Admixtures and Special Concretes

Prof. Manu Santhanam

Indian Institute of Technology Madras

Department of Civil Engineering

Lecture -14 Chemical Admixtures: Set controllers

Summary:

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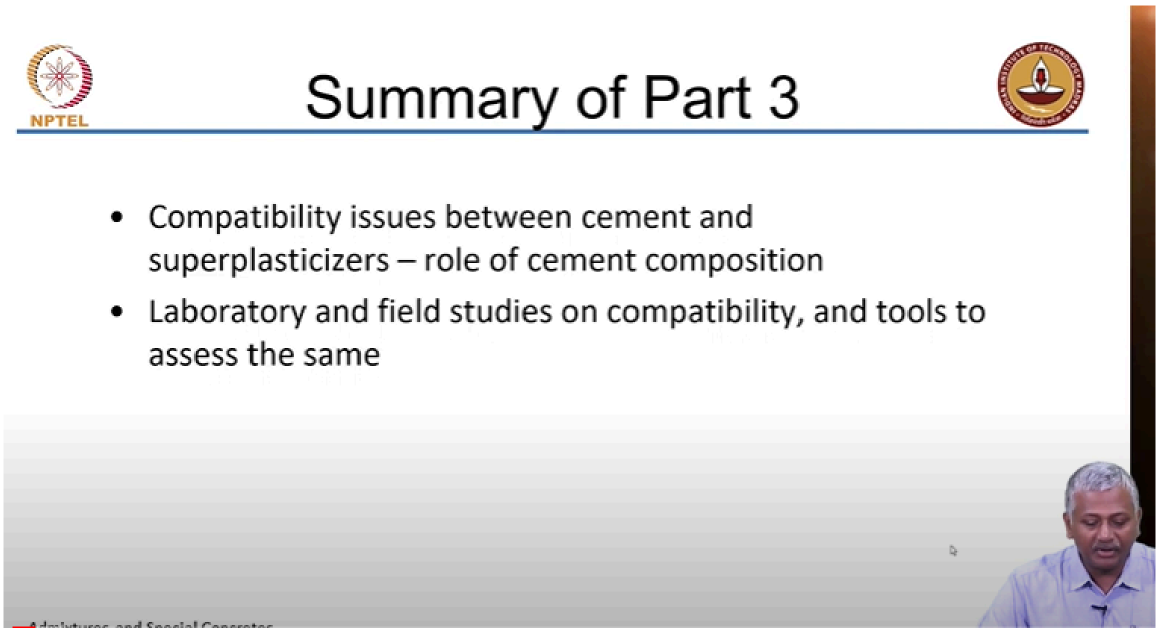

Okay, so in the last segment we talked primarily about what factors affect compatibility and we saw there is a whole range of factors. So one has to have a proper understanding of these factors before a combination of cement and super plasticizer is used in the field. It is not always very easy to do that, right? Because we know that half way through the project your cement source may change. Does that mean you completely alter your mix design? Now very often when any source change happens either in the cement or even the same source of cement sometimes you get different quality material. Let me give you an example. Let us say you are doing a project in Chennai and you are getting cement from any company that does not have an integrated cement plant close by. So they have what are called grinding units. So many cement companies set up grinding units in several locations. So what do they do there? They get clinker from their cement plants, they get the gypsum and they get any other additives like fly ash or limestone whatever it may be and do the final grinding alone at these plants and then they package and sell the cement from these grinding units. That is because it is easier to transport smaller amounts of clinker than to transport the full amount of cement from the integrated plants.

So now at these grinding units it is quite likely that the same cement company may be getting clinker from different integrated cement plants. So for instance there are several grinding units in the northern part of Tamil Nadu where they get clinker either from the Areolur belt which is about 250 km south of here or from the Tadipathri belt which is in Andhra. So the clinker obviously depends on the characteristics of the limestone that is available in these two locations. It turns out that when you make cement with the clinker obtained from Tadipathri or from Areolur it actually ends up giving you a very different characteristic. The cement ultimately has to meet the specs. It has to meet let us say if it is a 50 grade cement it has to have the required setting time, required strength all of those things are fine.

But the same brand of cement can behave quite differently when you use admixtures because of all the problems that we talked about previously. And in one such case this indeed was a problem. We saw that the primary source of the problem was the change in the cement clinker for the cement that was supplied to a particular project. And what happens on a construction site is that if something is not meeting the requirement the first person to get blamed is the admixture manufacturer. Why is that? Because that is something foreign that does not need to be there in the concrete. Cement is obviously important for the concrete but why are they putting this admixture it is something different. Some problem has happened so it may be because of the admixture.

