Admixtures and Special Concretes

Prof. Manu Santhanam

Indian Institute of Technology Madras

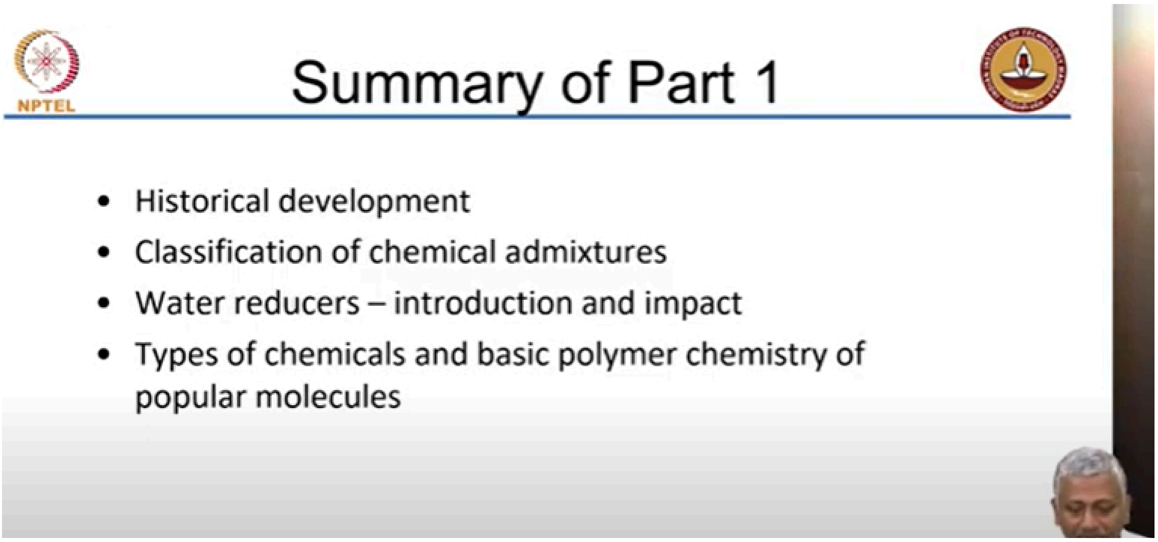
Department of Civil Engineering

Lecture 9

Chemical Admixtures: Water reducers - Part 2

Summary:

(Refer Slide Time: 00:40)



Summary of Part 1

- Historical development
- Classification of chemical admixtures
- Water reducers – introduction and impact
- Types of chemicals and basic polymer chemistry of popular molecules

Good morning all, so we continue our discussion on chemical admixtures, again what I am going to talk about is still from the same sections of the textbook. We talked primarily in the first part of the historical development of chemical admixtures about what kind of materials were actually used. We learnt about classification of chemical admixtures, we started talking about the introduction about water reducers and the impact that they can have on introducing sustainability in concrete.

