Admixtures and Special Concretes

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Lecture 15 - Chemical Admixtures: Set controllers – Accelerators

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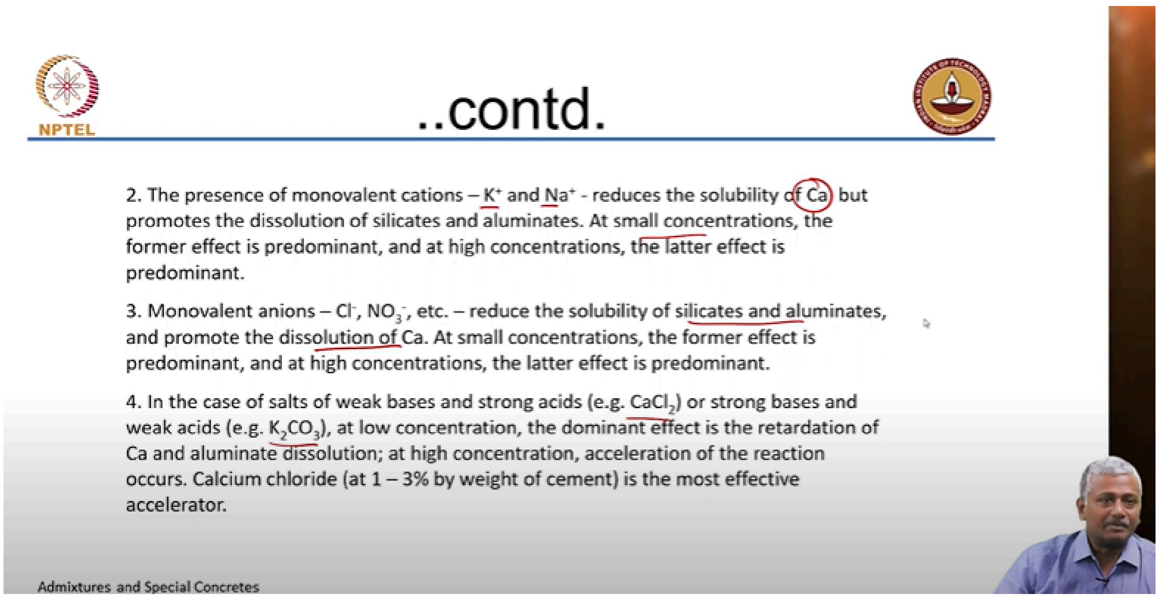

So we will resume where we left off in the last class with different types of accelerators or actually we were looking primarily at the commonalities between different types of chemicals when they are included in the cementitious systems. From the perspective of what kind of action from their side would dominate, right depending upon the type of anions and cations that are present in the admixture. The dissolution of this chemical into water will change the rate at which dissolution of cementitious compounds happens. So as I mentioned earlier the primary reactions of cementitious materials take place through a solution, a dissolution of the compounds and then reaction with water. So that rate at which the dissolution happens is either speeded up in the case of an accelerator or slowed down in the case of a retarder.

In some instances we saw that there are some reasons why certain chemicals can behave both as accelerator and retarder. In such cases you have to be very careful about the dosage that you use as we saw in the impact of the dosage here. In some instances at low dosage the retardation effect was dominant, at high dosages the acceleration effect was dominant.

Accelerating Chemicals

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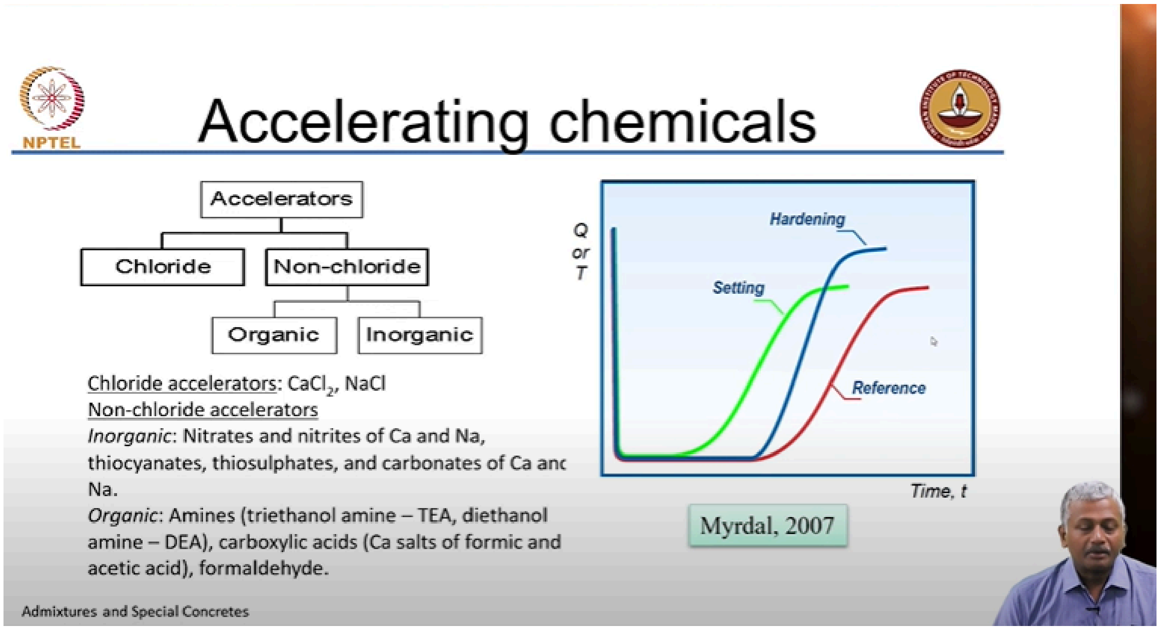

