Admixtures and Special Concretes

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Lecture 10

Chemical Admixtures: Water reducers - Part 3

Determination of Saturation Dosage:

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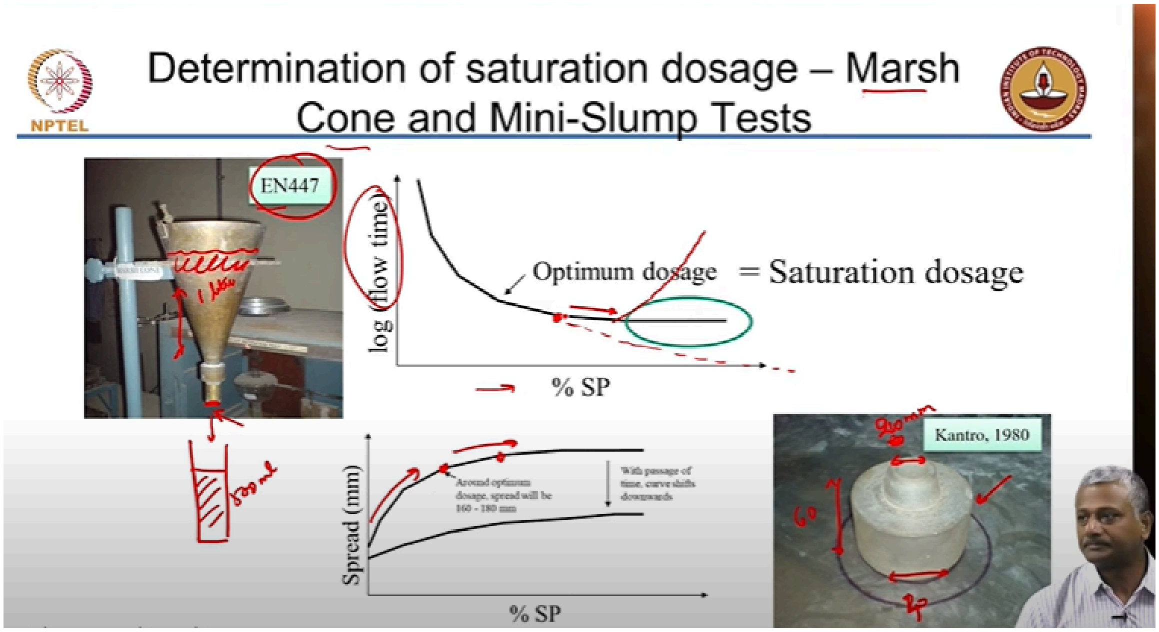

Determination of saturation dosage – Marsh Cone and Mini-Slump Tests

EN447

Optimum dosage = Saturation dosage

Around optimum dosage, spread will be 160 - 180 mm

With passage of time, curve shifts downwards

Kantro, 1980

So how do we check for the saturation dosage? There are methodologies that can be done in the lab not just in your research and development laboratories but also site labs because these are very simple methodologies. This is an EN approach, Euronorm 447 where they describe this marsh cone which was derived from an initial test that people used to do for grouts. So when we use grouts which have to be flowable you have to establish that flowability by checking the time that the grout takes to flow out of a conical flask. Now here instead of the grout we are using cement paste where you are going on adding additional superplasticizer dosage.

So let us say we choose the let us say you are going to work with a concrete where the design calls for a water to cement ratio of 0.4. So you make cement paste with the same water cement ratio 0.4 and you keep on adding a superplasticizer to this paste and check the flow. So you fill up this cone with about 1 liter of the cement paste and you stop the orifice at the bottom after the entire thing is filled up. You remove your finger from the orifice and let the paste basically flow out. You have a measuring cylinder which is placed at the bottom to check the time taken for 500 ml flow to happen. That is a typical procedure that is done for marsh cone. The orifice size has to be fixed whether you are testing a cement paste or a mortar. For cement paste typically we use 8 mm orifice. For mortars we use about 12 mm of orifice.