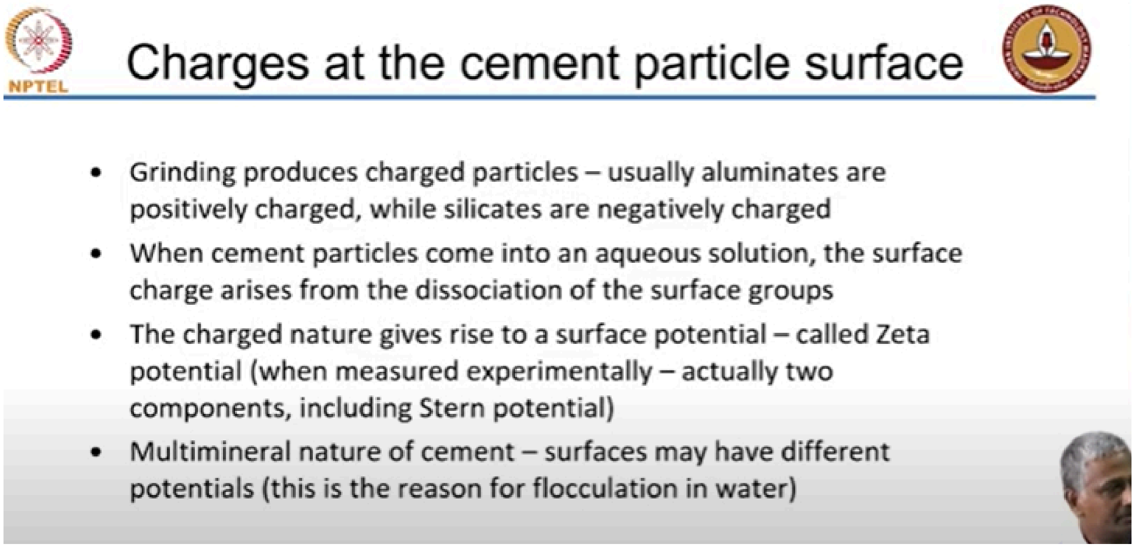
Why do we say water reducers are introducing sustainability in concrete? What was that one factor that we talked about where we can actually introduce sustainability in concrete by the use of water reducing chemicals?

Reduction in the cement content that is the primary impact. When we have water reducing chemicals we can lead to a reduction in the overall cement usage and that will contribute in the best way to the reduction of the overall carbon footprint of the concrete.

We also looked at types of chemicals and the basic polymer chemistry which is of course quite significant in understanding the degree of effectiveness of different chemicals. But at the same time from the perspective of why sometimes some chemicals work and others do not, why some combinations work and others do not. In such cases having some idea about the chemistry can be quite useful.

Charges at the cement particle surface:

(Refer Slide Time: 02:20)



Charges at the cement particle surface

- Grinding produces charged particles – usually aluminates are positively charged, while silicates are negatively charged
- When cement particles come into an aqueous solution, the surface charge arises from the dissociation of the surface groups
- The charged nature gives rise to a surface potential – called Zeta potential (when measured experimentally – actually two components, including Stern potential)
- Multimineral nature of cement – surfaces may have different potentials (this is the reason for flocculation in water)

Let us move on and look at what really happens that causes this classification of the cement particles. Now you know that in the final stages of cement manufacture the clinker is inter-ground along with the gypsum and any other additives that you may have like limestone or a fly ash. Typically this is done in ball mills where the particles are undergoing attrition and breaking down into very small particles.

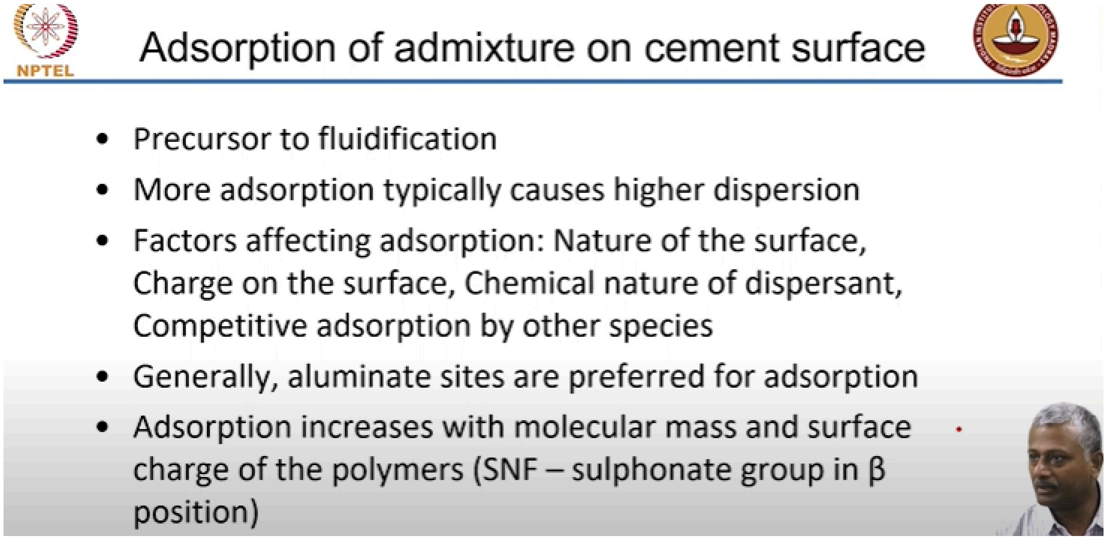
Now when you do this attrition and grinding of the cement the particles of cement have a net charge on the surface. Because you can imagine that you cannot obviously get perfect equilibrium in the atoms that are present on the surface as a result there is always some net charge on the surface. So usually aluminates acquire a positive charge whereas silicates acquire a negative charge when you do this process of grinding. So obviously when this kind of a cement or cement clinker is put in water there will be some flocculation or coming together of the charges. Opposite charges will attract and that will cause some flocculation of the grains to happen. This is a very common phenomenon even in food grains for instance like your atta. When you put atta in water you see that there are some grains of atta which will join together and flocculate. Of course there may be more the cohesive nature of the material itself rather than surface charges that is leading to this phenomenon. But yes, there are interfaces getting created even when the water basically wets each and every flour particle. There is obviously some new interface creation and this can actually also lead to some charges which are causing the particles to come together and make the flocs. So when cement particles come into an aqueous solution the surface charge arises from the dissociation of the surface groups.