So moving on from here let us now take a look at the type of chemicals that are used typically as accelerators and the types of chemicals used as retarders. So generally the broad classification of accelerators is in terms of the chloride accelerators versus non-chloride accelerators. There is obviously a reason we do this because initially acceleration was the primary or chlorides or calcium chloride was a primary source from which we obtained our acceleration of the setting of cementitious systems. So calcium chloride possibly is the best known accelerator but when people started realizing or understanding the impact of chlorides on the corrosion process it became increasingly difficult to use chloride accelerators except of course for plain concrete if you are going to be making plain concrete like concrete blocks for instance there is no harm in using chloride accelerators.

In fact for most of your block manufacturing purposes if you want to accelerate the rate of productivity of your system use of calcium chloride is a great way to do it. But because in reinforced concrete we have the problem of corrosion people have increasingly relied on non-chloride accelerators and these are typically nitrates and nitrites as we saw earlier anionic species including nitrates and nitrites are typical when we want to interact with the cementitious system and these are from calcium or sodium cationic sources. The other possibilities are thiocyanates, thiosulfates and carbonates of calcium and sodium. Now obviously it is not very easy to pick a particular chemistry so you have to look at several things. One is of course the effectiveness of how much these accelerators affect the overall capacity of the concrete to accelerate the set or retard the set.

Second is obviously the availability, are they available nearby or are they available in a local area of course construction chemicals are made available by the construction chemical manufacturers all across the country. But depending upon the distance to which the transportation has to be done that cost has to be considered and obviously the cost of the molecule itself will be a major determinant in terms of what you end up using. Organic chemicals are a lot more expensive as compared to inorganic chemicals but their action is a lot more uniform.

We saw earlier that organic chemicals belong to type 5 accelerators where they do not have any action until a particular dosage but beyond that dosage there is a constant acceleration of the set that means reduction of the setting time. So they are more dependable to really produce the kind of effects that we want and not worry about the dosage because even at low dosage they are not really going to act or do anything but if you are at a high enough dosage they will cause acceleration of the set. But these are going to be more expensive like triethanolamine, diethanolamine, carboxylic acids even formaldehyde is actually a good accelerator but for the purposes of formaldehyde being hazardous and not easy to handle it is not typically used as an accelerator.

So compared to reference concrete a setting accelerator will speed up the set. That means if you remember the heat evolution curve there was a period which we call as a dormant period during which the reactions are so slow that there is no perceptible heat evolution taking place. So the rate of heat evolution is very low. Now most setting accelerators will tend to lower or reduce the dormant period but beyond that the rate at which the hardening occurs may not be much different as compared to your reference concrete.

On the other hand you have hardening accelerators typically the ones which are thiocyanate or thiosulphate based where the setting may not be affected significantly that means the length of the dormant period is not getting changed much but the rate at which setting happens or the slope of this straight line portion of the curve is significantly higher compared to the reference mix. So you may want to use one or the other depending upon the type of application that you are looking at. If you are working in cold weather the primary impact obviously is on both setting and strength gain. So generally the setting accelerator will get you there but in some locations where your option is to go for strength gain but you do not necessarily want setting to happen very fast because you are delivering concrete through ready mix. If setting happens very fast the concrete will stiffen in the concrete truck and that is something you do not want.

You want the hardening to happen after the concrete is placed after the workability requirement is not really there. So in such cases you want to use a hardening accelerator.

I will give you an example. I used to work for a company called SICA Corporation in the US where we were trying out the chemical called SICA Rapid that was a hardening accelerator. It was called SICA Rapid and the primary impact of this accelerator was on this hardening stage that means the rate at which the strength developed once the setting happened. So here again the concrete was actually intended for a full depth repair of concrete pavement slabs. So what they were doing was closing down the highway at 9 pm at night. In the next 2 to 3 hours they would break the entire distressed concrete pavement slabs. The slabs that were not in good shape were broken up completely to full depth. 9 inches typically or 200 mm or 225, 250 mm will be the depth of pavement slabs. These are doubled concrete pavements.