So as you increase the superplasticizer dosage the flow time keeps reducing obviously because material flows out much faster. So beyond a certain point you are not seeing a major decline in the flow time that means you are reaching saturation. You can do the same thing with the flow table spread also no problem. You can do the same with the flow table spread but the only thing is there you need to probably have a flow table spread also includes the use of sand along with it. And otherwise you can use a mini flow spread which is called the mini slump cone in which case the top diameter is 20cm, bottom is 40cm and the height is 60cm. What is your typical slump cone for concrete? Now the ratio of the dimensions is the same; here we have 20 mm at the top, 40 mm at the bottom and 60 mm height. So this is a mini slump cone which could also be used to determine the saturation dosage. So as you can imagine as the SP dosage increases the spread which is seen in the slump cone increases but beyond a particular point you will not see a major increase in the spread. So that is your saturation dosage.

Now we talked about a case earlier where the superplasticizer of a molecule does not have any affinity for the cement at all. In such cases what will happen? As you add more and more admixture you will not reach saturation. So you may have a condition where this curve keeps going down completely. So that is an incompatible combination. In some other cases what may happen is you added too much admixture so bleeding starts happening. The water from your paste starts getting separated and because of that since water is lighter the water will come up on the top so you will have thick paste at the bottom. So what will happen to the flow time? It may start going up, flow time may go up again. Why because the paste is now falling in chunks it does not have the flow ability because the water has separated out. So you need to evaluate this test carefully. It is a simple test you do not need to make concrete once your design is ready to understand the compatibility between your cement and chemical admixture this test can be easily done at the job site.

Again just to define it once more, saturation dosage is the minimum extent of dosage required to produce workable concrete to induce the maximum potential of flow ability in cement paste assuming that adsorption is the sole cause of flow ability.

So what will happen if you increase the temperature? What will happen to the saturation dosage when you increase temperature? It will come down why? Will it come down or go up? Why will it come down? That means you need less admixture to adsorb why? What will temperature do to the adsorption rate? Probably are going to end up adsorbing more SP on to the cement but your initial workability may improve at higher temperatures but that is counter intuitive you know we always think that at high temperatures we are not able to maintain workability. It is not true we are not able to maintain workability over a longer time. Workability retention will be a problem at high temperatures. Attainment of initial workability will not be a problem.

Competitive Adsorption:

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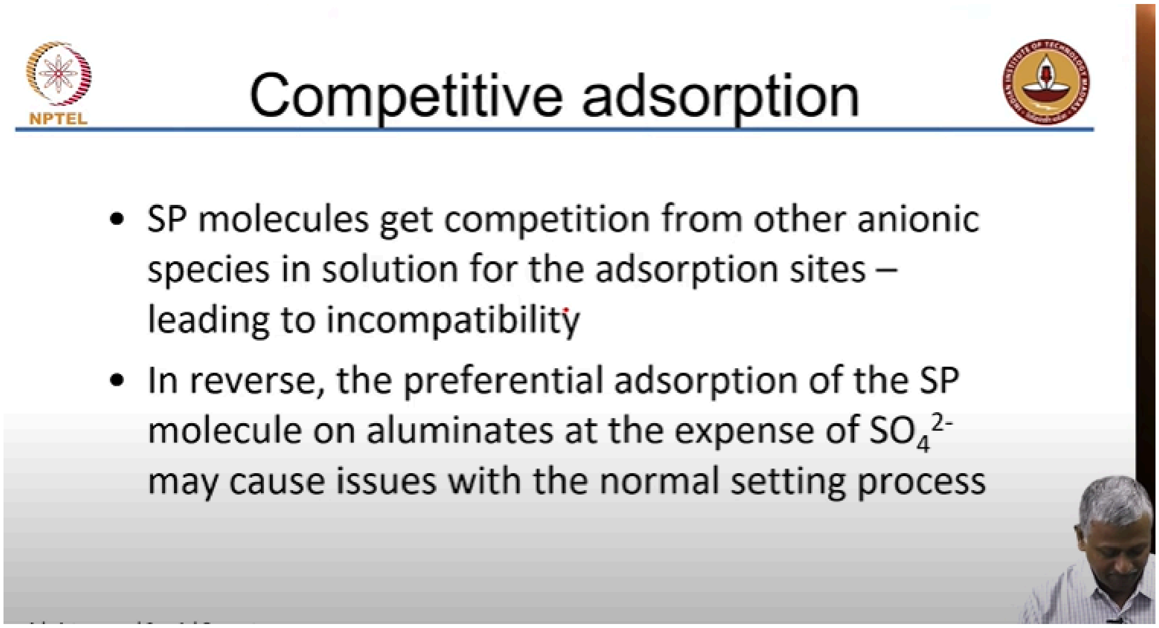