Because of this the admixture companies always have service people who run around between job sites. If there is a problem like this they run back quickly to their R&D and get minor tweaks in the formulation done until their admixture actually matches the demand of a particular job site. So the admixture formulations keep on changing as a result the same product may have 10 different types of formulations. So for instance if a product is let us say one of the products that is commonly used is Rheobuild it is an SNF admixture from master builders Rheobuild 1120. In one job site it may have 1120A and in another job site it may be 1120W. It is essentially the same compound but there have been minor changes so that it meets the demands of a particular job site. Now in this situation in this project that I am talking about they tried all kinds of things but nothing worked. So ultimately when we looked at the overall formulation we saw that there could have been some changes in the cement characteristics that led to this problem. And indeed when they went back they saw that the soluble sulphate part in the cements was changing significantly based on the clinkers that were available in different locations. So again cement companies are not always keen to accept that the problem lies with them but in some instances they have to see very closely about what is happening.

So again now just to give you one more example it is not only all of these factors there are other things also. For instance there was a project where we were looking at designing concrete which had very low water content about 130 kg/m^3 very low water content. Of course the PCE super plasticizer was used. Now when you have a very low water content I have already talked about the fact that you need to have an extremely good mixing process. On this site they were not at all prepared. They came with a tilting drum mixer that costs RM 500 or whatever the one they can move around on the site, the tilting drum type mixer. So that mixer which could mix about 0.5 m^3 in the first 4 or 5 batches of mixing could never achieve the level of workability that was required. But by the 6th or the 7th batch they had worked out how long they needed to mix to really get the system to be effective. If they had had the same concrete supplied with the pan mixer which they ultimately did they would have found a batching plant that was about 30 minutes away from this job site. They went to that batching plant and had the batching plant supply the concrete which was mixed in a pan mixer. Their workability was maintained consistently. So here they were on the site with a tilting drum mixer which was absolutely not up to the mark to mix a concrete which had such a low water content of 130 kg/m^3. So your choices of the concreting process and how ready you are on the site to actually apply the concrete also makes a big difference in the way that you can get your systems to be effective. And this is indeed a problem if you are working with concretes of very special characteristics self-compacting high strength all of those things which we will talk about in the later part of this course when we deal with special concrete all of these factors may affect the way that you get the required properties of the concrete.

Application of set controllers:

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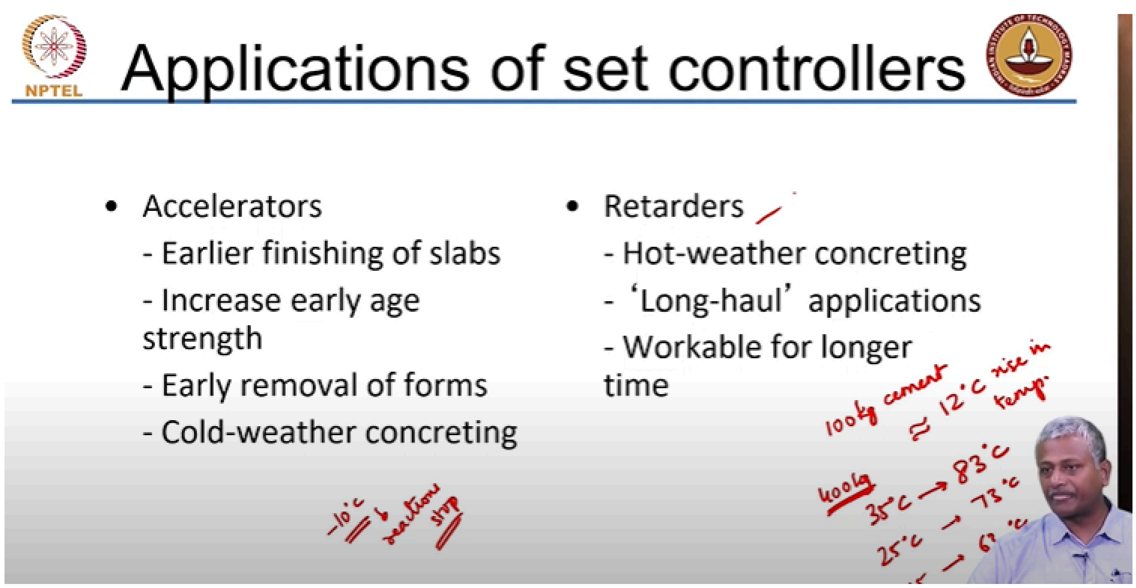

Now in this part of the chemical admixtures chapter we will take a look at set controlling agents accelerators and retarders. Now accelerators obviously are needed when you want early strength, earlier finishing of slabs, and early removal of forms or if you are doing concreting in the cold weather where because of the low temperatures you may have difficulty in attaining strength fast enough. So you want to accelerate the concrete mix because the cement reaction is slowed down at low temperatures.

