all it did was ensure that it took long enough for the cement particles and the any fine aggregate particles that may be in the system to start settling to the bottom and the water which was remaining on the top could be reused either in new concrete or for washing purposes. So, that way they did not have to waste the water that they got from washing and the material that collected at the bottom was simply settled. It did not set; it had just settled at the bottom and that could be simply removed and then discarded. So, that way they were able to reutilize this water because this is going to be a very important thing for us to do also because we do not want to waste all that water that goes into washing if that can be collected and reused this is a very efficient way of doing it.

Stabilization of returned plastic concrete, I talked about sugar instead of sugar. You can also use these gluconates that are much more effective and they will keep the concrete workable for a long time. So, concrete truck arrives on site it already has to wait for a long time before it can be used by the time it gets to be used the slump is not there the engineer on site rejects the concrete goes back by the time it reaches the plant concrete may have started setting you do not want that to happen obviously. So, you can stabilize and ensure that setting does not take place, but where does this concrete go finally? Anybody has worked for concrete RMC no one has experience with RMC people with L&T have you ever rejected a truck? It is actually a very rare occurrence that people do not reject trucks easily although they should be rejecting them much more often. So, these trucks do not know what happens to this concrete. Later I am getting recorded. Probably some concrete manufacturers will also be watching my lecture sometime, but still this is a question that always causes a lot of wonder because I do not know what happens to this concrete. Now ultimately it may get used up at a different site where similar concrete is actually required by the time it reaches the other site it may have started normally setting or sometimes they may go and dump in so-called low lying areas dump the concrete. God knows who classifies these low lying areas. The same thing with construction demolition waste we fill up these trucks with more and more waste that gets taken out of the city and gets dumped in some low lying areas. So, where are these low lying areas nobody knows? Anyway, all this has to be thought about in a big way, but when you have to transport concrete for very long distances.

I said previously that let us say you have to have concreting done on top of a hill and your concrete plant cannot be located for several reasons close by then your travel time may be sometimes 3-4 hours or even more. There are documented case studies where people had to travel 8-9 hours to deliver the concrete and they had a requirement of 1 day strength. So, here you retard, but you also want the 1 day strength. So, if you do some internet search you will find this compound called Delvo from the company which used to be called master builders earlier. They had this product called Delvo which could be used for this extended set retardation, but it was formulated in such a way with other ingredients added to it that once the concrete was actually placed and compacted and finished it could then start the strength gain process quite rapidly. So, it was not just a retarder, it had obviously some accelerating components in it.

Retarding Sugars:

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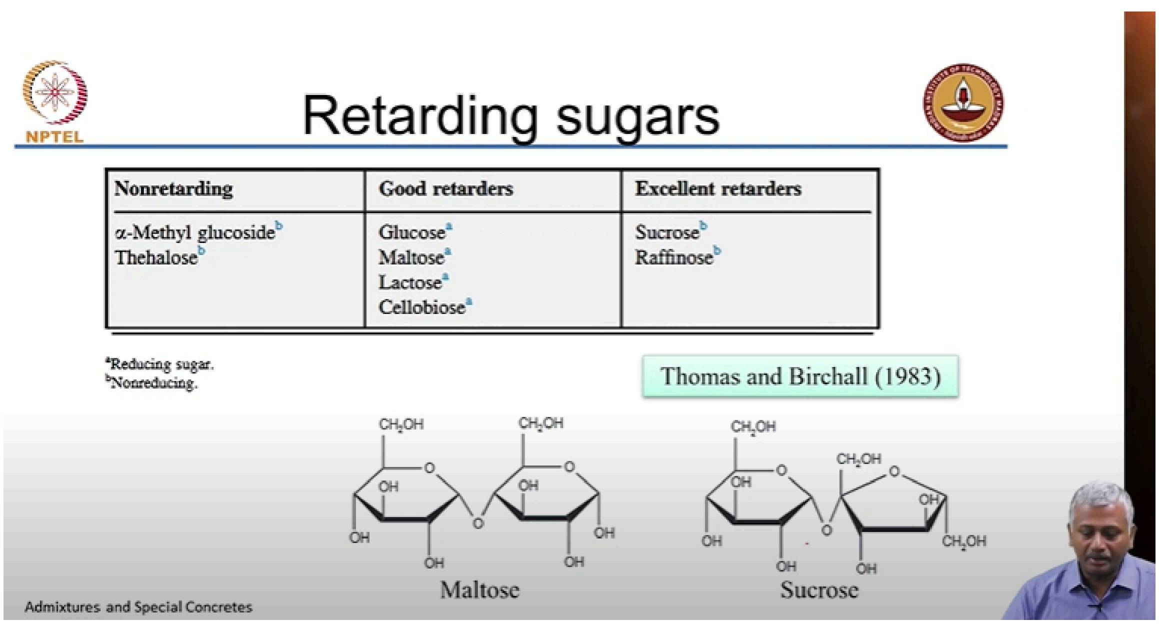

