Advanced Concrete Technology
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Lecture - 16
Chemical admixtures - Part 4

So far in this chapter we have been looking at the water reducing chemicals and in this lecture we will take a look at the set-controlling chemicals which are typically accelerators or retarders. You know very well about why these are used of course accelerators are used for early finishing of slabs or of other concrete sections, increasing the early age strength, early removal of form work or if you want to do concreting in cold weather.

For instance, in conditions where strength gain is expected to be slow you can accelerate the concrete to make it gain strength faster. Retarders on the other hand are just the opposite; you want to use them in hot weather conditions when the slump loss is rapid. You also use it for long haul applications and for keeping concrete workable for a very long period of time.

Now there are been instances where people have used retardates in applications where the concrete had to be in fresh state for more than 8 to 10 hours, that means even after 8 to 10 hours of travel the concrete should have had sufficiently high workability so there it could be used on site. So there are special conditions like that which stipulate the use of retarding chemicals inside the concrete.

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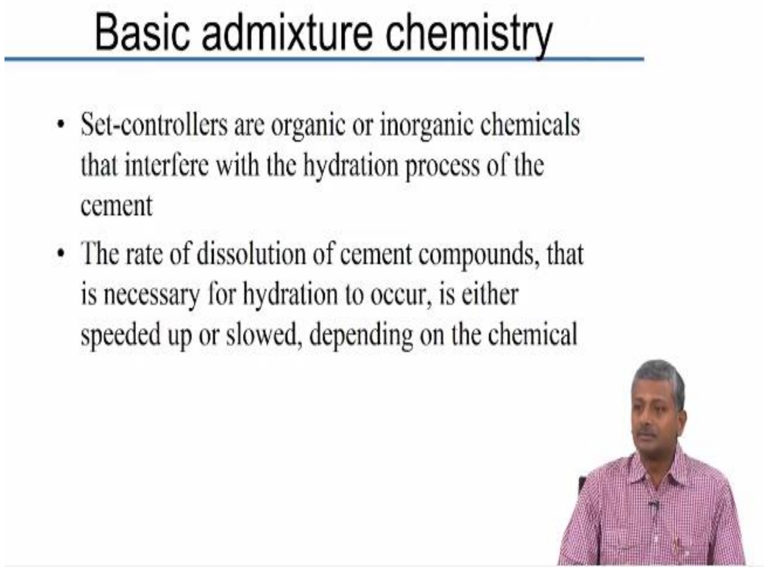

So how do these chemicals actually act? We know very well from chemical reactions that there are ingredients that sometimes are used in chemical reactions called catalysts that speed up the reaction. In cement chemistry the reactions are essentially of two types. The first one is a through solution reaction that means the rapid dissolution of the silicate and aluminates species into the surrounding solution initiates the hydration process and once that initial hydration barrier is formed you start diffusing the water through this hydration barrier and that leads to the rest of the process which is otherwise known as a Topochemical process; that means on the surface of the existing cement grains.

So here mostly the accelerators and retarders will have an influence on the early stage dissolution process. These are chemicals which will affect the dissolution of the different phases from cement grains. So the rate of dissolution of cement compounds is either slowed or accelerated and that leads to either a retardation or acceleration affect.

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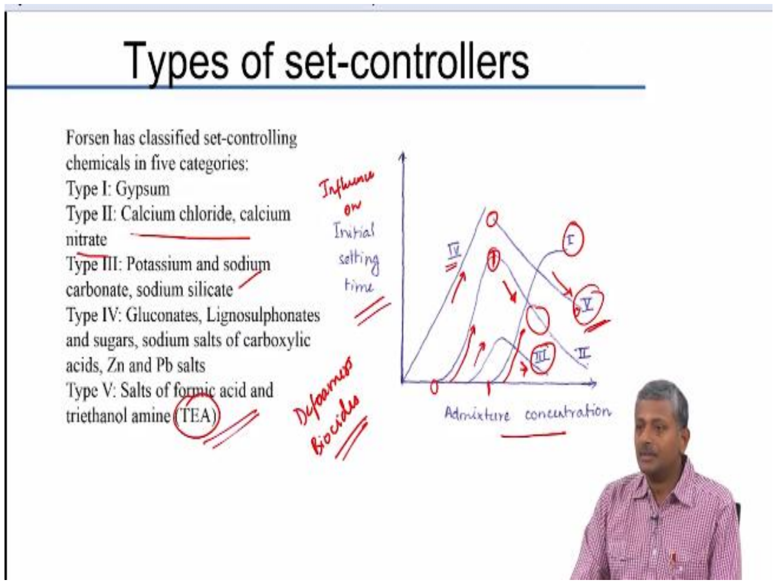

If you look at the family of chemicals which are included in set-controlling agents you will see that they often have varying sorts of actions. For example, at one dosage they may work like a retarder at another dosage they may work like an accelerator. So we will try and understand why this actually happens. So if you take a look at this diagram on the right, the y-axis is not exactly initial setting time but it is actually the influence on setting time..

So if you look at this first line that is Type-IV chemicals the setting time increases continuously when you increase the concentration of the admixture. This Type-V chemical, when you increase the admixture concentration the setting time decreases. I am not saying that I am starting off with the setting time at starting point and ending (where the line ends) here. What I just meant to say is with increasing concentration of the chemical the setting time keeps on decreasing. In the case of Type-I chemicals, the setting time is unaffected until a certain admixture concentration is reached and beyond that there is an increase in the setting time.

Type-II chemicals you have some minimum concentration at which the setting time starts increase but beyond the certain concentration you actually start seeing a reduction in the setting time, that means the same chemical at low dosages is acting like a retarder but at high dosages it is acting as an accelerator.