Can cement reactions keep on going if you keep reducing temperatures? At a given point typically we say that around minus 10°C the reactions will be stopped. So when you are doing concreting in freezing conditions it is very important to keep the temperature of the concrete high. Even if the ambient conditions are -10°C you have to ensure that the water has been heated up sufficiently well to get you the required temperature. On the other hand retarders are used when you want to do hot weather concreting. When the temperature outside is 45-50°C, if that heat makes its way into the initial temperatures of the ingredients of the concrete, obviously the concrete temperature is going to shoot up like crazy. We will talk about mass concrete later, but in general about 100 kg of cement produces an equivalent of 12°C rise in temperature. This is just a thumb rule; it can vary depending upon the type of cement of course.

For every 100 kilogram cement you have in your mix your concrete temperature will go up by about 12°C. So if you start your placement of the concrete at 35°C and let us say you have 400 kg of cement in your mix what is the temperature rise or what is the temperature of the concrete that can be expected the peak temperature is degrees 83°C, can be the rise in temperature or can be the temperature of the concrete. So in the same job site you try to lower it to 25° C. You are automatically cutting down the temperature rise by 10°C. If you go down to 15°C you are further cutting down the temperature of the core. It is beneficial therefore to place your concrete at low temperatures. This is in case of mass concrete structures where we expect that the size is too large and the concrete will start heating up significantly in the center.

For normal beams and columns where size is not so big we are not that concerned, but nevertheless if we have to maintain workability we need to ensure that the concrete does not start setting in this process and we have sufficient workability throughout the concreting process for that we need to use retarders. And for long haul applications in Mumbai every concrete they want 3 hours slump retention, because it is unpredictable how long it will take for you to reach the location. So to keep concrete workable for a longer time you definitely need this. There are actually other instances for instance you have to supply concrete on a hill and your nearest batching plant is somewhere far away. So imagine the time it takes to do the climbing to really get to the job site to really deliver your concrete. In such cases you definitely need retarders to ensure that the concrete does not start setting while it is supplied to the job site.

Basic Admixture Chemistry:

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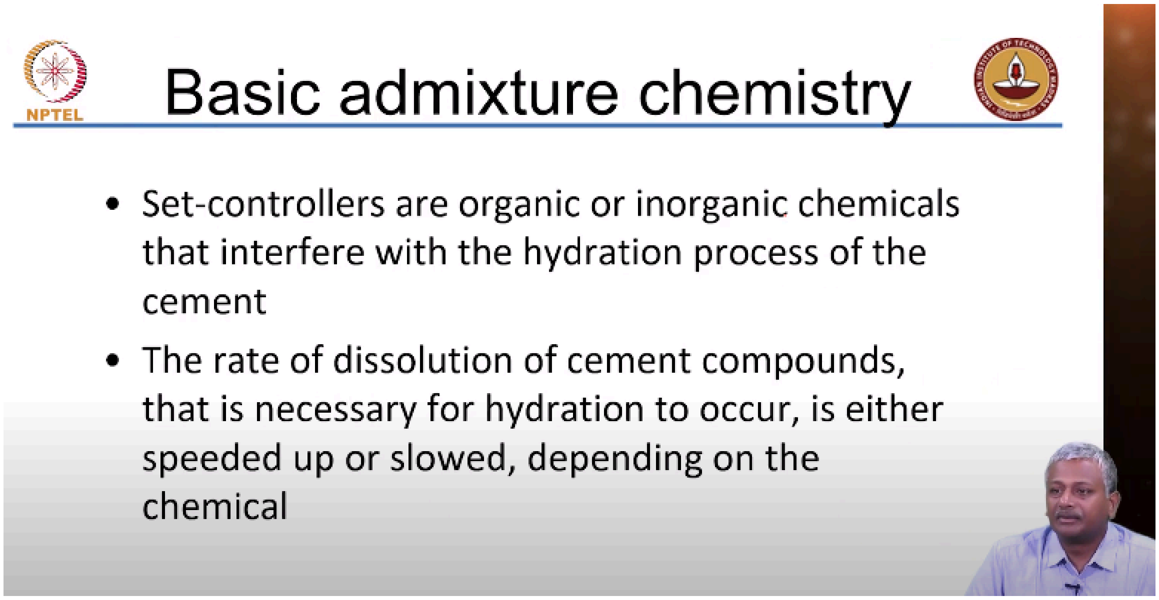

Now in terms of chemistry if you think about your general chemical reactions we talk about what are known as catalysts. Catalysts are chemicals that are added into the system that can increase the rate of combination of the reactants to produce the product. That is like an accelerator, an accelerator is like a catalyst in a regular chemical reaction.