Competitive adsorption

- SP molecules get competition from other anionic species in solution for the adsorption sites – leading to incompatibility
- In reverse, the preferential adsorption of the SP molecule on aluminates at the expense of SO_4^{2-} may cause issues with the normal setting process

So as I talked about there is competitive adsorption also that may happen in the systems. Superplasticizer molecules which I said are charged get competition from other anionic species in solution for the adsorption sites leading to incompatibility. Why does it lead to incompatibility? Let us say sulphate. Why is sulphate needed in cement or why is gypsum needed in cement? To slow down the reaction of aluminate.To have a much more controlled setting process. In the absence of gypsum aluminate will react with water and produce flash setting.

So without gypsum that is what happens but with gypsum the sulphate has to come to the surface of the aluminate and start reacting and prevent it from flash setting. Now imagine an admixture like a sulphonate, lignosulphonate, naphthalene sulphonate, melamine sulphonate. Sulphate, sulphonate same charge negative charge, aluminate positive charge.

So what will happen now? Instead of the sulphate from the cement that you want to come to the aluminate you may have sulphonate from the admixture that comes to the aluminate. So there is some competitive adsorption. The other way the preferential adsorption of super plasticizer on aluminates at the expense of sulphate may cause issues with normal setting.

So there are 2 aspects here. Incompatibility here means you are losing effectiveness of the admixture to provide workability. Because your admixture is simply getting adsorbed onto the aluminate and you do not have enough to adsorb on the other species. But since this admixture has now not permitted your sulphate to go and interact with the aluminate your normal setting process is going to get affected.

So here this is an interesting process. You are getting loss of workability but you are also getting delay in setting. Just imagine these are counterintuitive. We expect that when setting happens we lose workability. But here you may end up having both problems. There is loss of workability because admixture effectiveness is going down and since you have not permitted sulphate to interact with the C_3A your normal setting process is also going to get affected. So you have to be very careful when you start when you use lignosulphonates or naphtylene sulphonates.

Polycarboxylates do not have the same problem because as we will see later the mechanism is not by this surface repulsion, electrostatic repulsion it is more by the size of the molecule itself we will see that. So competitive adsorption has to be looked at carefully and these days just like when you make biriyani you add several masalas. These days when we make special concretes we add several admixtures. You can have a water reducer, you can have VMA, and you can have shrinkage reducer. Now all of these chemicals, many of them still work with the adsorption. They have to first adsorb and then lead to the effectiveness and because of that there is again competition between the admixtures.

So how do you resolve this problem? What can you do to resolve this problem? So here your challenge is to get the sulphate from the cement available to react with the C_3A before your adsorption by the polymer happens. Can you do this? How can you do it? You can delay the time of adhesion of the super plasticizer. So you add the water to the cement first to let this initial dissolution take place.

But there is another problem there. Water the gypsum that you use in your system does not dissolve fast. So that is another issue. So again this is something we will talk about in more detail. Compatibility issues we will talk about in more detail.