So they would break open the pavement at 9 o'clock starting at 9 o'clock. So by 12 they are ready to actually pour the concrete. So the application called for development of a flexural strength of up to 3.5 MPa at the end of 6 hours after placement. But because the concrete was being delivered to highway stretches which were far away from cities they had to ensure that the concrete was workable for a long enough time. And this was also an application that we did in the northern Atlantic region. So there was obviously the need to protect concrete from freezing and thawing that typically happens when you have cold weather cycles. So here we had the air entrainer to ensure protection from freezing and thawing. We had the super plasticizer obviously to provide workability that could retain the workability until the point of discharge. Then we also had this hardening accelerator. With this combination the mix proportion was strategized in such a way that after placement and normal consolidation by vibration and finishing it would take 6 hours for this mix to really achieve a strength of 20 MPa compression which approximately gave us about 3 to 3.5 MPa in flexure. So by 6 the pavement stretch is now open to traffic. So very rapid repair of pavements was possible. We were quite successful at marketing this across different state highway agencies and worked quite well that way. So one thing you also have to realize of course is this is a solution for early age strength. So accelerating chemicals typically may affect your long term strength.

Again I bring back my example of cooking. If you try to speed up your cooking process the end result is not that great. The taste is not always very good. You may happen to arrive at the right proportion by chance and get a good taste. But if you have a process that is slow and steady that takes you a fairly long time generally the result is good. Generally not always. Sometimes in your bid to experiment you may go wrong. But similarly in concrete curing if you are accelerating the curing process you have to pay the price in the long run. Generally the properties of accelerated concrete are not as good as that of normally cured concrete. So accelerated concrete could either be through accelerated curing like application of heat or steam curing which is typically done in precast companies or it could be done with the help of accelerating chemicals. In all of these cases you are ending up with a final concrete microstructure that is not as good as a normal concrete microstructure. Why do you think that happens? Why is this happening? If you go back to our initial discussion as to how cement hydrates and fills up the pore space around it. Now what we are doing by acceleration is causing a rapid hydration on the surface and maybe we are not allowing the remaining water to get diffused through this initial hydrate membrane that is formed and hydrates the rest of the cement. As a result what happens is we are left with a lot of open porosity. We develop strength fast but a lot of open porosity still remains in the system which does not get closed by the slow hydration of the cement. Same thing happens in heat curing also. We get a lot of open porosity in the long run. So more than strength the real impact is on durability.

When you accelerate the setting of concrete you will end up with a durability level that is not comparable to the durability of normally cured concrete. So one thing that you do in precast concrete even if it is heat cured or accelerator system or whatever it may be post acceleration. So let us say in this pavement we got strength at 1 day or 3.5 MPa which was enough to open the highway section. Now if you leave it like that there is very little chance of the strength development to continue happening at a steady rate throughout. So in such a case it helps to actually do further moist curing of the concrete after the initial strength has been attained.

So in precast yards what they do is typically they have these large pre-casting beds where the concreting is completed and then the heat curing cycles are given. Beyond this the concrete which has been set and obtained the right strength is shifted to the storage yard. In the storage yard it is very helpful to continue to spray water or to keep the concrete moist until the time when it is going to be used in service. It is a very good practice to do that because the provision of a moist environment enables that whatever moisture still remaining inside continues to slowly hydrate the cement and close up or block up all the pores that are still open in the system. But we do not do that often. These concrete are just lying outside because you have attained the initial strength. In many cases the attainment of strength is to ensure that you can transfer the pre-stress to the concrete. Once that is done your objective is gone. You have already met your objective but really if you want to make the concrete more durable the moist curing beyond the initial curing to attain the strength is very important.

Calcium Chloride:

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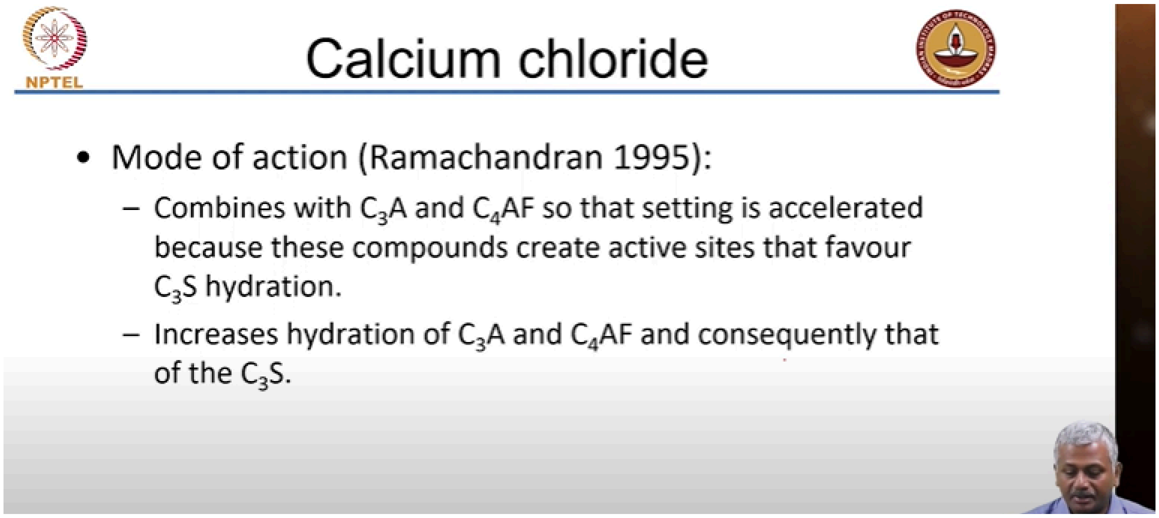