Retarder acts opposite to that. So primarily set controllers are either organic or inorganic chemicals that interfere with the hydration process of the cement. Now super plasticizers did not have a direct interference with the hydration process. But they did have indirect interference. What is that indirect interference? They adsorb in the cement grains, preventing the cement grains from directly reacting with water quickly enough. So there is some, the more admixture that you add the more retardation that will happen. So that is not a direct indication but indirect indication of an ability to retard. But in the case of these chemicals we have almost a direct involvement in the way that the reactions actually happen.

So the rate of dissolution of cement compounds that is necessary for hydration to occur as we discussed earlier, cement particles, the compounds of cement first lead to a dissolution and reprecipitation to start forming your hydration products. So this rate of dissolution either speeded up or slowed depending upon the chemical that you use. So an accelerator will speed up the dissolution, a retarder will slow down the dissolution.

Types of Set controllers:

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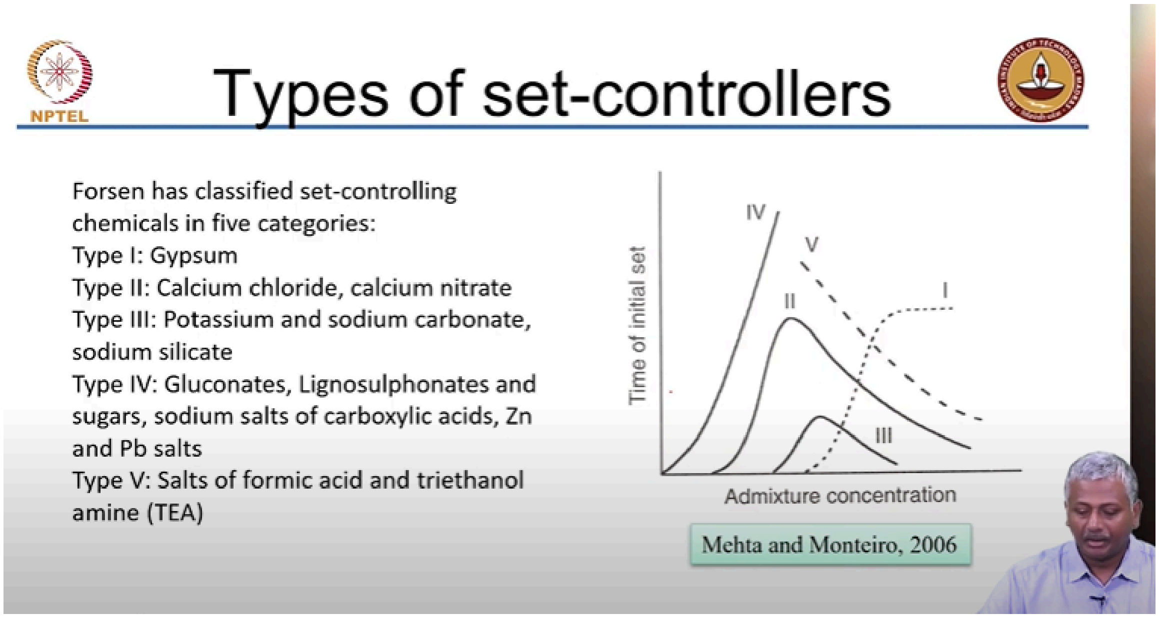

So this was work done by cement chemist previously Forsen. He did a classification of set controlling chemicals into five categories. Now what is plotted here as a time of initial set is not the actual time, it is basically an increase or decrease in the time. Which means that if the curve is going up that means my initial set is going on increasing as compared to a mixture without any admixture, without any of these chemicals. If it goes up and comes down that means at small doses there is increase in setting time or retardation, at high dosages there is reduction in setting time or acceleration. So that is how this curve needs to be interpreted. It does not mean that your setting time goes up to a certain point then starts dropping, it is not like that. So you can almost think that at one concentration you are leading to retardation, at another concentration you are leading to acceleration.