The same thing with Type-III chemicals that they have this sort of behavior going up and then coming down that implies that at small dosages the Type-III chemicals are increasing the setting time or retarding the concrete and at high dosages they are reducing the setting time or accelerating the concrete.

So what are the chemicals which make up these types of set-controlling agents? Type-I is Gypsum. Gypsum is essential at significantly high dosages to ensure that the aluminates do not react with water to lead to flash set. So Gypsum acts like a retarded or a set-controller in certain specified dosages. But Gypsum is not typically used as a retarding agent additionally; whatever is added to the cement is added already as a set controller. Beyond that we do not really add additional Gypsum in the system, unless we want to optimize the extent of Gypsum that is existent in the system. We talked about that when we looked at the heat calorimetric in cement chemistry, that often times when we substitute cement with mineral admixtures since the quantity of Gypsum reduces we want to optimize that to ensure that our reaction happens in the correct time.

Type-II chemicals are calcium chloride and calcium nitrate which are known to be the best accelerators. Calcium chloride especially is known to be the best accelerator. Now what is interesting about Type-II is that they start accelerating only after certain dosages, that means you need to have certain minimum dosage built-in for them to act as an accelerator otherwise they act as retarders at very low dosages they will act as retarders. So calcium chloride you need to use at sustainably high doses to cause a reduction in the setting time or accelerating the concrete mix.

The third type is potassium and sodium carbonate and sodium silicate and these are also are retarders in the beginning but then they become accelerators when you cross a certain dosage,. Type-IV is typical water reducing chemicals like Gluconates, Lignosulphonates, and sodium salts of carboxylic acids, Zinc and lead salts. These are uniformly retarding your concrete with increasing concentration there is more and more retardation. These are the same, most of them the organic ones, as your regular water reducing chemicals.

Then finally, the constantly accelerating chemicals essentially the salts of formic acid and triethanol amine lead to this Type-V behavior where with an increasing concentration of the admixture you have a continuous reduction in the setting time.

I have not really discussed much about formulation of different super plasticizing chemicals but typically if you look at the formulation let us say of a typical sulphate naphthalene hydrate; because we want to build-in some slump retention characteristics into SNF, the construction chemical company would typically mix it with some Lignosulphonates. The Lignosulphonates helps to increase the slump retention time, so most formulations of SNF would have Lignosulphonates.

If you look at formulation of Lignosulphonates because that causes retardation; often times will have a small spiking with these Type-V chemicals especially the triethanol amine. The TEA is often used as an ingredient for formulation of Lignosulphonates which would cause major retardation but to ensure that the retardation is not major but ‘controlled’, you can actually add some amount of triethanol amine into the formulation.

One more interesting thing is many of these the Lignosulphonates and SNFs may have Air-entraining properties if you use at certain dosages. So they ensure that the air is not entrained at the concrete very often they also add deformers, which are chemicals that can kill the air bubbles that are forming in the system.

And often times, for example, for the organic polymers you may actually promote bacterial growth in the system because there is lot of sugars. So to make sure that does not happen we also put biocides.

But I essentially wanted to tell you that to ensure good slump retention SNF typically Lignosulphonates is blended along with it and to ensure not excessive retardation in Lignosulphonates, triethanol amine is blended along with it. So there are different ways of actually controlling the kind of product that you come out with so that the properties of concrete are well controlled with respect to that.

So one common way of finding out if your admixture has outlived its life is that when you look at the admixture drum, it would have been bulged. This happens especially with sulfonated naphthalene formaldehyde and Lignosulphonates and you have been storing it for long. This bulging happen because of the action of bacteria that start generating gases and that sort of bulges out of the drum. So when you go to the construction site if the admixture is been stored for too long in the external heat, will often find this happens because that is the conducive environment for the bacterial growth and that causes gas formation and your barrel start bulging. At that point your admixture will start becoming unutilizable.

So coming back to set-controlling agents again these are different types of behavior that come across based on the type of chemical and we need to be extremely careful with the dosage because the same chemical can act as a retardee or an accelerator.

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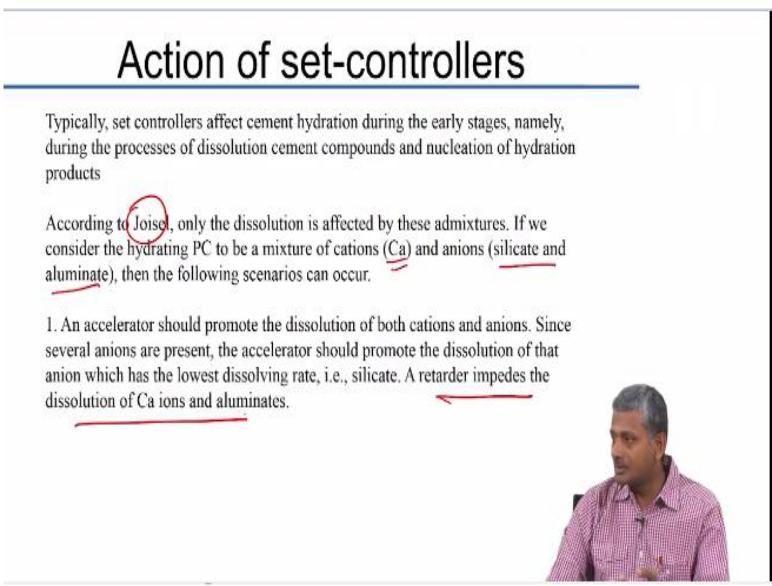

So why does this happen? We talked about the fact that accelerators or retarders are going to be affecting the dissolution stage of the hydration process. Joisel was one of the chemist who proposed the theory of how these chemicals are actually acting. What he said was you can separate your cementitious ingredients into a mixture of anions and cations. The cation is calcium and anions are silicates and aluminates.