Electrostatic Repulsion:

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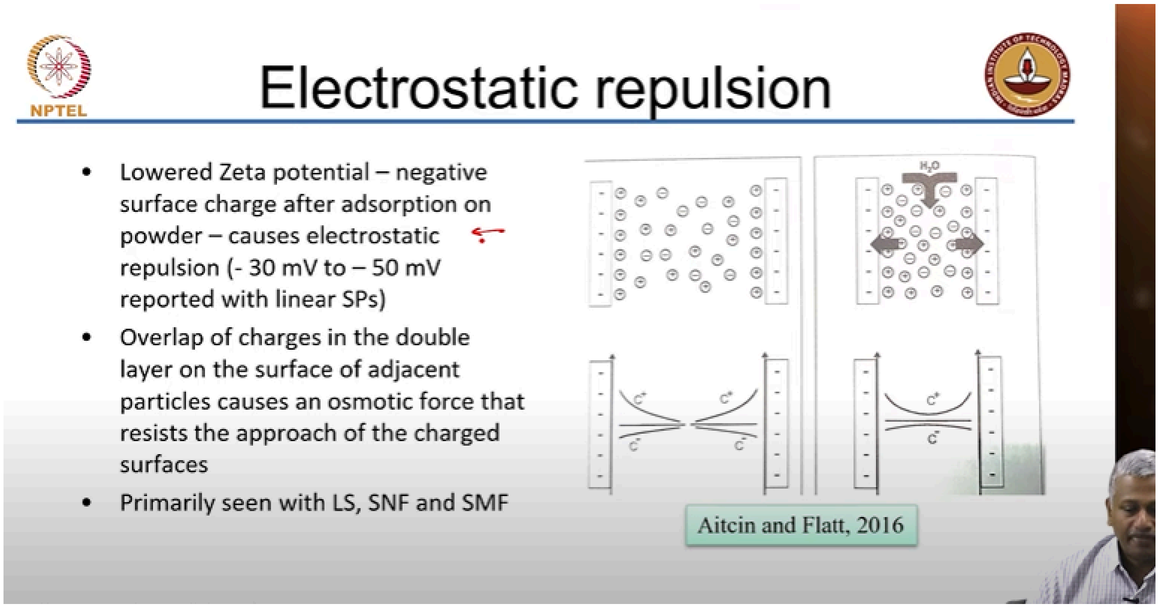

Electrostatic repulsion

- Lowered Zeta potential – negative surface charge after adsorption on powder – causes electrostatic repulsion (- 30 mV to – 50 mV reported with linear SPs)
- Overlap of charges in the double layer on the surface of adjacent particles causes an osmotic force that resists the approach of the charged surfaces
- Primarily seen with LS, SNF and SMF

Aitcin and Flatt, 2016

So the first mechanism of producing this workability is electrostatic repulsion. As we discussed many polymers like lignosulphonates, naphthenosulfonates they have negative surface charge. As they wrap themselves around the cement particle they give an overall negative zeta potential. So there is lowering of the zeta potential that happens for the cement particle surface. So people have actually measured this about -30 to -50 mV have been reported for certain linear super plasticizer molecules. So essentially what is causing the separation of cement particles is this layer formation on the top charged layer formation which leads to this double layer on the surface of adjacent particles which causes osmotic force that resists the approach of the charged particles. Essentially like charges repel to put in simple terms. So negatively charged cement particle surfaces are going apart from each other and this as I said you typically see in your sulphonates which give this negative charge onto your surface. So surface electrostatic repulsion it happens after adsorption. So the steps are first is adsorption then your lowering of zeta potential and then your electrostatic repulsion.

Now the same adsorption phenomenon also happens for the other types of molecules like polycarboxylates or vinyl copolymers those are also getting adsorbed onto the cement particles.