So what are these types of chemicals? If you take type 1 is gypsum which is typically used as a set controller in cement, you have a certain minimum concentration that you need to add to really induce this set control and then the time of setting increases and then more or less remains constant, it does not really increase too much beyond that.

Type 2 is calcium chloride and calcium nitrate which are well known as accelerators but interestingly when you look at these accelerators you see that there is a dosage of these chemicals where the set time is actually increasing and there is a dosage where you get the acceleration. What does this go to show? This tells you that this chemical has opposite effects at different concentrations. So you need to be very careful in designing the concrete mix with the right dosage of the chemical. At too low a dosage you are leading to retardation, at high dosages you are causing acceleration. So you need to ensure that you have high enough doses present in the system.

Type 3 again has a similar effect of increase in set at low dosages and acceleration of the setting at high dosages. But what is the difference here? Type 2 and type 3. What is the difference? The impact of the admixture is lesser for type 3 as compared to type 2. Type 2 has the maximum impact, type 3 has less impact.

Type 4 what does it tell you? It is a constant retardation. If you keep on adding more and more retardation actually happens. And type 5 they are not effective at low dosages but at high dosages it is constant acceleration. There is constant acceleration of the set. These are salts of formic acid and triethanolamine whereas type 4 are basically your major retarders that are typically used. Lignosulphonates, sugar, sugar is a very well-known retarder. Most truck drivers carry a packet of sugar with them to prevent the concrete from settling inside the truck. Wasting concrete is obviously much more preferable than wasting the truck. Concrete solidifies in the truck that is a loss of several lakhs of rupees. Whereas regular concrete which is about Rs.5,000/m^3, it is only about Rs.30,000 that you are losing if the concrete gets wasted.

Action of Set controllers:

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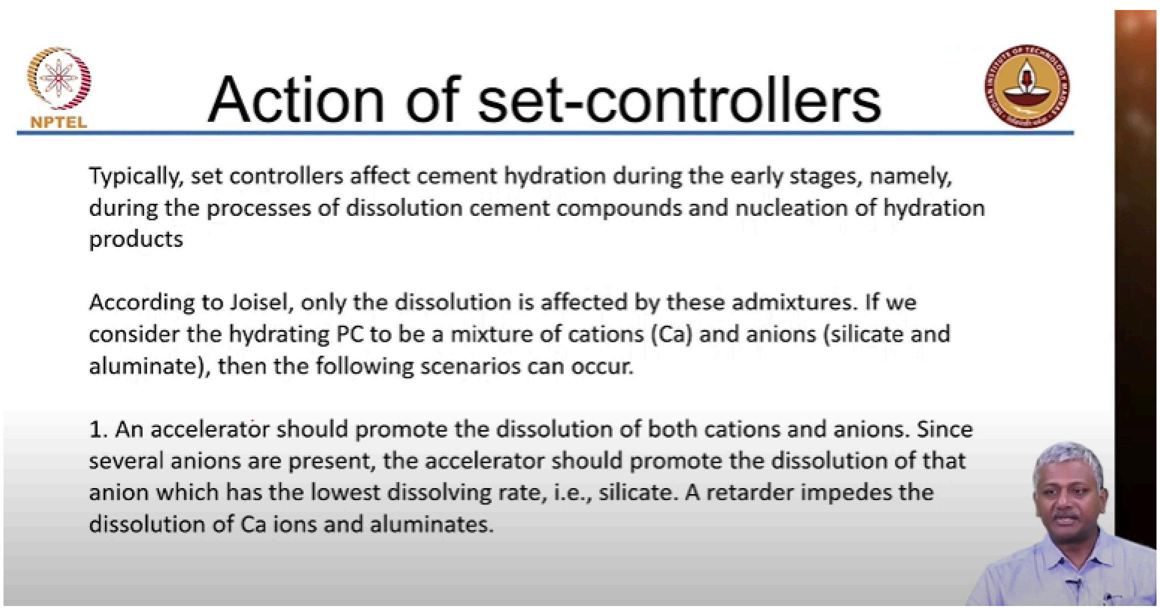

Now it is interesting to note that certain types of chemicals behave both as retarders and accelerators. So we need to understand what chemistry is. So as I said the primary effect on the cement chemistry is during the dissolution process of the cement hydration. Now again another scientist named Joisel, he said that the dissolution is affected by these admixtures. If we consider the hydrating Portland cement to be a mixture of cations, all the compounds are calcium based so there is only one cation that is calcium and anions either silicate or aluminate. Let us not even consider C_4AF in the system because that is hardly reactive, it does not react much at all.