An accelerator should promote the dissolution of both cations and anions. Since you have silicate and aluminates two types of anions are present. The accelerator should promote the dissolution of the anion that has the lowest dissolving rate. So aluminates are rapidly reacting and Silicates are less rapidly reacting. So the accelerator should prompt the dissolution of silicate. So retarder impedes the dissolution of calcium ions and aluminates. An accelerator increases the rate of dissolution of calcium ions and silicates. So accelerators will increase the rate of dissolution of calcium and silicate, a retarder will impede the dissolution of calcium and aluminate.

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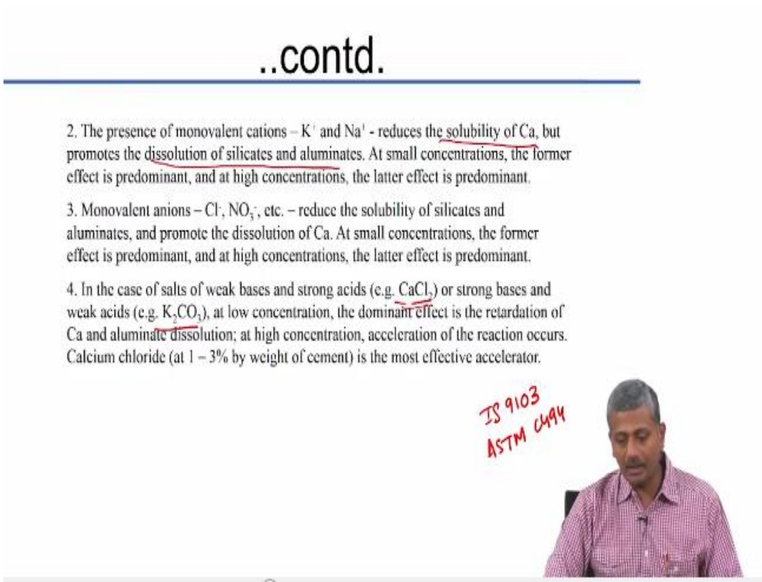

So if the chemical that you add have monovalent cations like sodium or potassium, since you will have a common ion affect when you introduce these chemicals into your mixture because of the higher presents of the positive ionic species contributed by the admixture, there will be a reduction in solubility of calcium but an increase in the dissolution of silicates and aluminates.

Positive ions are put to suppress the positive ionic species but you are increasing the rate of dissolution the negative ionic species. But all these cannot happen simultaneously, so what happens is, at small concentrations the effect of separation of calcium is predominant where as at higher concentration the effect an increase in dissolution of the silicate and aluminates is predominant.

In other words, the same chemical acts as a retarder in the lowers dosages and an accelerator at higher dosages. Now if you have monovalent anions like chloride or nitrate the opposite effect happens. Chloride and Nitrate anion species will tend to promote the dissolution of calcium but retard the dissolution of silicate and aluminate.

So at small concentrations, the effect of retardation is predominant; at high concentration the effect of accelerator is predominant. So calcium chloride, and calcium nitrate are extremely good accelerating chemicals only at very high dosages. At small dosages they may end up retarding system. Now when you have calcium chloride it is a mixture calcium and chloride or you have potassium and carbonate at low concentration, the dominant effect is the retardation of calcium and aluminate dissolution. Whereas at high concentration, the silicate dissolution is accelerated.

So you need to be very careful about how you use these chemicals, what is the dosage and you need to decide on that dosage through adequate testing in your system. Now I have not touched upon the standards for chemical admixtures, but I just would like to point out that Indian standards is IS 9103, and that deals with chemical admixtures for concrete, it talks about all different types of chemical admixtures. Similarly, ASTM standard is ASTM C494. The standards define a specific concrete mix that you need to make with and without the admixture and test the properties in the fresh and hardened state. The fresh state properties include the slump and the setting time of the concrete and then the hardened state properties include the compressive and flexural strength and also the rate of shrinkage that you have in your system. So all those properties have to be satisfied for your admixture to be deemed qualified to be used in concrete. Based on how what kind of properties they satisfied they can be classified into different types of chemicals as per the ASTM or IS codes.

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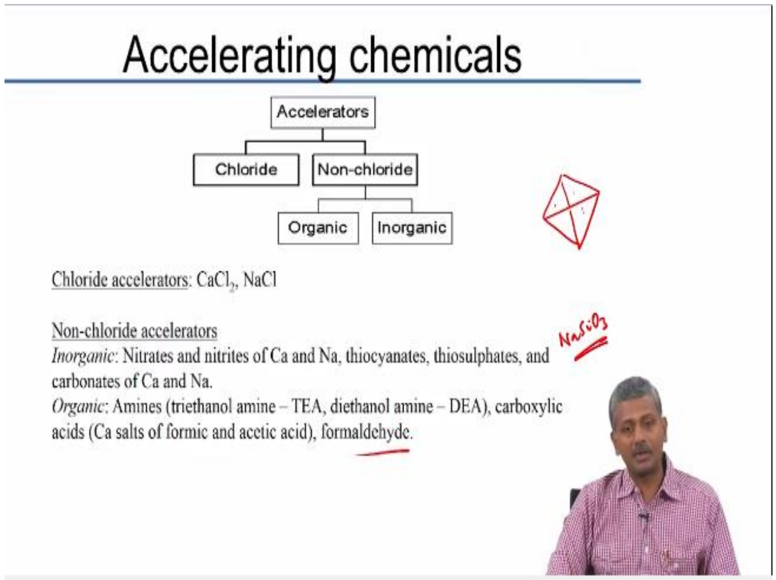