Steric Repulsion:

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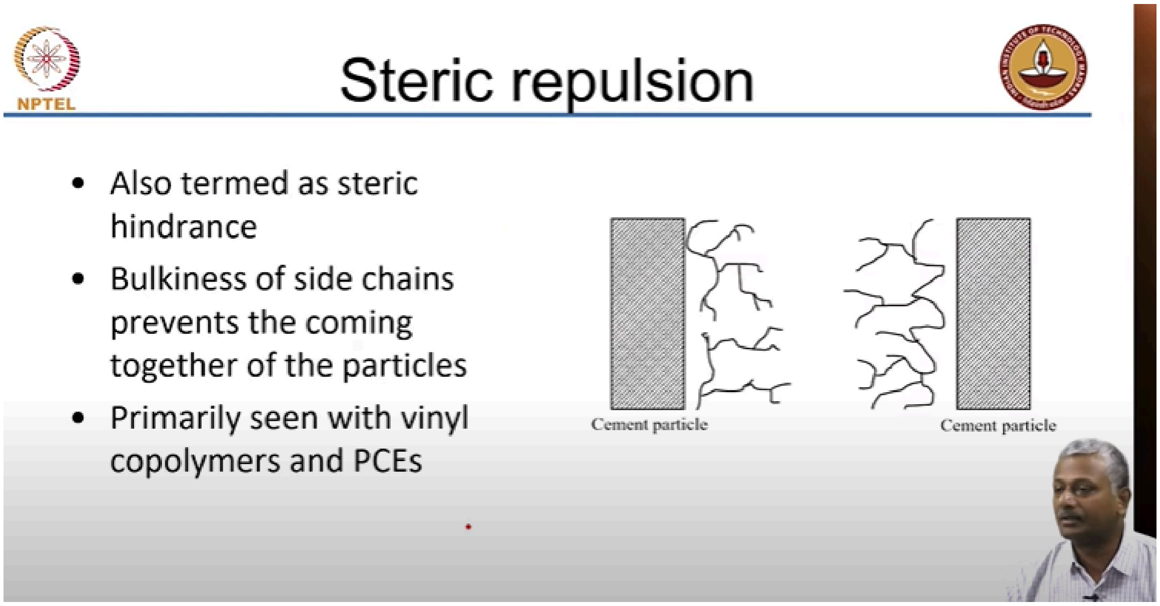

Steric repulsion

- Also termed as steric hindrance
- Bulkiness of side chains prevents the coming together of the particles
- Primarily seen with vinyl copolymers and PCEs

But they are producing repulsion through this steric hindrance or steric repulsion. What is steric? Steric means related to the structure of the molecule. So you have this polymer chain that is getting adsorbed onto the cement but you have these side chains that are so bulky that they are preventing particles from coming together. So even here adsorption happens but beyond that you have steric repulsion. So bulkiness of the side chain we saw the polymer structures in the last class where polyethylene oxide has multiple units of that in the side chain. So when you make these bulky side chains it prevents the coming together of the particles and that is called steric repulsion.

Now the charged system the electrostatic repulsion based admixtures the charge will diminish as the cement starts hydrating. As a result you may not get effectiveness for a longer time but with steric repulsion you get that effectiveness for a longer time because it does not rely on the surface charge. It does not rely on your maintenance of surface charge for a long period of time.

Influence of structural aspects of PCE:

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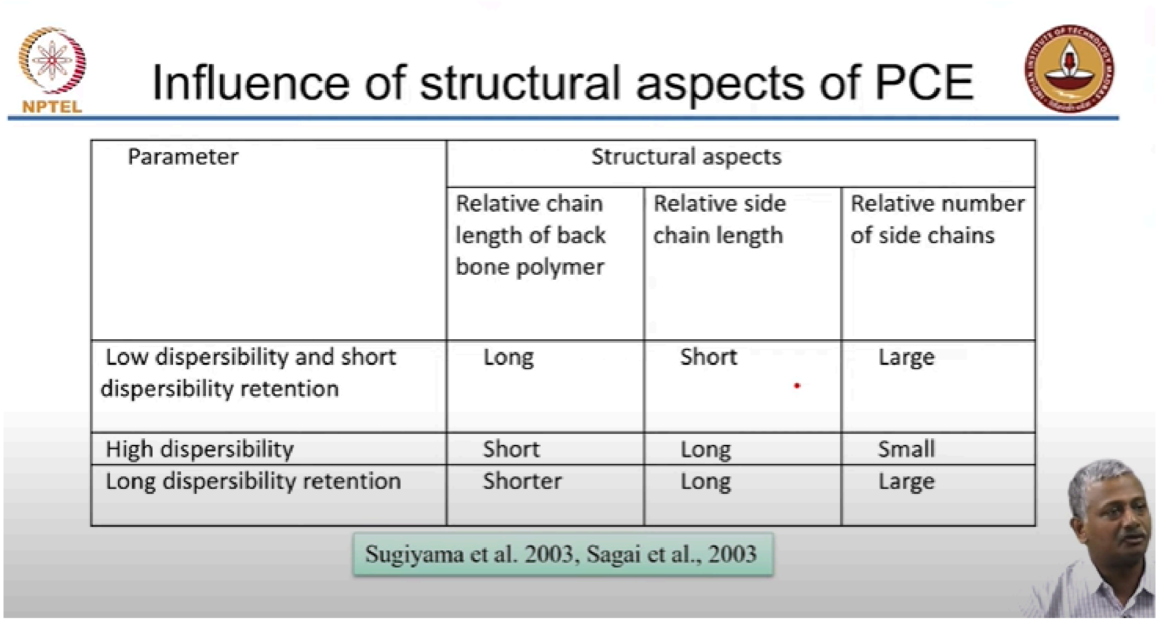