So you have anions which are silicate or aluminate. So the following combinations according to Joisel can happen. One accelerator should promote the dissolution of both cations and anions. So it should promote the dissolution of the cation which is calcium and it should promote the dissolution of the anion which has the slowest rate of dissolution that is silicate. Because it eliminates you know well that they react fast, silicates react slowly so the accelerator should affect the silicate. A retarder should be just the opposite. Retarder should impede the dissolution of calcium, it should also impede the dissolution of which anion? Aluminate, because it is a faster reacting anion.

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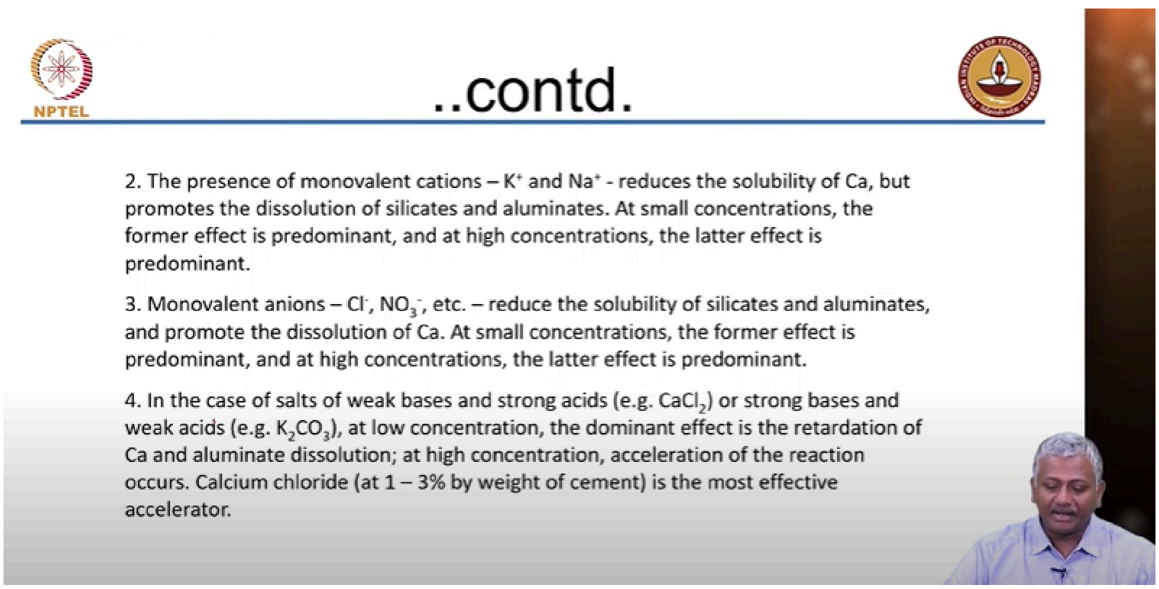

Now it turns out that when you have these monovalent cations in your admixture, sodium and potassium, they will reduce the solubility of calcium but they will promote the dissolution of silicate and aluminate. Why? Because you are having an admixture that is rich in monovalent cations, sodium and potassium. They are reducing the solubility of calcium. Chemistry you may have heard about the common ion effect, you have more positive ions in your system, and it prevents more positive ions from coming into solution. It would like to get more negative ions in the solution to maintain some equilibrium.

So at small concentrations it turns out that this reduction in solubility is dominant but when you have large concentrations of sodium and potassium in the system, the contribution to dissolution of silicates is dominant. That is why we see this kind of a relationship. At small concentration that is retardation, at high concentration that is acceleration. Same goes to show for monovalent anions like chlorides and nitrates. They reduce the solubility of silicates and aluminates, negatively charged species but promote the solubility of calcium. It turns out that at small dosages this is dominant, at high dosages this is dominant. So that means that if you use a chloride based accelerator, you need to add high enough dosage so that the dissolution of calcium becomes the dominant phenomenon. So obviously we are using mixtures of ions, calcium chloride or potassium carbonate and so on when you have a low dosage, the dominant effect is the retardation. At high dosages the dominant effect is the, but calcium chloride is the accelerator that cannot be used in reinforced concrete because chloride will induce corrosion. So we have to look for non-chloride chemicals. Calcium nitrate is an option. Calcium nitrite is also an option because it also acts as a corrosion inhibitor which we will look at later.