What are the primary compounds that are present on the cement? So you know tricalcium silicate, tricalcium aluminate and so on and so forth these can also lead to development of surface charges. So this net surface charge that is present not just because of the grinding but also because of the dissolution is called the zeta potential. The surface charge creates what is known as surface potential or zeta potential. Now of course when you measure experimentally there are two components to this including what we know as stern potential but we will not get into the discussion there in detail.

Primarily you need to imagine that when you are putting a cement grain in an aqueous solution there is a surface charge and that is often the reason for the flocculation that happens eventually if we do not use a water reducer. Now surfaces in cement grains because of the different types of compounds that are present, surfaces may have different potentials and this is what is causing the flocculation, as I said when you have opposite charges particles are coming together and forming flocs. And when you start forming flocs what is going to happen is these flocs or bunches of grains are attracted together and they start trapping the water inside. And obviously to produce workability in your concrete you need the water, the water creates this flowability. So if you are trapping the water, the water is not available to create workability. So what we need to do is ensure that the particles are getting dispersed and for that we use the super plasticizers.

Adsorption of admixtures on cement surface:

(Refer Slide Time: 05:43)



Adsorption of admixture on cement surface

- Precursor to fluidification
- More adsorption typically causes higher dispersion
- Factors affecting adsorption: Nature of the surface, Charge on the surface, Chemical nature of dispersant, Competitive adsorption by other species
- Generally, aluminate sites are preferred for adsorption
- Adsorption increases with molecular mass and surface charge of the polymers (SNF – sulphonate group in β position)

When the admixture or super plasticizer which we learnt in the last lecture was a long chain polymer. When this polymer is brought into a solution with the cement it starts getting enveloped on the surface of the cement. It adsorbs on the surface.

What is adsorption and how is it different from absorption? Absorption is basically on the surface, absorption is a bulk uptake of the liquid by the solid. So before fluidification the adsorption is a very important step where the polymers basically are wrapping themselves around the cement particles. The greater the adsorption there is going to be a greater dispersion.

Now why is this dispersion happening? Because of several things. But there are several factors which will affect the amount of polymer getting adsorbed on the cement surface. This includes the obvious nature of the surface.

- If you have a smooth surface versus a rough surface that could be one aspect.
- The composition of the surface obviously, charge on the surface, what is the net charge, is it positive, negative, what kind of charge is present.
- Chemical nature of the dispersant, whatever polymer you are using, what is its chemical nature, what is its composition
- Competitive adsorption by other species. Now please remember cement is not just C_3S, C_2S, C_3A and C_4AF there are other species like sulphates which are coming in. So these sulphates also are negatively charged and they will also get attracted towards certain cement surfaces. There is charge in the polymer that also attracts it towards the cement surface. So competitive adsorption can actually happen. So that is a very important thing to remember when we move forward to understanding the aspect of compatibility of cement and super plasticizer.