Influence of structural aspects of PCE

Parameter	Structural aspects		
	Relative chain length of back bone polymer	Relative side chain length	Relative number of side chains
Low dispersibility and short dispersibility retention	Long	Short	Large
High dispersibility	Short	Long	Small
Long dispersibility retention	Shorter	Long	Large

Sugiyama et al. 2003, Sagai et al., 2003

Now because of this interesting formulation of the polycarboxylic ether molecules you can actually make different types of molecules to get different types of performance. So let us say you want low dispersibility and short dispersibility retention. Can you give me some examples of an application where you want less workability and less retention of workability? Any example of a concrete which needs to be applied with less workability and less retention of the workability?

Pavement, concrete pavement. Concrete pavements do not need too much workability at the same time if it is workable for a longer time then you are not gaining your strength fast enough. So in this case you go with a backbone polymer that is long so that adsorption really happens but then side chain length is short so you do not really get too much repulsion and you have a large number of side chains which go and attract themselves to the surface, adsorb themselves on the surface and you do not really get a retention of this workability for a long period of time. You want high dispersibility let us say self-compacting concrete in such cases your backbone polymer may be short but your side chain length has to be quite long to provide you the excessive workability and of course when you want retention of the same thing you still have to go with short and long but a large number of side chains to provide you that effectiveness for a longer period of time.

So what I am trying to say here is, I mean these combinations may not work out all the time but what I am trying to say here is you can now play around with the molecule and control the length of these side chains, control the length of the main polymer chain to acquire specific polymers that work for your particular application.

So because of PCE now we can actually engineer the super plasticizer for any application like for 3D printing, like for self-compacting concrete, for all of these slip forming so you can actually now start looking at functionalities being brought in. The side chains need not just provide dispersibility, the side chains can also have some functional groups that can lead to other things like I said earlier we have super plasticizers and VMA added separately. Now the side chain itself could have molecules that lead to the viscosity modification also. So all of these aspects can now be brought in so in other words we can make the admixture multifunctional and that is the main advantage of PCE. So although they are expensive the multifunctionality helps you reduce the extent of other chemicals that are needed for producing various different effects in your special concrete.

Comparative evaluation of SP types:

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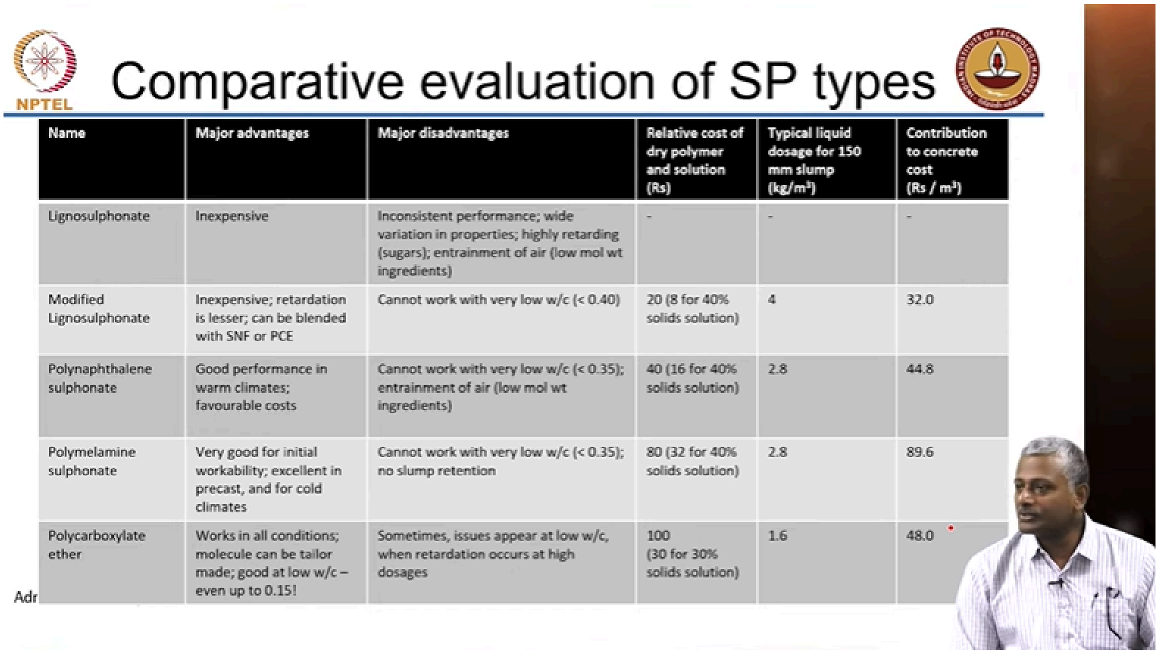

Comparative evaluation of SP types

Name	Major advantages	Major disadvantages	Relative cost of dry polymer and solution (Rs)	Typical liquid dosage for 150 mm slump (kg/m³)	Contribution to concrete cost (Rs / m³)
Lignosulphonate	Inexpensive	Inconsistent performance; wide variation in properties; highly retarding (sugars); entrainment of air (low mol wt ingredients)	-	-	-
Modified Lignosulphonate	Inexpensive; retardation is lesser; can be blended with SNF or PCE	Cannot work with very low w/c (< 0.40)	20 (8 for 40% solids solution)	4	32.0
Polynaphthalene sulphonate	Good performance in warm climates; favourable costs	Cannot work with very low w/c (< 0.35); entrainment of air (low mol wt ingredients)	40 (16 for 40% solids solution)	2.8	44.8
Polymelamine sulphonate	Very good for initial workability; excellent in precast, and for cold climates	Cannot work with very low w/c (< 0.35); no slump retention	80 (32 for 40% solids solution)	2.8	89.6
Polycarboxylate ether	Works in all conditions; molecule can be tailor made; good at low w/c – even up to 0.15!	Sometimes, issues appear at low w/c, when retardation occurs at high dosages	100 (30 for 30% solids solution)	1.6	48.0

Adr

At least this aspect we should talk about. In construction projects everything finally boils down to cost. You give the new product, how much does it cost? That is what the first question anybody asks you is. But the cost is not an absolute term, it is a relative term so we have to pay attention to what we are talking about.

So let us say we have lignosulphonate, it is inexpensive, it is a first generation admixture, it is available typically as a water reducer, and we simply use it at high dosage. But the problem is when you start using SP as a super plasticizer there is inconsistency in the performance. It is about variation properties, it retards, it entrains air, so there is lot of problems. So we would not even consider it for comparison of the costs and performance. But let us look at a case where we can modify the lignosulphonate.