So again I am just giving some examples of retarding sugars, like your good retarders typically include glucose, maltose, lactose and cellobiose and excellent retarders could be sucrose and raffinose. You have done some understanding of this sugar molecule in your basic sciences back in probably 9th or 10th standard. So, I have just given you the structure of sucrose and maltose here. So, these compounds obviously are again of the aromatic type and they have very varied effects on the way that they can act.

Effects of glucose:

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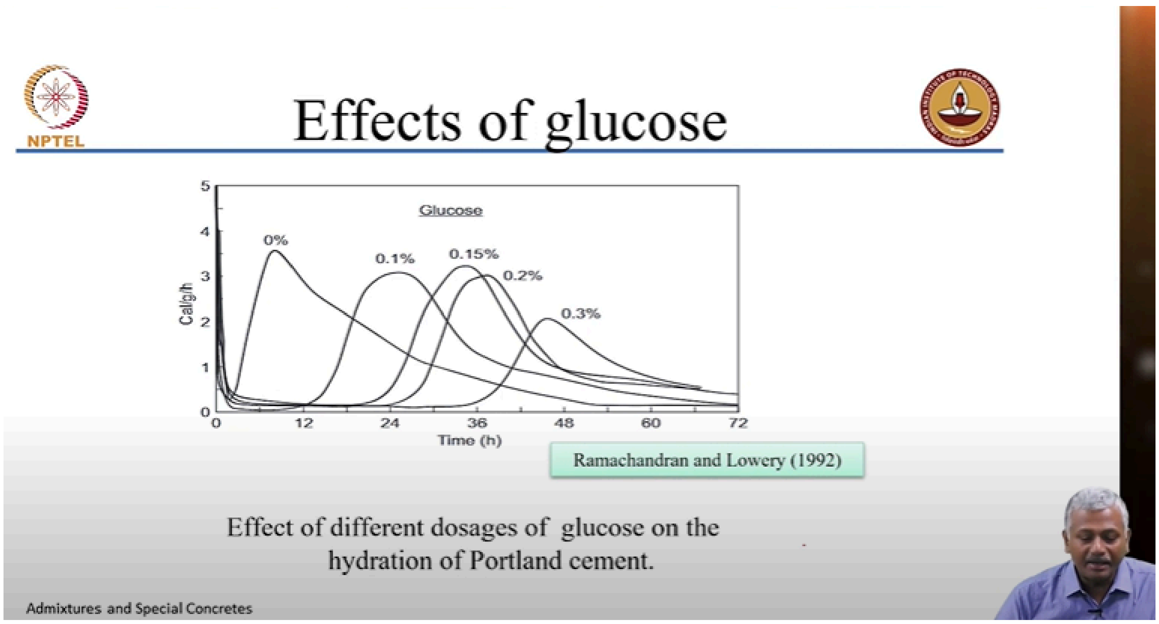

So, when you add glucose into your cementitious system what you are again doing is extending your dormant period. All setting accelerators shorten the dormant period all setting retarders extend the dormant period. It may also turn out that the total the actual peak heat that is liberated in your system may also start getting reduced as you add more and more of the retarder because this is all rate of heat evolution cal/gm/hr. So, the rate at which heat evolves is represented by that peak. It does not mean the total heat evolved. Total heat evolved will depend on how much reaction is actually taking place. It is just happening slowly so if you plot the total heat that is evolved let us say in joules per gram or calories per gram versus time it will slowly keep getting built up. Let us say if that is for normal concrete for retarded concrete it may have a much gentler slope, but ultimately it may reach the same level as long as the hydration continues to the same extent. So, that is the total heat developed, but the peak heat rate may reduce when you add more and more retarder like glucose in this case.