So just to give you the idea about what type of chemicals constitutes acceleraters, you can divide accelerators into two types Chloride and Non-chloride. Chloride accelerators are like calcium chloride and sodium chloride. Unfortunately, although they are very effective they cannot be used because you are increasing the chloride concentration of the system and that leads to corrosion of the reinforcing steel. So today calcium chloride is permitted only in plain concrete not in reinforced concrete. Non-chloride accelerators have to be used because you cannot use chloride accelerators so inorganic chloride accelerators include Nitrates and nitrities of calcium and sodium you can have thiocyanates of sodium, thiosulphates or carbonates of calcium and sodium. These are all extremely good accelerating chemicals.

Sodium silicate also is an accelerating chemical, sodium silicate, which is not listed in slide. Organic chemical includes triethanol amine, diethanol amine, carboxylic acids in terms of salts of formic and acetic acid and also formaldehyde is a good accelerating chemical. Formaldehyde is extremely hazardous and cannot be used directly. Those you have took biology in your high school would have used formaldehyde as a preservative for biological species. So here formaldehyde is also a good accelerator species but unfortunately because of the hazards of handling formaldehyde we cannot be using it. In fact in most of these chemical admixtures drums you will see the hazard symbols listed very carefully. These are the requirement that you need to list the hazards which maybe there in your system. Typically hazards are listed in a diamond shape; with each quarter of the diamond has a specific meaning with respect to the hazards that are in the system like flammability and hazardous ingredient and so on.

For every chemical admixture you typically get a datasheet. The datasheet not only tells you what the chemical admixture is capable of doing, how it should be used and so on and so forth. It also tells you what are the hazards ingredients present in the material, how you need to handle it, how you need to store the material and so on. So all these have to be done with extreme precaution on the job site.

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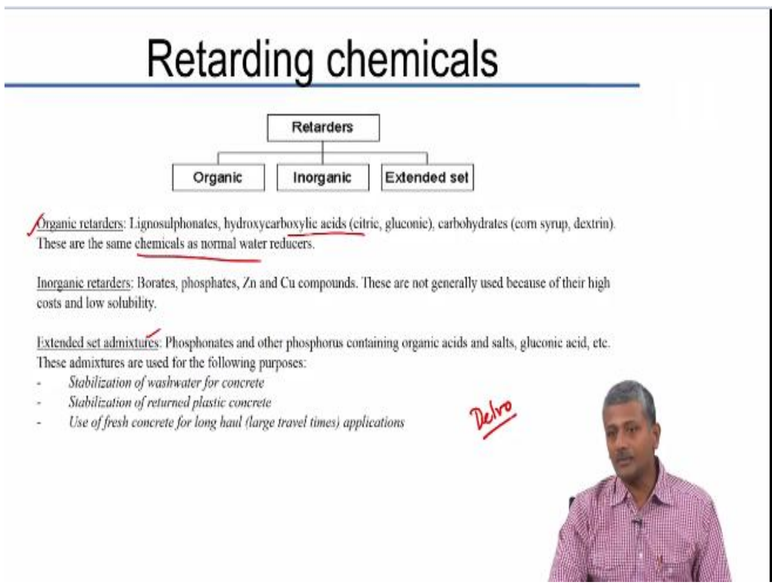

Retarding chemicals, we talked about this is already that organic retarders are the same as regular water reducers. You have the Lignosulphonates, hydroxycarboxylic acids, carbohydrate and so on, these are the same as your regular water reducers. Inorganic retarders are Borates and phosphates of zinc and copper. The problem with this is, many of these admixtures which are inorganic, are quite expensive.

Interestingly, amongst the accelerators, the inorganic accelerators are fairly inexpensive but amongst retarders the organic retarders are inexpensive and inorganic retarders are expensive. We have the special class of admixtures called Extended set admixtures, phosphonates and other phosphorus containing organic acids and salts, gluconic acid and so on. So these are to keep your concrete in a fresh state or without setting for a very long period of time.

One thing that we do not really worry about much in India is that after the truck which delivers the concrete, once it goes back to its yard there is water which is use to flush out all the remaining concrete and other cerements inside the truck. Here we do not really worry too much about the environment the water simply goes out into the soil; we just wash it out and we do not really take care of that water which is coming out.

But pH of cement paste is very high with high alkalinity of pH 12 to 13 or sometimes even more. When you are washing out this water and you permit that to mix with the ground water you are contaminating the ground water and making it a lot more alkaline,. So there are strict environmental standards in several countries, mostly a lot of European countries have this problem where this wash water from the truck cannot be used or cannot be simply discharged into the ground. So what they do is they collect the wash water, store it in drums, add these extended setting chemicals inside so that water and cement or cementicious material are there inside do not harden but they simply settle at the bottom of the drum. From time to time they clean out the bottom of the drum and they extract that water and after sufficient analysis of the water quality they can reuse it for either again for washing or if the water is good enough they can as well reuse it for making concrete itself. I think it will soon happen in India also that we have to start worrying about what damage this will cause to the environment. So wash water stabilization is one of the common needs for your extended set admixtures.