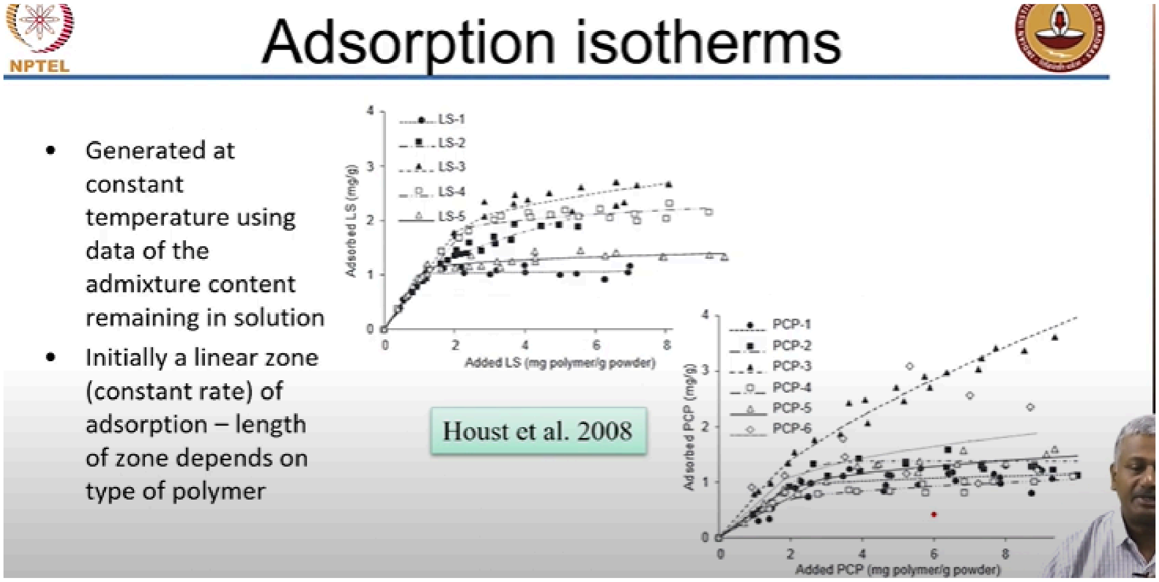
Now aluminate sites are generally preferred for adsorption primarily because they have a net positive charge and most of the admixtures or polymers have a net negative charge. So there is a greater attraction towards the aluminate. So in some instances this can lead to a major reduction in the effective amount of chemical available for producing workability. A lot of it may just get lost on the aluminates and not really look at the entire range of cement particles that are actually available.

Now we talked a little bit about polymer chemistry. We saw that the polymer chain length is very important. The longer the chain the more complete will be the adsorption. So adsorption generally increases with the molecular mass because molecular mass is directly linked to the chain length and also the surface charge of the polymers and here also we took a look at the case of SNF polymer, where we saw that the sulphonate group in the beta position seems to have a much higher surface charge allocated to the polymer chains as opposed to the sulphonate in the alpha position. This alpha, beta are all positions around the benzene ring. Now of course for organic chemicals benzene is or benzene related products are probably found in several different organic species. In polymers also as you saw in the structures that we talked about in the last class the benzene ring was quite uniformly found in most of the structures. So the sulphonate group in the beta position is one of the reasons why certain times the admixture may work very well and other times when you do not have the process that leads to this formation you may not get the same level of effectiveness and this can actually happen with the same product.

As a civil engineer in the field sometimes we are baffled as to why this is working one time the next day it is not working. One of these factors that contributes to that variability in the effectiveness could also be this aspect.