Now we are causing retardation and I talked about the fact that in lignosulphonate molecules there may be some sugars present that can cause retardation. Let us say you do some fermentation and remove the sugars and we said that there is air entrainment present. So you can modify the formulation in such a way that the air entraining molecules are removed. We will talk about that later. So when you do that you can create what is called a modified lignosulphonate.

There you can have controlled retardation and reduced air entrainment now. The problem with this again is the lignosulphonate has its own limitations in working with extremely low water cement ratio. So you cannot even imagine it being used for water cement ratios less than 0.4. Now let us say the relative cost of the dry polymer is 20 rupees or 20 units, arbitrary units 20 units. So if you take a typical liquid that is available in the commercial sense, most liquids that are available for admixtures are either 30% or 40% solution. That means active ingredients are about 40%, remaining is just water. So it is important because if you sell it as a liquid it is easier to disperse in concrete mixtures. If you sell it as a powder you need to take all that additional precautions. So most of the admixtures are sold as liquids. So 8 let us say for a 40% solid solution, let us say the cost becomes 8 now. For a 150 mm slump in concrete we may require around 4 kg/m^3 of the modified lignosulphonate. That means our cost becomes 32 rupees per cubic meter for using modified lignosulphonate.

You come to poly naphthalene sulfonate, it works well in conditions which we have in India and it is very good for warm climates. It has a cost which is not as high as polycarboxylates but then again when you go for very low water cement ratios of less than 0.35 it is not very good. In some cases it can also lead to air entrainment especially if the poly naphthalene sulphonate molecules do not have too many, and do not have an adequate chain length. If you have a dimer or a trimer present it will act like a surfactant like a detergent and produce more and more air in the system. So here the relative cost of the dry polymer is 40 rupees let us say. Again for a 40% solution you get 16 rupees as the cost. You do not need as much to produce the 150 mm workability. So if you multiply the two you get the cost to the concrete to be about 44 rupees or 45 rupees.

Similarly polymelamine sulfonate problem is it does not work well in cold climates at all. It is very good for initial workability, it produces excellent concrete, it is an ideal concrete for precast conditions but it does not retain workability long enough, no slump retention. It also cannot work at very low water cement ratio so you cannot really imagine it being used for very high strength concrete. The cost is higher, about 80 rupees let us say for the dry polymer or 32 rupees for a 40% solid solution. So that means again let us say you need 2.8 kg/m^3 to produce 150 mm slump nearly the same as SNF. So your overall cost is quite high now 89.6 rupees.

Polycaboxylate we talked about the fact that it works extremely well, it is the material that is the admixture of choice when we want to make high strength concrete even as low as 0.15 which we will talk about later ultra-high strength concrete can be prepared. In such cases polycaboxylate is the only way to go. Some issues of retardation can happen at very low water cement ratios when you add too much dosage that is obvious. Cost is going to be high, let us say 100 rupees. Now typically these are sold at about 30-33% solids. So let us say 30% solid so you have 30 rupees as the cost of the solution. You need less dosage to acquire the same level of slump because we want to produce 150 mm slump only; it is not a major demand in terms of workability.

So actually if you look at it your cost contribution to concrete is only 48 rupees which is only slightly higher than your sulphonated naphthalene formaldehyde. It is lower than melamine formaldehyde, it is higher than modified lignosulphonate no doubt but let us say you want to choose a concrete where you want to produce 200 mm slump. You may not even be able to make it with modified lignosulphonate; you can only do it with polycaboxylate or SNF. In such cases your contribution of the cost to the concrete is what matters to produce concrete of a given effectiveness. It is not the unit cost of the material but how much it actually costs for the concrete to achieve that level of performance.

So we have to change the way in which we look at the cost. The cost to achieve performance is what we desire. Like a Mercedes and an Ambassador are very different in initial cost but if you think about maintenance in the long period of time, maintenance for an Ambassador, many of you probably do not even know what an Ambassador is, you do not get to see any more in the streets. So you have to spend a lot more for maintenance to get it running to keep it running for a long period of time. Mercedes does not but of course when you do have to spend on maintenance on a Mercedes you are done. So that example does not totally apply to this condition because there is no maintenance here.