Sometimes your truck which goes to the job site has to come back with the concrete because the concrete is rejected, the slump is not met. This scenario rarely happens in India because mostly we add water at the end but I am not just talking about the India it is happens all over the world. When I worked for a construction chemical company in the U.S., and we were doing a field trial of our product which was of a new water reducer and so here we were at a ready-mix concrete plant and I was waiting along with my colleague with all the testing equipments to test the properties of the fresh concrete. So there every time fresh concrete is delivered you check the slump, you need to check the air content and then you need to prepare your cylindrical specimen for compressor strength testing. So we were waiting and then this truck was getting filled up with concrete from the plant. I was waiting for too long nothing happened, then after sometime I heard the truck driver honking twice and then again there was a little bit of mixing and then again there were two honks. So I was asking my friend why is this concrete not coming, what is the problem with this truck and why is he honking. So my friend told me that the truck driver with the sound of the concrete in the truck can actually tell the slump of the concrete. As the slump is not sufficient every honk he indicates 10 gallons of water to be i.e, 38 liters of water per honk.

So four times he honked, so you can imagine he has added nearly 120 liters of water in a concrete truck which is probably about 6 cubic meters. So the water cement ratio is totally going haywire but now the driver is very happy with the sound of the concrete in the truck. So he comes and deliver it to us obviously the slump is good, but we had no idea whether our water reducers actually worked or not. So the same kind of stuff that happens in our country, happens also in a so called developed country like the United States. So concrete construction everywhere is not taken seriously.

Nevertheless if such a situation arises that the concrete is rejected and if the driver has to bring it back then one of the common strategy is to simply add the extended set admixture into the concrete so that it does not set inside the truck. There are now interesting chemicals which can actually retard for a long time but then start accelerating once the concrete has been delivered. So now this is special type of admixture which is called Delvo and this Delvo is available from this company called Master Builder which is otherwise known as BASF now.

Delvo is an interesting chemical or it is a mix of chemicals that can retard the concrete for nearly 12 hours. So you can actually have a travel time of nearly 12 hours especially when you are trying to deliver concrete to very high reaches in the mountains and you do not have sufficient concreting capability at that height. So you make concrete in your plains and then send it up to the mountains so that the even if the travel time is 12 hours the concrete is still fresh. But then once it is placed, the other affects starts coming into play, that is acceleration. So within one day this material is able to deliver a strength that is equivalent to a normal concrete.

You might have also heard of Oil-well cementing. In Oil-well cementing when you drill into the ground for extracting oil, the drilled holes should be kept stable. So you need to maintain the stability of this hole and prevent the holes from collapsing. So for that they send out a cement which is an Oil-well cement, which is an interesting combination of accelerating and retarding chemicals. It has to retard enough so that the cement can flow for a very long distance into the drill hole. But once it is in position it should start hardening fast because then it will prevent the collapse of the soil around it. So again you can combine these accelerators and retarders quite effectively into working for different kind of situations.

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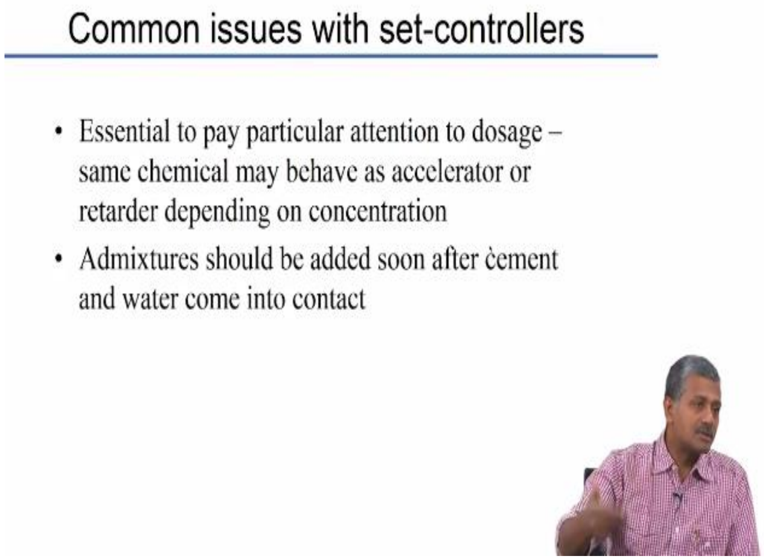

Hence same chemical can work at different dosages as either retarder or accelerator. Generally, in terms of dosing it into the concrete it is added soon after the cement and water coming to contact or sometimes it is mixed with the mix water and then added to the concrete mix.

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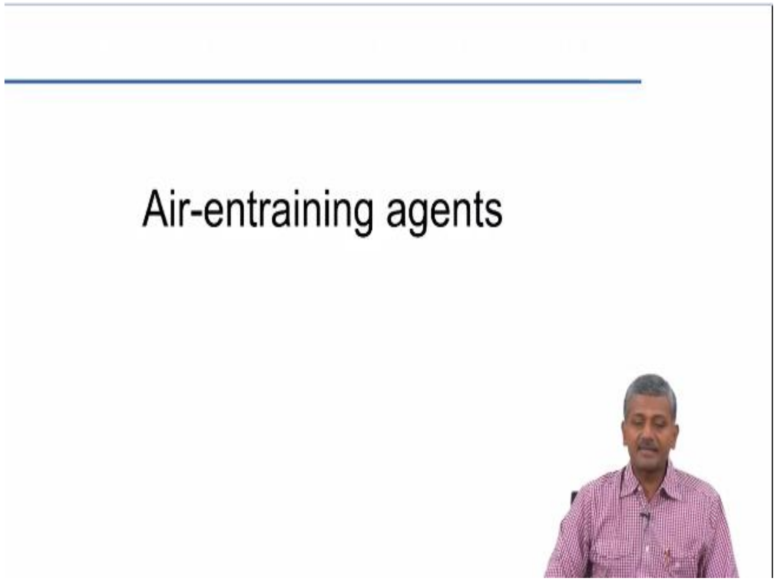

The next class of chemical that we will talk about is Air-entraining agents.