Adsorption Isotherms:

(Refer Slide Time: 09:52)



Adsorption isotherms

- Generated at constant temperature using data of the admixture content remaining in solution
- Initially a linear zone (constant rate) of adsorption – length of zone depends on type of polymer

Houst et al. 2008

Now with adsorption typically chemists like to create what are known as adsorption isotherms. Isotherm means something at a constant temperature. So essentially you are looking at the extent of adsorption happening at the same temperature.

So what you do is you have a solution in which you have cement and water and you add more and more quantities of the admixture to the system. With time what will happen this admixture will get adsorbed on the cement but some of the admixture may still remain in solution. It may not have enough surface available first of all if you overdose. So there is already some limit to dosage of the chemical that can be added. You can only coat so much of the cement surface with the admixture you cannot continue to coat more and more.

So some admixture will remain in solution.

So this is for instance for lignosulphonate adsorbed lignosulphonate versus added lignosulphonate. You see here what is happening initially: all of the lignosulphonate that is added is getting adsorbed. But then later there seems to be some sort of a saturation with respect to the adsorption. There is no more admixture getting absorbed and the remaining admixture remains in solution.

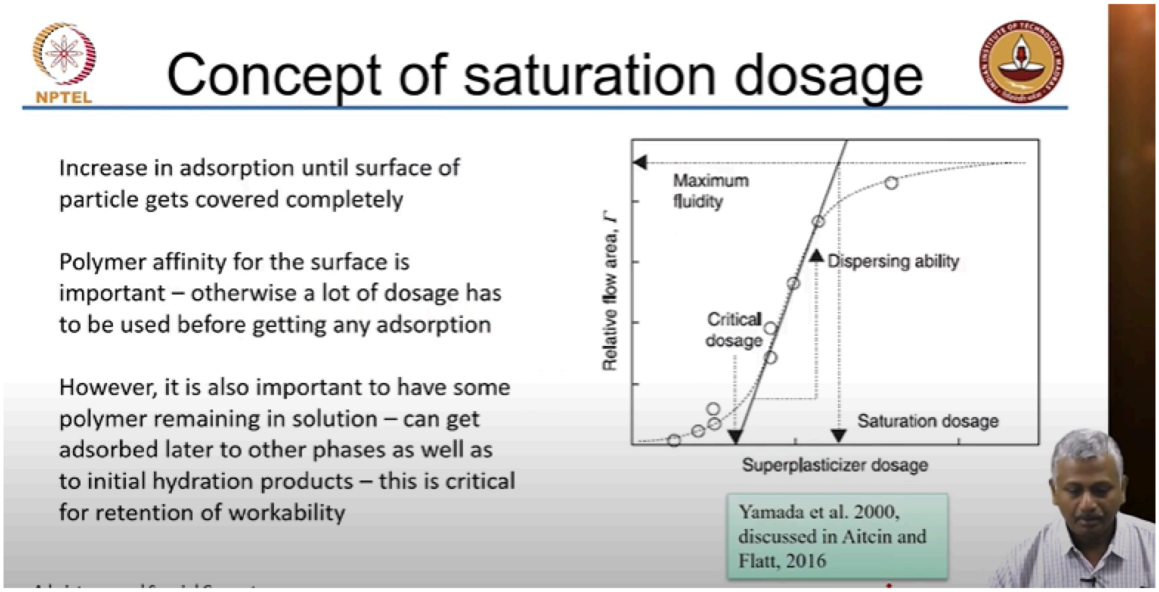
Now is that a good thing or a bad thing this admixture remains in solution. Why is it bad? Because you are wasting chemicals. Too much chemical you are overdosing and that remains in solution does not do anything. But if you think about it the admixture that is getting absorbed in the cement, the cement is also going to hydrate slowly. And in the initial stages if you have ettringite and CSH that are forming as we discussed in the chapter on cement chemistry. So initial products are getting formed. Now if you still have admixture remaining in solution it may go and start adsorbing on the initial products also. So what does that mean? It will further give you workability. It will delay the setting for sure but it will also give you extended workability. So it may be bad from the perspective of overdosing that you are wasting your money on something excessive but it may also lead to some effectiveness with respect to a longer retention of your workability. So what do you want? For instance if you are working in a precast company, so in precast do you really worry about workability retention? Probably not. You make the concrete to discharge in the forms and directly you may produce your components.