Now calcium chloride people have done extensive studies on it. It combines with your aluminates so that setting is accelerated because these compounds create active sites that favor C_3S hydration. And secondly of course they are also calcium chloride as we discussed earlier increase the rate of dissolution of the calcium as well as the silicate species.

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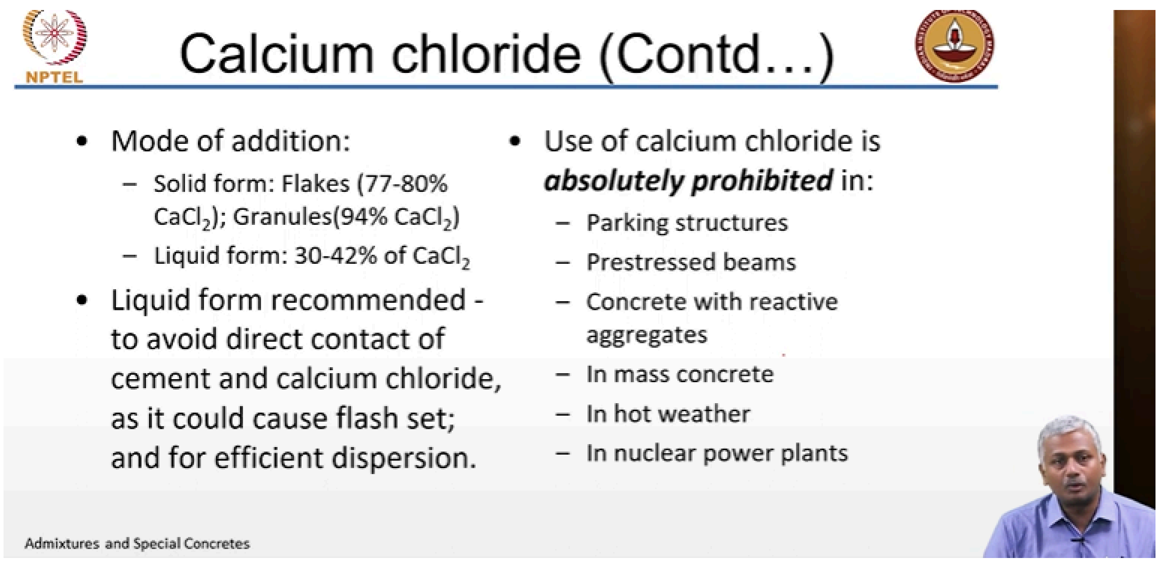

Now as I said in the past people used a lot of calcium chlorides. So there were different forms in which calcium chloride was made available. There were flakes, granules that could dissolve in water almost immediately because calcium chloride is highly soluble or about 40% liquid form of calcium chloride also was available. Liquid form is generally recommended because what we do is we want to restrict direct contact to the cement with the solid calcium chloride because locally what that would do is create a very rapid set locally. Liquid form means your calcium chloride has been diluted sufficiently enough and then when it is mixed with the water it gets further diluted and then you can control the setting better that way. So dispersion of the product happens better. So most compounds are actually sold in a liquid form. Very rarely you will get super plasticizers or accelerators or retarders in a powder form.

You do get pre-packed formulations. In some cases when we are going for a repair for instance you have these bagged repair systems where cements and admixtures everything is mixed together in a powder form, dry form. When you go to the site all you need to do is mix water and that is typically also given very clearly for one bag of this product to mix so much water. And when you do that all the products that are inside the system dissolve and come into the liquid form and then you have the normal process of hydration. All patching mortars, repair mortars and everything is typically sold in the form of bagged products.

Now for obvious reasons you want to prevent calcium chloride usage in parking structures, pre-stressed beams wherever you have a lot of problems with reinforcement corrosion. Now you also want to restrict its use in nuclear power plants for obvious reasons because you do not want to cause anything to the concrete that will lead to any disastrous failures. Nuclear power plants are obviously very important structures and such facilities have to be having a very high level of safety to prevent any radiation leakage. In terms of mass concrete and hot weather concrete you do not want to further accelerate the concrete system because of the presence of high temperatures and the presence of the high heat development because the mass concrete will lead to much higher rates of hydration. Now the parking structures is a very interesting story not from the point of view of use of calcium chloride in concrete as an admixture but the use of calcium or magnesium chloride as a salt that is or even sodium chloride as a salt that they spray on the surface of the pavements to prevent skidding during icing of the pavements.