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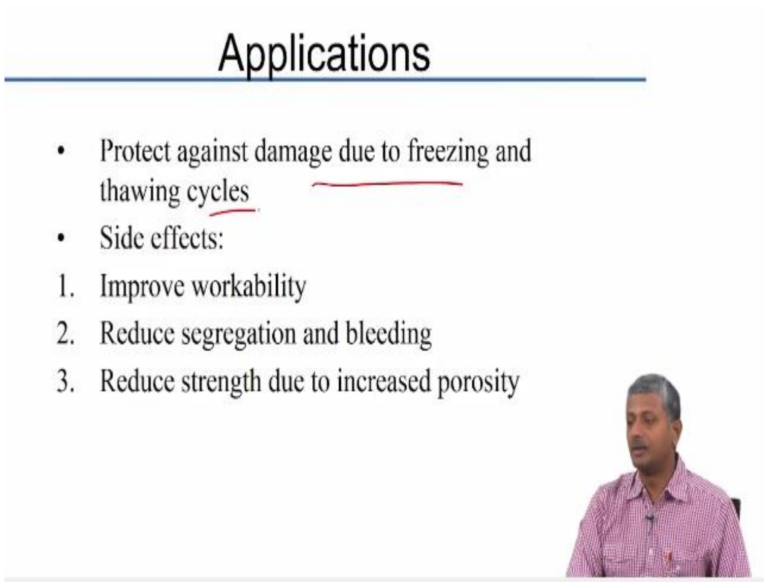


Now again Air-entraining agents are used for very specific purposes that is protection of damage against, freezing and thawing. Interestingly, a lot of people use air-entrainers in India even in the situations where we do not really have any freezing or thawing conditions. And the common understanding among these people is that air-entrainers are being added to increase workability.

But that is not the correct reason. Air-entrainers do increase workability but that is only a side-affect. They increase workability because you are introducing air bubbles in the concrete and the air bubbles will act like ball bearings and increase the flowability or plasticity of the concrete..

But that is not the main reason why you use Air-entrainers, you use it primarily for improving resistance to freezing and thawing.

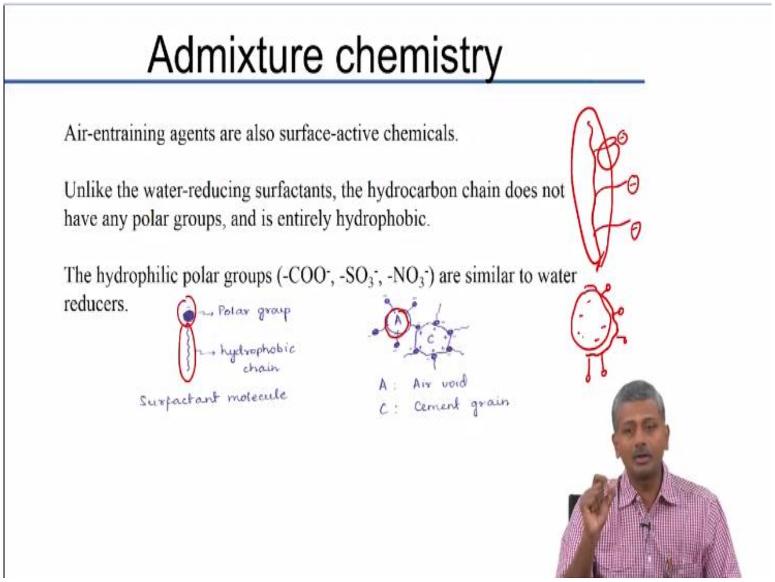
So what happens during freezing conditions? Water transforms to ice that means you have a volume expansion, water is the only material which expands on freezing, all the other materials when you reduce temperature will tend to contract. So this expansion and then subsequent contraction where this ice turns back to water so that means there is, swelling and shrinkage. So this cycle of swelling and shrinkage is what concrete cannot take and starts cracking.

So failure due to freezing and thawing is a major problem in several countries which are beyond the Tropic of Cancer, especially in the North Atlantic region. There you can get severe cycles of freezing and thawing because the diurnal variation in temperature can be as high as 20°C, 30°C. So high temperatures in the winter will reach about 5°C to 10°C and low temperatures can go up to –20°C, –30°C like that.

So you can have such large variations which will lead to problems of freezing and thawing. We will discuss the mechanisms in our last segment on durability. But to ensure that the air bubbles are present in your concrete they will provide space for your water to transform to ice. So they will accommodate the expansion and prevent your concrete from cracking.

So the side effect obviously is that it improves workability because of the ball bearing effect and it will also reduce segregation and bleeding, because these are surfactant chemicals. The main important characteristic is that because you are putting air in your system you are going to increase the porosity and as a result your strength will be lowered. So if you are adding air entrainers to your system to increase workability that is not the right thing to do because you are going to end up reducing your strength.

So one other use of air entrainer because of its improved workability is in plasters. You can use air entrainers in plasters because there the strength is not very important but the applicability is very important. **(Refer Slide Time: 31:34)**



So just like water reducers air entrainers are also surface active chemicals. As discussed earlier, the water reducer molecules have a long chain and then side chains. And these side chains have some polar groups attached to it. When this chemical wraps itself around the cement particle these side chains orient outwards of the polar groups and give a negative charge to the cement. That is how the water reducers are acting.