But in a ready mix it is different. Your truck has to travel long distances, you need to maintain workability for a longer time. So there it is important that you have some admixture remaining in solution after some time. So it is a little tricky to just design concrete with exactly the saturation dosage of your chemical.

This is polycarboxylate. Again this is the extent of adsorption that is happening but again these are all isotherms generated for different types of chemicals that have been used. So the linear zone basically says that all that is getting added is getting adsorbed and then of course your saturation happens and then you have almost completely the extra admixture that you add is not getting adsorbed. Now that is where we are getting to next.

Saturation Dosage:

(Refer Slide Time: 13:20)



Concept of saturation dosage

Increase in adsorption until surface of particle gets covered completely

Polymer affinity for the surface is important – otherwise a lot of dosage has to be used before getting any adsorption

However, it is also important to have some polymer remaining in solution – can get adsorbed later to other phases as well as to initial hydration products – this is critical for retention of workability

Yamada et al. 2000, discussed in Aitcin and Flatt, 2016

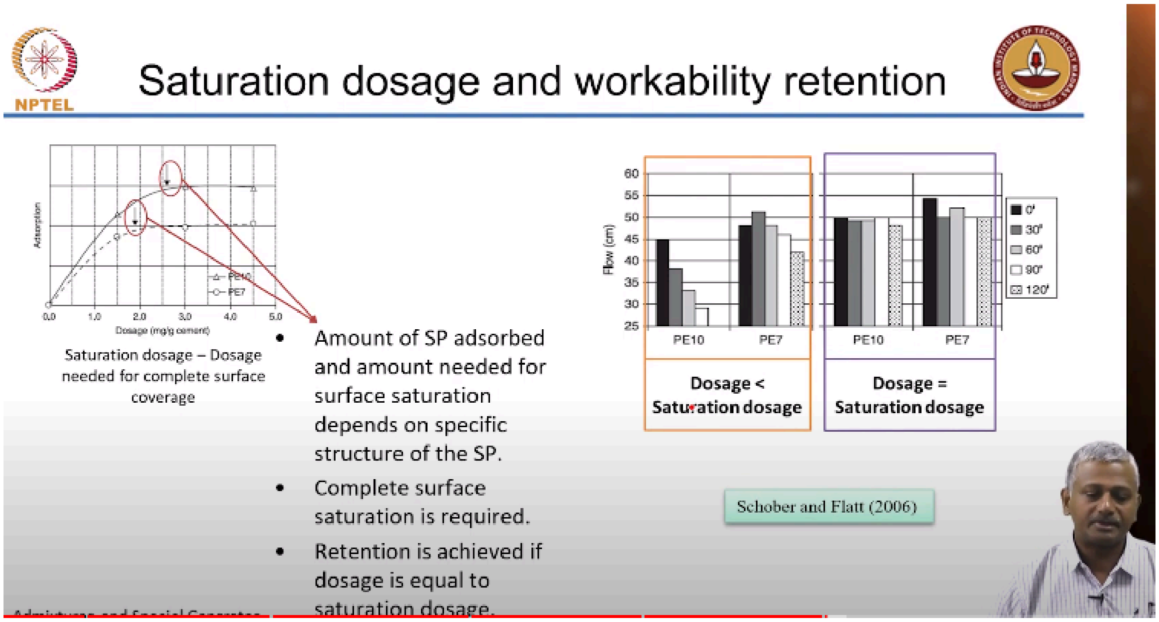
What is the saturation dosage and how do we determine this? So the concept of saturation dosage again is indicated by the fact that you only have so much adsorption that can actually happen. So increase in adsorption until the surface of the particle gets covered completely. Now all this also goes to say that your admixture has to be uniformly available in your concrete and somebody had raised this question that we are using only such a small quantity of the admixture, how does it get available to the cement? It gets available because the admixture is water soluble. It mixes with the water and is available throughout the volume of the concrete and your mixing also is very important. You need to mix properly. If you do not mix properly you will not really have the admixture available to all of the cement. So that is definitely something that you have to look at. So polymer affinity for the surface is obviously important otherwise you need to keep on increasing the dosage to get any adsorption. If the polymer is not at all going and sticking to the surface you have to keep on adding more and more and you will probably not complete that adsorption at all. So that kind of a combination of cement and superplasticizer is called an incompatible combination where the saturation does not happen at all. You keep on adding more and more but you do not see its effectiveness to the extent that you want to see.