In most countries where icing actually happens on the pavement either they spray sand to increase the friction or they spray salt because what does salt do? It melts the ice or it basically depresses the freezing point of the water so water does not transform twice. So because of this they spray salt and the vehicles that drive over these pavements the carry the salt with their tires and when they come to the parking garage and park there the salt slowly drips and the salt is highly concentrated now because it is all dried up and when it starts dripping onto the parking garage floor the slab of the parking garage is likely to just diffuse into the concrete and create corrosion. So that is how they actually started looking at these impact of the de-icing salts that were used for de-icing of pavements on the corrosion that they caused to concrete parking structures. So again all of these were related and people could then figure out de-icing salts can create a lot of difficulties because while they may be diluted by the time that they are fully sprayed onto the surface of the pavement because they are actually sticking onto the tires they are getting more concentrated they start dripping slowly onto the parking garage and create this corrosion. Now just to give some idea about the effectiveness with respect to increasing the hydration rate of tricalcium silicate.

Accelerating Chemicals:

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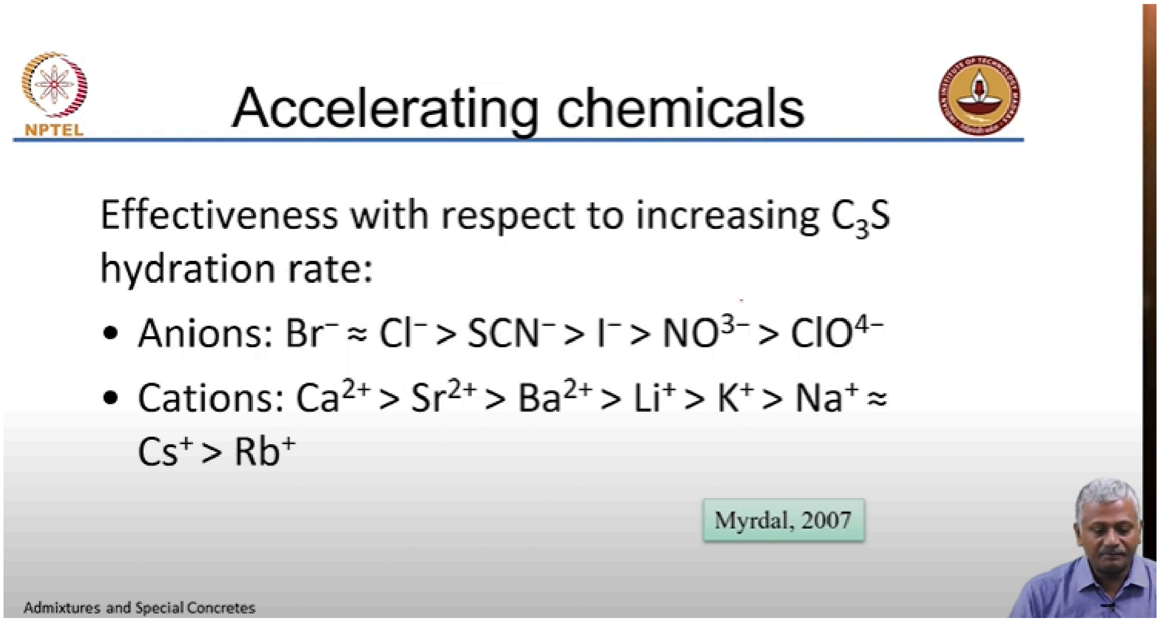

This is basic studies that have been done with different species of accelerating compounds. Among the anionic species of course the chloride is the best even bromides are good but a lot more expensive then you have thiocyanate, iodide, nitrate, and chlorate. So these are the order decreasing order in which you have the effectiveness of chlorides are most effective.

Cations calcium bearing cations are the best then strontium, barium, lithium, sodium, potassium, cesium and rubidium. Some compounds are more difficult like barium or cesium or rubidium because these are more expensive. So you have to probably work only with calcium and sodium which are most easily available as elements on the surface of the earth. What are the major elements that you can find on the surface of the earth? Silicon is most abundant. Silicon then aluminum then you have calcium and then you have iron. If you go deeper down into the earth's crust obviously there is more iron but on the surface silicon is the most abundant. So between these 4 calcium, aluminum, iron and silicon they make up nearly 80-85% of the oxides that are found on the earth's surface. So already these are the compounds that we use already in cement manufacture.