But in this case unlike the water reducing surfactants here we do not really have a long chain. We only have these short chains with a polar group. So you only have a hydrophobic short chain and a polar group at the end for the air-entraining molecule. So all it does is this hydrophobic chain is orienting itself towards the air bubble. So this A is depicting an air bubble in the system and the polar group orients outward.

Since the polar group is orienting outwards it is again giving you the same effect that it is dispersing or dispelling all the grains of cement and the air bubbles and preventing them into coming into contact. The air bubbles are generated during the mixing process. When mixing happens the air bubbles are generated and because of the action of these surfactants the air bubbles get stabilized.

You have seen this on a day to day basis when you add detergent to your water and agitate it the air bubbles that form remain stable. And unless you apply a very high pressure they do not really break. Same thing in concrete; these air bubbles remain stable and do not break even when you do the compaction of the concrete. The large air bubbles will easily break but when the bubbles are small they will not break easily. And those are the kinds of bubbles that are generated by air-entraining chemicals.

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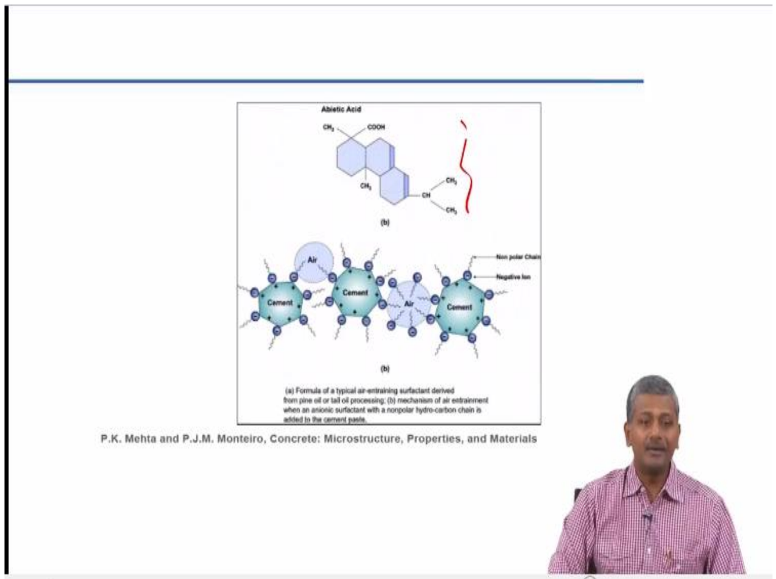

So this is a snapshot from Mehta and Monteiro book which tells you the working of air-entraining chemicals. The picture in the top is the basic molecule of the air entrainer. Mostly air entrainers are derived from again tree extracts like vinsol resin.

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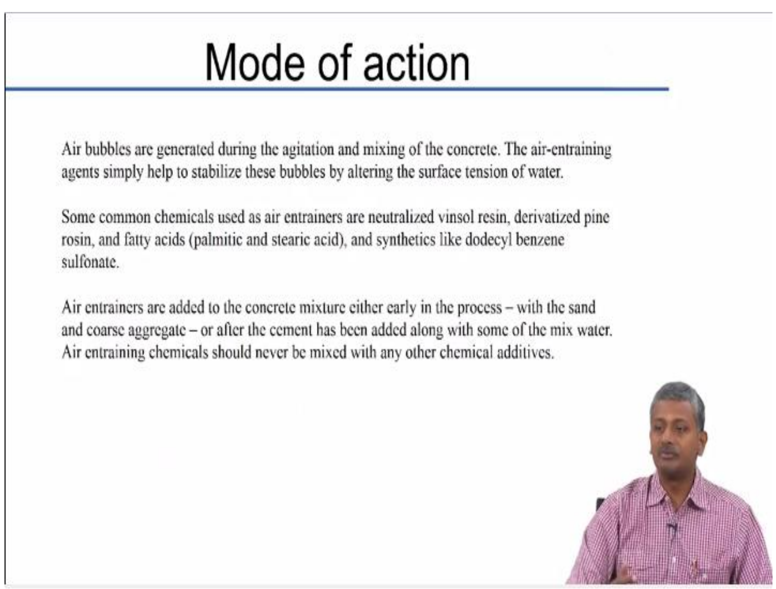

Or you can also have some fatty acids like palmitic and stearic acid which can be quite useful. Most of these air entrainer chemicals are also something that you might find in your daily use soaps, detergents and shampoos. Most of them are quite similar to the action of air-entraining chemicals. So you see these ads where the detergent molecule goes wraps itself around the dirt and brings it out. I do not know if that really happens but that is what they show in the animations that come with these ads. Interestingly ads portray construction materials completely in a different light. So the popular misconception amongst the public is that cement and concrete are one and the same thing. If you go anywhere people say I am building a cement road. You cannot build a road with cement you need concrete to build the road.

So that is a misconception amongst public that cement and concrete are one and the same. Unfortunately, what these tend to convey especially in terms of cement is that the higher the cement strength the better the concrete. So as a result of that in the market when you talk to consumers and masons they seem to think that the cement strength is very high and it will be good for all applications. And that is what led to all these problems with the plaster. In the past that people started using very high strength cements and because plasters had a high surface area shrinkage and other effects lead to lot of cracking in the plasters. And then people started realizing that they are not doing the right thing. Cement companies were also to blame because they were not promoting the cements correctly for different applications.

So now many cement companies have started off coming up especially with respect to plaster; they come up with their own plastering compounds or plastering additives or plastering cements or plastering mortars. The problem with that is it is going to be quite expensive as compared to your regular cement mortar. So convincing anybody to use these plastering mortars would be a difficult task.