Now as I already talked about this in the previous slide that you do not want only admixture that is adsorbed but you want to probably dose a little bit more than that to have admixture available in solution which gets adsorbed on to the other hydration products which helps in retention of workability. So if you look at the workability here as a relative flow area per se versus superplasticizer is a dosage as you increase the dosage of SP your workability goes up. Beyond a certain point it seems to go up quite critically but beyond again another point you are probably not going to be able to see much of an enhancement of your workability. That means you are reaching a level which is saturation which causes your concrete to have probably no extra impact of the additive that you are putting in. In economics we call it the law of diminishing marginal returns. Here the returns are the workability and you are pumping in more and more of the admixture in after a given point you really do not require any more admixture to provide initial workability but again you need to remember this aspect that retention of workability could be made possible by the extra chemical that you add in the system.

So your saturation dosage is where you do not really see any further significant increase in your flowability. Now there is one more thing marked which a critical dosage is. Now critical means below this dosage you are actually seeing no effect at all. Your admixture is not making any effect at all. Now this critical dosage obviously will depend on the type of admixture that you are using. We talked about the first generation admixtures including Lignosulfonates. Second generation was poly naphthalene sulfonates and the third generation is polycarboxylic ether or vinyl copolymers. Those have maximum effectiveness so the critical dosage for those will be much smaller whereas for lignosulfonates already you may have to put in quite a bit of material to get the work started.

Saturation Dosage and Workability retention:

(Refer Slide Time: 17:20)



Saturation dosage and workability retention

Saturation dosage – Dosage needed for complete surface coverage

- Amount of SP adsorbed and amount needed for surface saturation depends on specific structure of the SP.
- Complete surface saturation is required.
- Retention is achieved if dosage is equal to saturation dosage.

Dosage < Saturation dosage

Dosage = Saturation dosage

Schober and Flatt (2006)

So again this is just an example of saturation dosage and workability retention.
So here there are examples of 2 polyethylene or polycarboxylic ether admixtures that are formulated in this study. So the amount of super plasticizer adsorbed and amount needed for surface saturation depends obviously on the type of chemical that you are using. So

obviously it depends on the chemical composition here the cement is not getting changed so you are not really having any difference in that. So you need complete surface saturation so it turns out that it happens at two different levels for these two chemicals. Now retention is achieved if dosage is at least equal to saturation dosage equal or more you need greater amount than saturation if you really want retention. So what is given here is the flow in terms of the time 0 minute, 30 minutes, 60, 190 and 120 and you see here that if the dosage is less than saturation dosage you see a drop in workability, significant drop in workability whereas at saturation dosage you seem to have very little reduction in workability. And if you are going excess of saturation dosage you may actually even prolong that further but you have to live with the retardation that happens in the system.

Many times in our construction sites there are problems with concrete setting and this concrete setting problem generally arises because they overdose.