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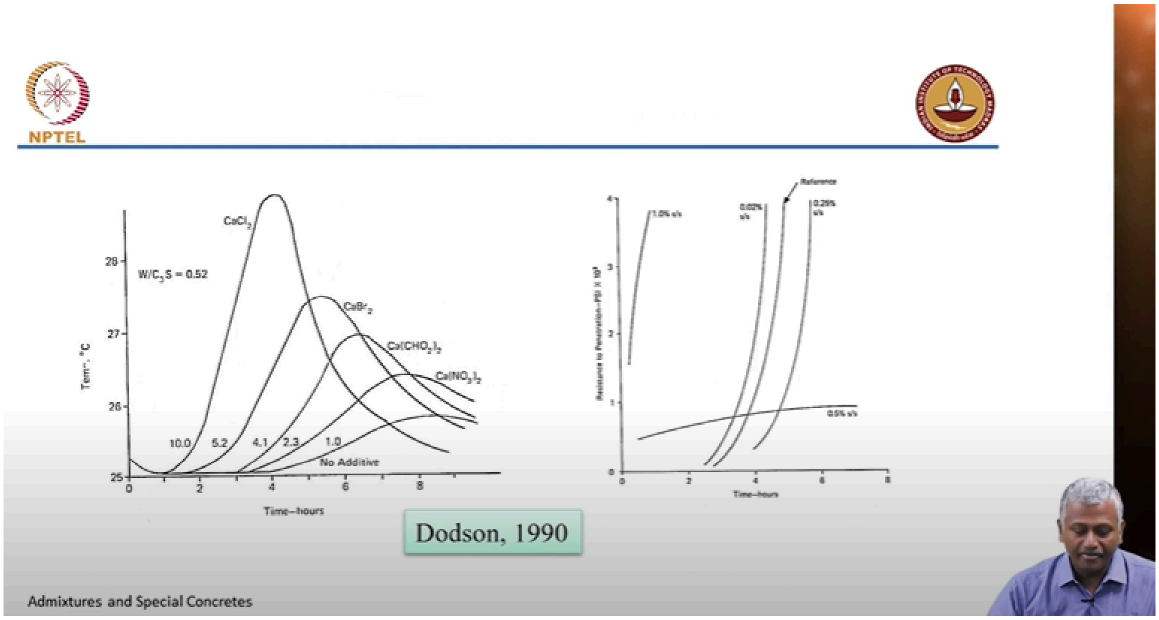

So again this is research published from Dotson. It is actually a book by Dotson on chemical admixtures that shows this data. So this again plots the effectiveness of different admixtures calcium chloride, calcium bromide, calcium formate and calcium nitrate which are used as accelerators. What they are looking at is the reference one without any additive. What they are looking at is the relative shortening of the dormant period that is reported from your heat curve. So that very clearly you have an impact of using these accelerators in the heat curve.

Sprayed Concrete Accelerators:

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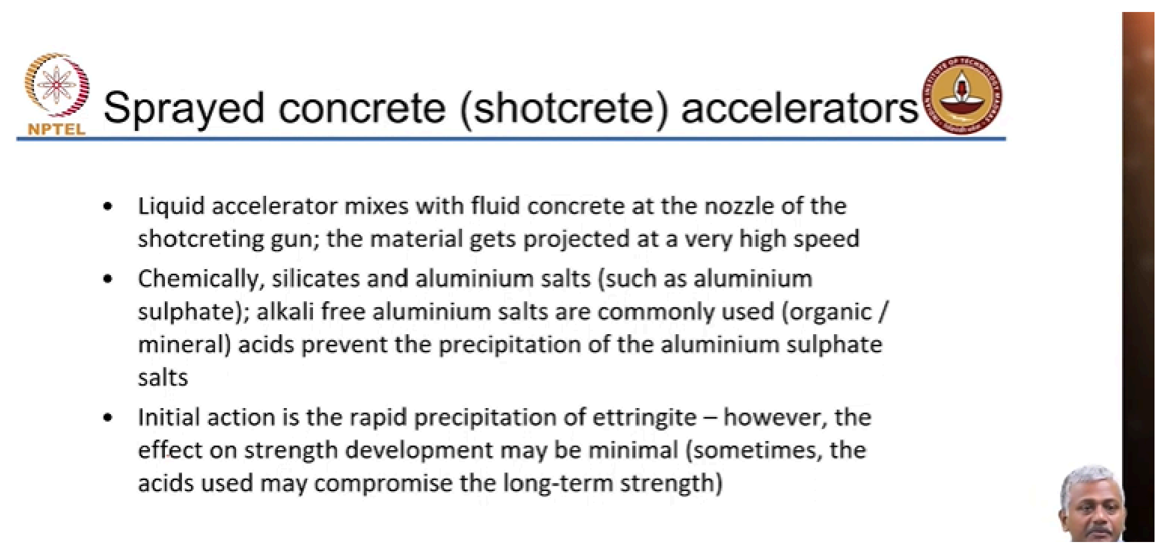

Now in some instances we have to work with shotcrete. Many of you would have come across these applications of shotcrete for tunnel linings for instance. So you can use shotcrete to stabilize the soil once the boring has been done. Either you can actually put a tunnel lining in terms of a curved slab or you can use shotcrete to stabilize the soil and ensure that there is no collapse of the soil. So this shotcrete has to have the property of being very cohesive and then sticking on to the surface hardening very rapidly so that it does not permit the soil to fall. So all this has to be done very quickly even when they cut slopes to make your highways and stuff like that to prevent the massive landslides from happening the rock surface has to be often stabilized and shotcrete is also used quite extensively in such applications because the soil may be quite loose to make sure that it does not start sliding further you use shotcrete. So we can do shotcreting typically in two ways, one in the wet process or in the dry process again. I think some group will work on shotcrete during the project. So the wet process means that you mix the concrete completely and then shoot it out at high velocity through a gun.