So many companies are trying to change that strategy and coming out with plastering cements that can be used with any sand and water and you can make your own mortar. So again, you need to be careful about what the ads show you; but in terms of air entrainers of course we are talking about surfactant molecules which are similar to your detergents and that are why I wanted to bring that out.

So the air entrainers are typically added early in the process, right after the aggregates have been mixed into the mixture. Because any water that is in the system when you are trying to agitate it will start generating the bubbles and air entrainers can stabilize those bubbles which are forming even very early in the process.

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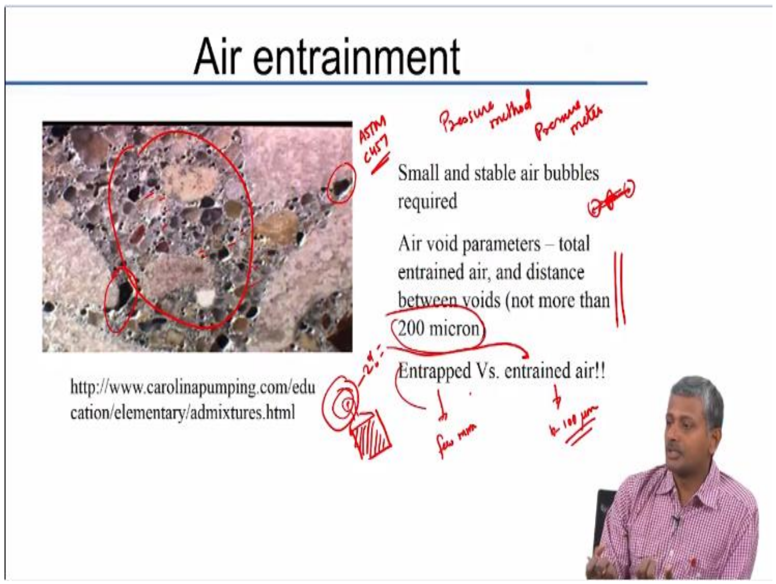

And after the air has been entrained in the concrete you need to be sure that the air entrainment is to the extent that you desire. For that, what you need to do is check the air content first of all of the fresh concrete. What typically people do is use the pressure method for air content determination using an instrument called the pressure meter. So this pressure meter has a chamber which is filled up with the concrete fully. The standard compaction of three layers, each layer compacted 25 times with the damping rod is done. And on top of this there is another chamber which has a dial gauge attached to it. This top chamber is fitted completely on the bottom chamber and then there is an inlet through which you can actually put in water. So you fill up the top chamber completely with water. Then this water is pressurized by the application air pressure. When you pressurize it the water will start seeping into the voids of the concrete. Once the voids get filled up, the chamber on top which was earlier filled completely with water will now have some air in it. So when you release the pressure this air will actually come out as it was pressurized, and the extent of air coming out will be directly indicated by the dial gauge here.

So it is a very simple measurement but it takes good amount of practice to actually get this done right the first time. So using this you will not only be measuring the entrained air you will also be measuring what is called the entrapped air. Entrained air is what you are actually purposefully introducing it to the system because of the use of the chemical. Entrapped air is what is there in the system which cannot be gotten rid of even after compaction. So for example in the picture shown above, you see that there is a large air void between the aggregate there, because the paste was simply not able to get in there. These are entrapped air bubbles. You can see very clearly the entrapped air is of much larger size as opposed to the entrained air. You can see the small bubbles which are circular they or spherical bubbles which are in the system, those are your entrained air bubbles.

So if you remember our discussion on different sizes of voids and pores in the system, the entrapped air is of the order of few millimeters and entrained air is generally 1 to 100 micrometers; more likely 10 to 100 micrometers. So you are generating these very small spherical air bubbles which are stable because of the effect of the air entraining agent.

The larger bubbles will tend to collapse as much as possible but you still will get some entrapped air in the system. So when you are measuring air with the pressure meter the water is going to penetrate both entrained and entrapped air. If you have done the mix design process for concrete you know that for a particular aggregate size you always assume that there is some amount of air that is going to be in the system.

For a 20 mm aggregate size, if you go as per IS 10262 method of mix design you will assume that about 2% or 1.5% of air is present in your system. So whatever air you get from the pressure meter you subtract that 2% or 1.5% and the remaining balance is the entrained air. These numbers 1%, 2% for different size of aggregates is only indicative and need not be the correct.

So that is why in this process we ensure that we do a standard compaction so that this process can be compared from one lab to the other. So this entrained air is what is important in this system. Not only is the total air content important, the way in which these air bubbles are distributed is also important. So what you need to ensure is that the distance between voids in this system should not be more than 200 microns. How do you check that? In a fresh concrete obviously you cannot check that.

Wait till the concrete gets hardened, take a section through the concrete, put it under the microscope and do an analysis under the microscope and determine the distance. So there is actually an entire ASTM procedure which is dedicated to the petrographic analysis of hardened concrete ASTM C457. There it tells you how to calculate these air void parameters; not just the size and the shape of the air voids but also the distance between the voids.

Why do you think this 200 micron distance is there? So let us say there are two air bubbles and there is a pore connecting the air bubble. There is water in the pore and when expansion of the water happens to ice, the excess water starts getting pushed out and it makes its way towards the air bubble. So 200 microns ensures that the excess water does not have to travel a long distance in the capillary because any movement of water in the capillary will be associated with a very high capillary pressure and that will be what is causing your failure or cracking due to freezing and thawing. So if you have more air bubbles close together, the distance that water has to travel in the capillaries will be less. So less hydraulic pressure will be generated and there will be less chance of cracking in your system.