Now why do you think they overdose on construction sites? Why do they overdose the admixture? To keep the workability for a longer time but why? So there is loss of workability as the concrete is getting transported so they will shoot for a higher slump at the concrete plant so that when it gets to the job site it will at least satisfy the slump requirement at the job site. But what else? Why do you think overdose happens? What are the other reasons? Practically, I am not talking technically from an admixture view point, practically what else happens? The concrete truck is there, it is starting from the plant and coming to the job site. What other situations do we overdose in? Your truck arrives at the site, then what happens? Exactly, the site is not ready to take the concrete. The truck is simply standing on site. What happens during this time? The slow rotation but the concrete is losing its freshness, it is losing its workability. So you may have some extra admixture on the site. Now when you do this, you are obviously pushing your admixture content much above your saturation dosage.

So I was involved in one such project where they called me after three days, three days of concreting they called me and they showed me a column where they had poured the concrete. After the first day, the foremen basically tapped the surface, top of the column, the concrete seemed to be dry so he thought it was hard, opened the formwork, the entire thing collapsed, concrete collapsed. When I went there on the third day, I could actually still feel the concrete not fully set. It had not hardened, I mean it was still, they had cleaned up mostly but I could see some samples lying down. So this concrete I could also smell the admixture very clearly. Sulfonated naphthalene formaldehyde has a very clear cut smell. So you could smell the admixture. Then I went to the QC lab, I told them okay you would have made concrete specimens from this batch, can you show me the specimens? So they went to the curing room or curing tank and pulled out the specimens. Specimens were perfectly fine. We tested the specimen, it gave the strength that we require at 3 days, perfect, and no problem. But the concrete in the structure is not set, what is going on here? Why? So, when did they make the specimens? Before the concrete actually was delivered to the site, the truck stopped by the QC lab, discharged the concrete, the specimens were prepared, nicely consolidated, stored in ideal curing conditions, perfect concrete but at the site extra admixture is added, severe retardation that is not set.

So the problem is even if you design concrete to meet a certain target requirement, the way you execute also is very important. Now with concrete just like food, again I have come back to cooking, fresh food tastes better, just like that I am not saying concrete tastes better but fresh concrete, readily newly mixed concrete always has the best characteristics. If you continue to wait longer and longer, you run into these problems and to sort out those problems you have to do all kinds of things. Earlier in the days when people were not using admixtures very much, they used to add water. At least today they do not do that, adding water obviously is problematic from other viewpoints, strength and durability, admixture of overdose may not really affect your strength and durability overall. While the concrete takes longer to set, I have actually seen cases where concrete is not set for seven days also. You can imagine the extent of overdose they did or maybe the compatibility was not established before they undertook the project.

So in such cases all you need to do is just wait, eventually setting will happen, eventually concrete will harden, it may not be poor quality in the long term. But with water addition obviously your water cement ratio is totally gone beyond what you wanted it to be and you end up getting low strengths. Again those are also examples that we have seen quite a bit in projects. Sometimes without understanding the requirement of how concrete should be designed for a particular project people go with designs that they already have. As a result they use combinations of materials including the wrong choice of chemical admixtures and the wrong estimates of the water content required for the initial workability or workability retention. So this is again a problem that we have looked at in several sites. Now how did this problem come about because they ultimately determined that the concrete from the cubes itself was not coming close to the 28 days strength. So we went and took cores from the columns and for a M35 concrete the strengths we were getting were between 10 and 15 MPa, 10 to 15 MPa for a M35 concrete. Now what is happening there? Obviously it is a case of adding water, the concrete was not designed for the required initial workability or retention of workability. So to make up for lost time and to ensure that the project went ahead they added water and ultimately got a strength only of 10 to 15.

Now what do you do? The structure is already up, what do you do now? You probably can try jacketing. So here the designer has to come back in again and see whether at that strength of concrete is the column able to take its loads. It turns out in most cases it is able to take the load. It is able to take the load in most cases even if it is like 10, 15 MPa strength. We have over designed the structure so much it is still working no problem. But what is the problem there? Durability is the problem. We are not going to get durability where we have designed for a 50 year life. We may end up with a 10 year life because our concrete quality is poor. So always people only look at designers, they do not understand what is going to happen over the long term in terms of durability of the concrete. The corrosion will initiate much faster because your cover concrete is going to be of poor quality.