A dry process means the concrete is mixed dry and it comes to the tip of the gun and there the admixture is added and then the mix basically shoots out. So the liquid accelerator mixes with fluid concrete at the nozzle of the shotcreting gun and material gets projected at very high speed to ensure that there is sufficient impact to get the material to stick on to the surface so chemically these compounds sprayed accelerators are basically silicates and aluminium salts such as aluminium sulphate. Generally the alkali free aluminium salts are commonly used.

So why do you need your aluminium salts to be alkali free because you do not want the salt to start getting crystallized in your system. So if you have an alkaline salt it will start basically crystallizing your aluminium sulphate salts in the system. So you want alkali free aluminium sulphate as a shotcreting accelerator.

Now you are adding additional sulphate so if you think about the chemistry of a system how the cement chemistry typically is? We have aluminates reacting with gypsum. They form ettringite in the initial stages but because sulphate is not available at plenty this ettringite slowly gets transformed to monosulphate that is the low sulphate form of calcium sulphate. So in this scenario when you are putting an additional sulphate system inside your concrete it is going to create more and more ettringite formation and if you remember the structure of ettringite from our initial discussion it is present in the needle type form and causes rapid stiffening of your concrete. So the formation of massive amounts of ettringite causes rapid stiffening and since the sulphate balance is so high you put so much sulphate in there this ettringite will not transform back to monosulphate anymore. So this will remain as ettringite. Now this ettringite, although it affects the initial setting and strength gain, the long term strength contribution of this ettringite is not going to be significant. Sometimes this ettringite may also start decomposing in the long term and that may lead to a long term loss in strength.

Acids that are used in your system because it is alkali free the acids that are used in the formulation may also compromise the long term strength. So all of this has to be carefully studied before implementing it in concrete. Now alkali free accelerators have now started making inroads into concrete in a much larger fashion because of the advent of 3D printed concrete and that is something we will talk about when we get to 3D printing separately.

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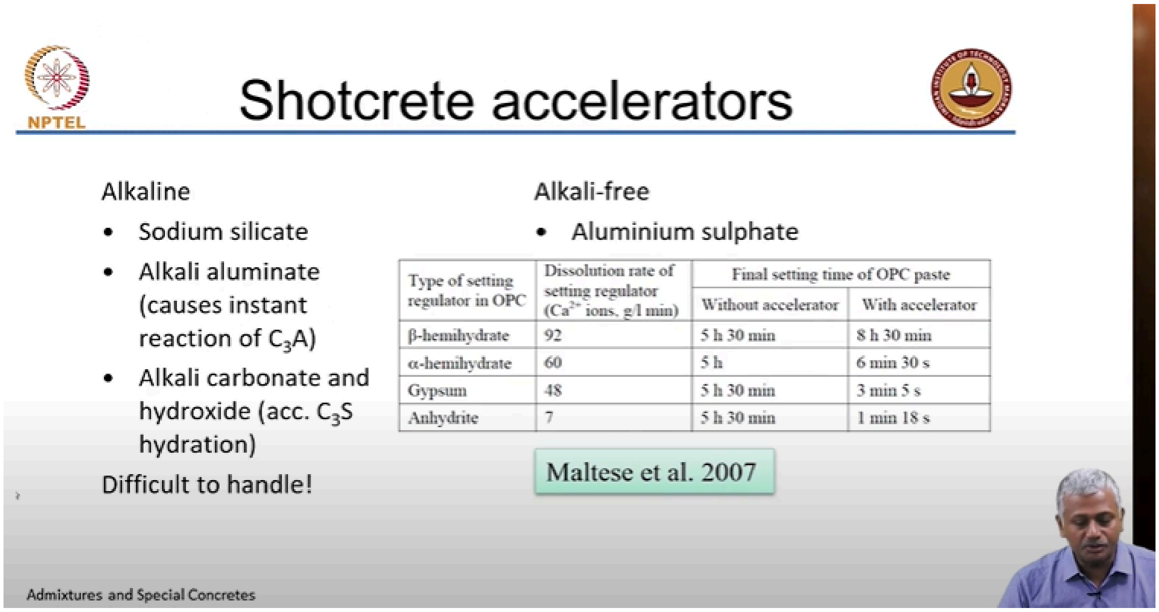

So just to give you some chemistry of these accelerators, you have alkaline accelerators of course like sodium silicate, alkali aluminate and alkali carbonate and hydroxide. These are difficult to handle as I said because they have very high pH levels, it can be extremely caustic. On the other hand the alkali free accelerators like aluminium sulphate are quite useful. Just to give you some idea about the effectiveness of these materials, you can see that the type of setting regulator in OPC is given here.