Effects of sucrose:

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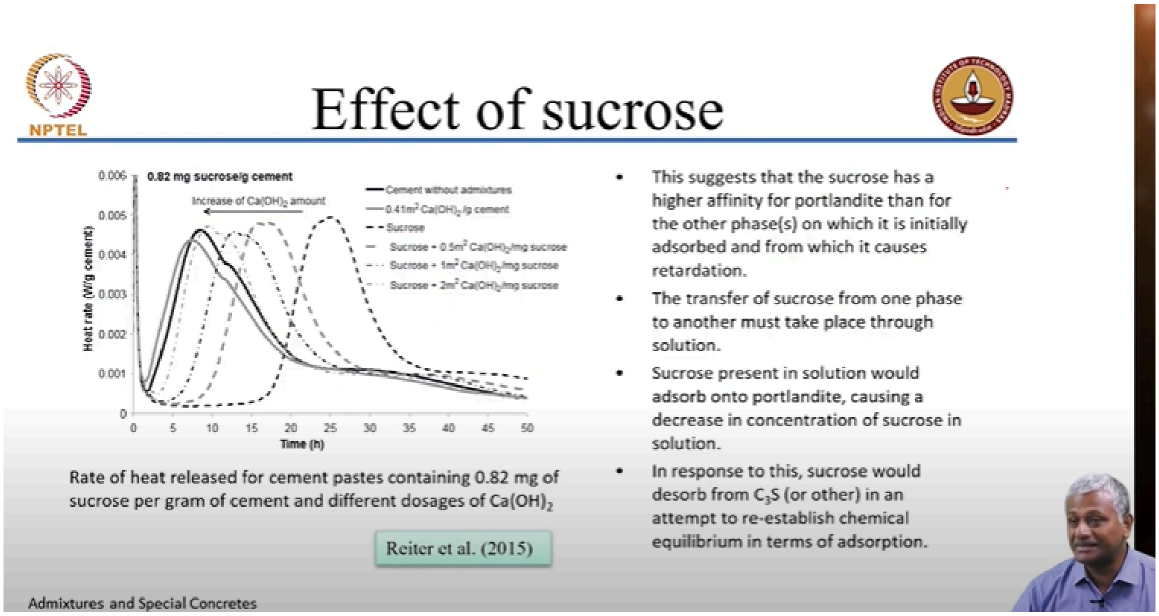

Now, sucrose is quite interesting because the effect of sucrose can be a little bit of a confusing one. Sucrose is a very good retarder no doubt, but what happens is if you have lime in your system. If you have calcium hydroxide in your system you tend to lose effectiveness of the sucrose as a retarder. Sucrose has an affinity for portlandite or calcium hydroxide than for other phases and it does not really express itself in the same level of retardation. So, with sucrose with different levels of calcium hydroxide you are seeing that with increase in calcium hydroxide levels the efficiency of retardation of sucrose is dropping.

Now, this does not mean that for normal cement sucrose will cease to be a good retarder just because there is enough calcium hydroxide, but between cements which are likely to generate different levels of calcium hydroxide in the system you may have a different efficiency of the sucrose happening. So, you have to look at this chemistry carefully before you actually arrive at the right dosage to be used in your system.

Retardation by Superplasticizers:

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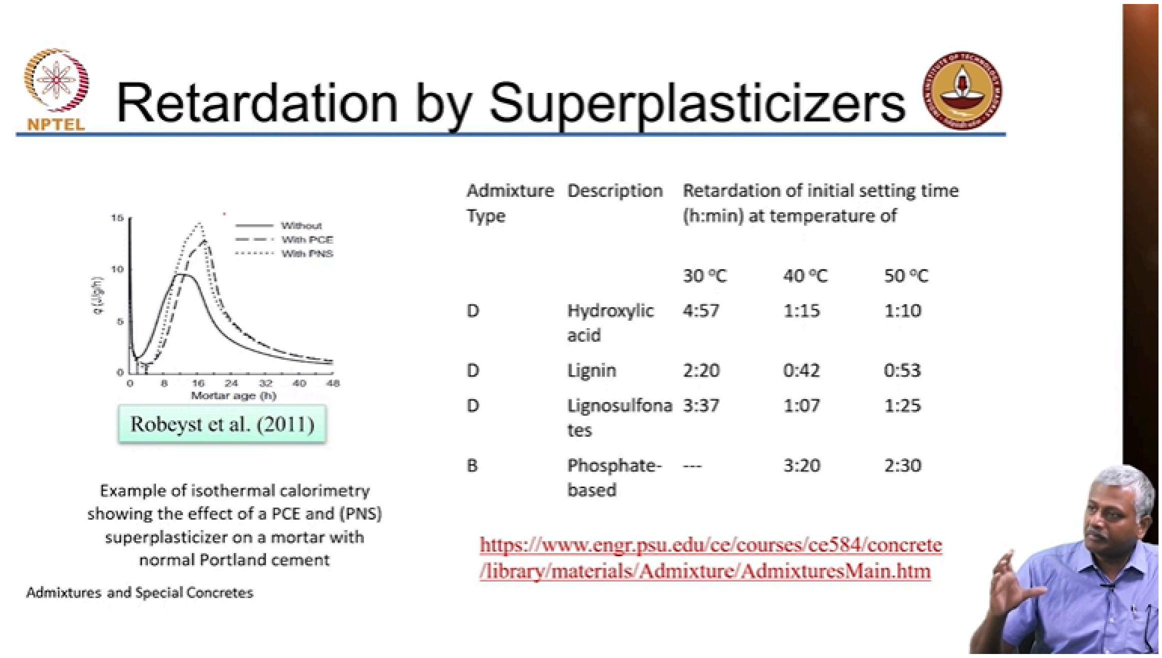

Now, as earlier saying super plasticizers which envelop the cement particles prevent hydration from happening and the extension of this to a longer period of time let us say by polycarboxylates will further retard the hydration of the cement. So, super plasticizers can have an impact on the retardation of cement hydration also.

So, this is an example again of the heat curve. So, the study of the heat curve is often a very good example to determine the relative rates of reactivity or kinetics of the reaction. So, we will see later that these heat studies are also used extensively in understanding the impact of mineral admixtures like fly ash or slag or calcium clay for instance. So, this is for cement mortar what you see is with different forms of super plasticizers there is a minor shift in the time at which the peak occurs.

There is a minor increase in your dormant period, but interestingly the peak heat rate is higher when the super plasticizer is being used. Why do you think that happens? Why is the peak heat rate higher? What is that saying? You have caused an increase in your dormant period that is retarding your concrete, but the peak heat rate that means the rate at which the reactions are happening are much higher once the reactions start happening. Why is that? Please remember particles in the presence of super plasticizers are nicely dispersed. So, each and every particle now has access to water ideally. It is not going to be happening in a practical sense, but ideally each and every particle has more access to water. So, the hydration or rapid dissolution of the C_3S can happen quite significantly when you have super plasticizers. That is why the heat rate is actually going up, but the time at which this heat rate actually happens is extended. So, at different temperatures the relative effect of these super plasticizers could be quite different. For instance, hydroxy-carboxylic acid or hydroxylic acid at 30°C is causing a retardation of 4 hours and 57 minutes. At 40°C it is only 1 hour and 15 minutes.

Lignin is causing about 2 hours and 20 minutes retardation of the initial set at 30°C, but at 40°C you are having a major reduction in this time. So, what this goes to show is when you start using these retarders they may not have the same effectiveness at different temperatures. So, when you plan projects you need to be aware of these issues. Luckily for us obviously we know the range of temperatures within different segments of the project. So, we can plan appropriately to use the retarders at the right kind of retarders at the right dosages.

Mechanism:

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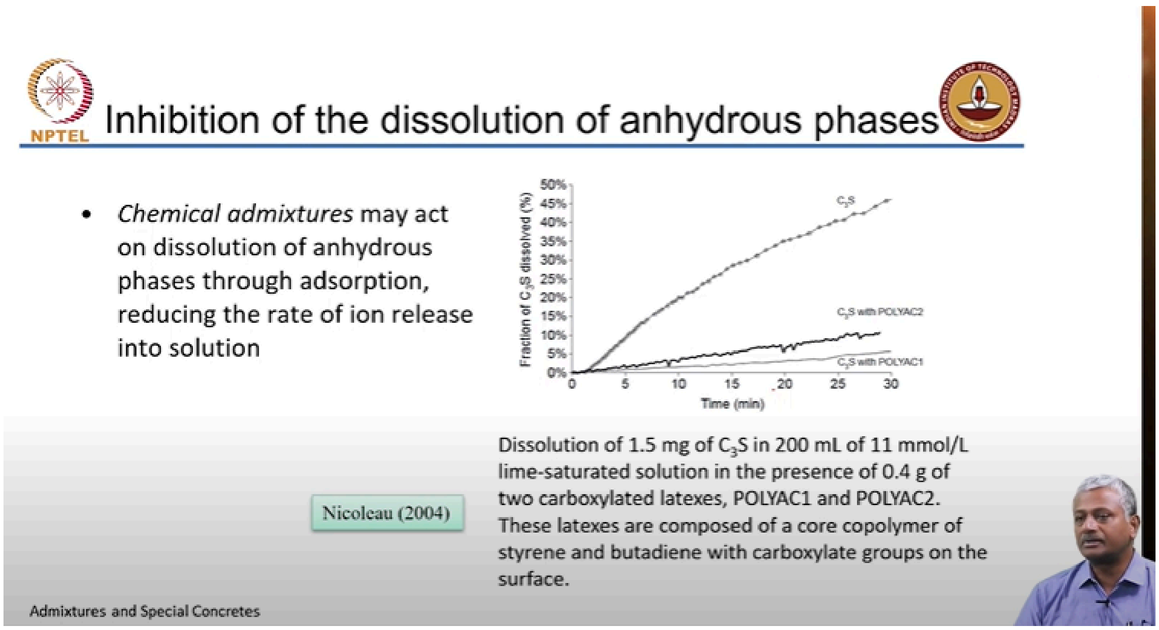

We come back again to this mechanism. As I said, accelerators and retarders affect the rate at which dissolution of cementitious phases happens. So, again the mechanism may again depend on adsorption. So, these molecules are getting adsorbed onto the cement surface and preventing the rate at which they are dissolving in the solution. So, what is presented here is the fraction of C_3S dissolved versus time for no admixture case, and this is the admixture polyacrylate 1, polyacrylate 2. So, there are 2 different polyacrylates that are used in the system. 1.5mg of C_3S is taken in a diluted solution of lime saturated.

Why is it lime saturated? Because we do not want any leaching. If you put cement in water, calcium will start leaching into the water. When you use a lime saturated solution you prevent that leaching. So, all you are seeing is the extent of calcium dissolving in the system just because of the effect of the hydration process not because of the leaching process.

This leads us to another interesting question. In laboratories you take concrete cubes and put it in water, store it in water. But there is also another method of storage: you can store it in a room where humidity is controlled to 100% in a spray of moisture. So, there is a difference here. When you store it in water the calcium bearing species are leaching out. Even the alkalis in the system are leaching out into the water. This thing does not happen when you start spraying the moisture.

Similarly here if you had chosen a condition in which the C_3S is simply put in water, leaching of calcium may actually happen rather than the dissolution leading to hydration. So, here that is why lime saturated solution is being used in the presence of two carboxylated admixtures. So, you can see very clearly that the fraction of C_3S dissolving is much lower at the initial time periods of 0 to 30 minutes. So, because of this adsorption and stabilization of the polymer molecule adsorption on top of the cement particles it is preventing calcium from dissolving.

Surface retarders:

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Now in some applications we want to give a texture to the concrete surface. We want to have an exposed aggregate surface just for aesthetic purposes. In such cases we can use what are called surface retarders. After the concrete has been placed and finished, after a few minutes of the finishing of the concrete we can spray the surface retarders. What happens when you spray the surface retarders is only the surface of the concrete the cement does not set. So, after a certain period of time when the concrete inside has already set but the surface is not set all you do is take a water jet and remove the cement paste from the surface. So, that leaves us with textures like this where aggregate can be exposed and gives a nice aesthetic appearance that is called a surface retarder. It is not a retarder for the entire concrete but only for the surface of the concrete.

So this was a short segment because much of admixture chemistry is similar to what we talked about in water reducers action. So, that is what these chemicals also are doing. They are again long chain chemicals that are acting by adsorption and preventing dissolution of your calcium bearing species. I also want you to do a self-study on the standards ASTM C494 and IS 9103. These are the two standards ASTM standard and IS standard. Just take a look at what these standards talk about in terms of these standards are primarily for the use of water reducing and regulating chemicals like accelerators and retarders. Try to see the way in which they define the effectiveness of these materials, how they should be tested, how they should be certified and how they should be used. ASTM C494 and IS9103.