If you use different forms of hemihydrate, we talked about gypsum, its utilization as a set controller in cement paste. So different forms of gypsum when they are present in your system, they are having different rates of dissolution. This is your natural anhydrite or hard burnt anhydrite which has the lowest dissolution rate. Gypsum as you move on towards hemihydrate, you increase the dissolution rate. So setting time of OPC paste without an accelerator is about 5 – 5.5 hrs at this dosage in this study that was done by Maltese. But what happened is that when the aluminum sulphate accelerator was used, it turns out that it actually retarded the system with beta hemihydrate. So there is some secondary competition going on between the sulphates from the accelerator and sulphate from the beta hemihydrate which is high solubility. But when alpha hemihydrate or gypsum was present, look at the effect of setting time, 6 minutes, 3 minutes.

An anhydrite which was very slowly soluble absolutely did nothing while the accelerator went and created ettringite formation and caused setting to happen in 1 minute. So here we are looking at systems that are getting severely accelerated and this is obviously important from the point of view of shot treating because you want the material to stick and harden almost immediately.

So again what I wanted to present with this table is to show that when you use chemicals of different types which have common anionic species, there could be some competitive reactions that will affect the rate at which setting and hardening takes place. So you need to be very careful utilizing concrete. So again this could be for instance if you had this beta hemihydrate in your cement, your effectiveness of the accelerator is not going to be there. So you have that problem. You need to ensure that you understand the form in which hemihydrate is present. How this is typically done is when you get the cement, you also do what is called an X-ray diffraction study of the cement that gives you all the phases that are present, the sulphate phases, the C_3S, C_2S and so on and based on that you can actually ensure that you add the right type of chemical to the system.

So with that we come to a closure of the accelerator section. No questions? All clear? Yes? Sir, for the calcium chloride system for addition we talked about the big granules in liquid but liquid as we can see the concentration is almost half of what the granules and that is so would not it require much more quantity? Yes certainly.

So liquids will require much more quantity. You need to obviously have storage spaces in your ready-mix concrete plants. Cost wise would it be better to… Well transportation of large amount of liquid is obviously more expensive as compared to transportation of powder. Powder is much more efficient. One could obviously transport the powder and convert it to liquid in the storage plant right wherever you are storing this admixture that could be done. But for that you need an efficient mixing to happen. But yeah liquid systems are much easier to use as compared to the solid powders. We again sometimes the admixture companies also they play an interesting game. When I started working for the admixture company I was wondering why all these liquids look the same color. Everything looked this caramel brown color. They used to add this coloring agent which makes everything caramel brown. So you will have no idea unless you of course get used to the smell of the admixtures the naphthalene sulphonates will have different smell, the lignosulphonates will have different smell and so on. So after understanding that aspect I realized that they do not want to confuse the customer too much by giving different colored products. So everything looks that brown. With the advent of these poly-caboxylates things have changed quite a bit.

So there we start seeing much more colorful chemicals. Some are colorless, some are amber, and some are yellow and so on and so forth. So people have now started getting used to the idea of admixtures. In the beginning everything was the same color brown, all caramel brown every time. And that also led to some very interesting situations. So this was from my experience in the US where all these ready mix concrete plants, they actually have different tanks typically for different admixtures. So I was working in New Jersey which is in the northern Atlantic region. So freezing and thawing is a common problem. So they always need to entrain air in the concrete. And then they used to have a tank for air entrainment, they used an air entrainer, another tank for super plasticizer and so on. Very often what they would do is they would switch these tanks. So when the tank gets empty they would put the next product in. So the air entrainer tank gets empty and they put a super plasticizer in. So what that does is if there is any remnant liquid left over there is some incompatibility in the liquid form between the air entraining agent and any other admixture which what it does is it tends to solidify the air entraining molecules, the air entraining compounds typically your Winsol resin will come to that in the next segment. So it gets solidified and what it ends up doing is blocking the pipes. So when you want to dose the new super plasticizer in the system it does not come out because the pipe is getting blocked. Now very often the concrete user does not understand what is going on, the concrete manufacturer.

So I used to always get these coke bottles filled up with this solidified gook and these guys would say no, no, if you filled the wrong tank the truck driver was in a hurry so he filled up the wrong tank. All of the time the same thing happened. So these liquid admixtures which look exactly brown in color lead to that kind of a problem if you are not aware of what the chemical is. So we need to handle it with care because all of these chemicals have their own different effects and for instance you do not want to add the quantity of air entrainer that you add for the super plasticizer that is going to be disastrous. Your concrete will lose strength tremendously because you are putting too much air in the system.