

## Admixtures and Special Concretes

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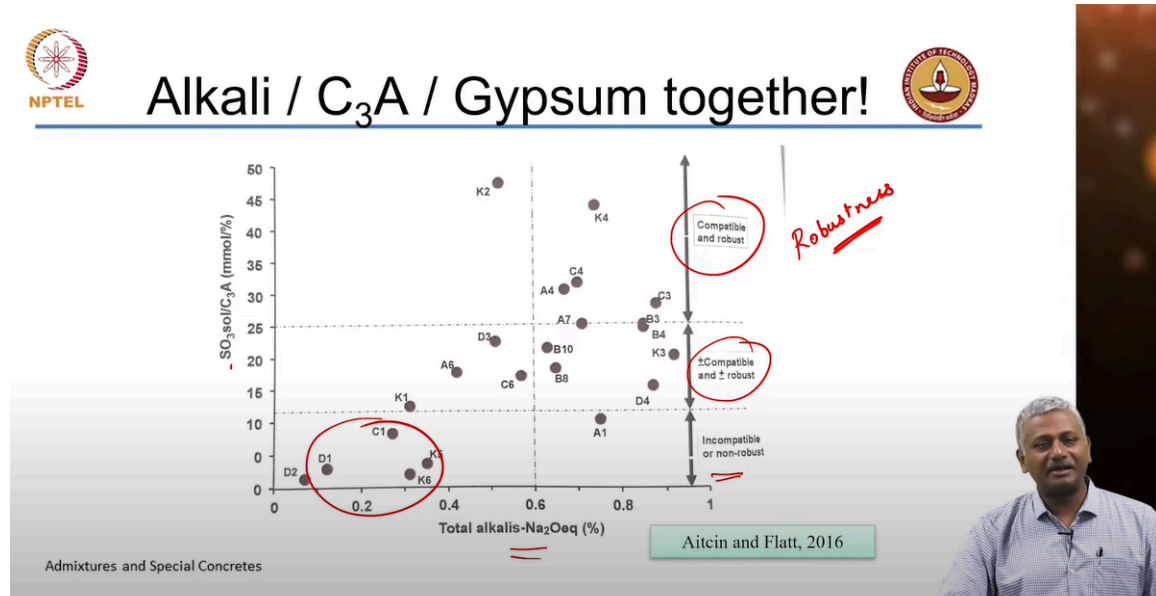
Indian Institute of Technology Madras

Department of Civil Engineering

### Lecture 12 Chemical Admixtures: Water reducers - Part 5

Alkali /  $C_3A$  / Gypsum together:

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Now, of course, life is not always so simple that you can separate out each effect and study that individually everything happens together. So, here all of this is taken together for instance the sulphate to  $C_3A$  ratio and the alkali content of the cement. So, here what we are talking about is you can divide your composition into different regions. If you have very high alkalis and you also get much higher sulphate to  $C_3A$  ratio not  $C_3A$  to sulphate, but sulphate to  $C_3A$  ratio you can have compatible and robust combinations. Now in between they describe it as compatible and robust with some negatives it is not always compatible and robust, but when you have very low solubility of the sulphate to  $C_3A$  ratio irrespective of the alkali content especially at low alkali content you have a problem with respect to compatibility. So, you need to add additional alkalis or alkalis sulphates there to really get your compatibility happening.

Now, what is robustness? It is a very interesting term as far as concrete mix design is concerned. When do you call a concrete mixture robust? So, we make concrete mix in the lab and we expect that to perform the same way in the field. We make concrete mix designs typically in the form of  $\text{kg/m}^3$  of material. We design the mix with a particular water cement ratio, we expect a certain workability, a certain strength.

When we take it to the field there could be variations on a daily basis with respect to the moisture in the aggregate. You may want to check the aggregate moisture as often as possible, but it is not practically possible to do this for every mix that you make.

How much is the capacity for a mixer in a typical batching plant? Any ideas? At least a half cubic meter, but what is the size of the batch that is typically prepared in the lab? How many kilograms? Each cube is how many kilograms? 150 mm cube, about 8 to 8.5 kg. If you have to make 6 cubes you need at least 60 kg of mix. You would not mix more than 100 kilograms anyway because mix is typically available in labs of that size. 100 kg is hardly anything,  $100/2400$  if you want to convert it to cubic meters. That is hardly anything. There the size is  $0.5\text{m}^3$ .

In such instances there may be variations in the moisture content that you find in your system. Now robust mix is that which still results in the ideal combination of workability and strength despite minor variations in water content and in super plasticizer content. You have to imagine that everything that you do in the lab you cannot translate as it is into the field. There will be variability, there will be much greater variability than you see in the lab. You should be able to still afford some degree of change from the actual mix design. You do not do it intentionally, but even if that happens your workability and strength should not get affected. So a robust mix is something that is designed in such a way. So if you have to really take up a design to be robust you should be doing all of these things in the lab. It is not just one mix design, you should also vary your super plasticizer dosage and water content up and down by at least 5 to 10  $\text{kg/m}^3$  meter for the water and a small amount for the super plasticizer to ensure that your concrete mix is still able to retain its property. Because all that will affect the long term performance.

Even for instance when you make a mix for a concrete and a project, the project duration need not be just a month. Your project duration could be a year, sometimes 2 years, 3, 4, 5 years. That mix design that you made on day zero now has to be valid for the full five years when you are working with possibly different batches of cement, you are working with different batches of admixture, and you are working with different sources of aggregate. How do you ensure that your mix is good enough to last for five years? Nobody can be such a genius that they can produce a single mix that will last for five years. That is where you need to assess this robustness before you really take these mixes to the field. And again, I keep talking about this in many fora that this aspect of concrete mix design is really given a very shabby treatment in most construction projects. So

typically when the site is ready to receive concrete that is when they ask for the mix design. That is the kind of preparation that we do for concrete mix design. But if you have to look at all of these effects, I am only talking about workability here. So if you think about long term properties, strength, shrinkage, durability, all of those things need time to get evaluated. So unless you have time you cannot really do this. You cannot just rely on the fact that I used this concrete mix 10 years ago, let me use the same thing. And in most projects unfortunately that is still the mentality that is being followed.

### Influence of calcined clay:

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The slide, titled "Influence of (calcined) clay", features the NPTEL logo on the left and the IIT Bombay logo on the right. It contains two main diagrams. The left diagram shows "Clay platelet" as a blue layered structure with "Surface adsorption" of "PCE" molecules (represented by blue hand-like shapes) on its surface and "Intercalation" of PCE molecules between the layers. The right diagram is a detailed cross-section of a "Montmorillonite layer" with a thickness of 1.77 nm. It shows "Silanol groups of clay layer" (Si-OH) and "Interlayer water as bridging molecules" (H<sub>2</sub>O) between two layers. A "Polyglycol" chain is shown intercalated between the layers, with its oxygen atoms interacting with the silanol groups and water molecules. A citation "Plank et al. 2015" is placed between the two diagrams. Below the diagrams, the text reads "Intercalation between layers; adsorption on high surface area". At the bottom left, it says "Admixtures and Special Concretes". A small inset photo of a man is visible in the bottom right corner of the slide.

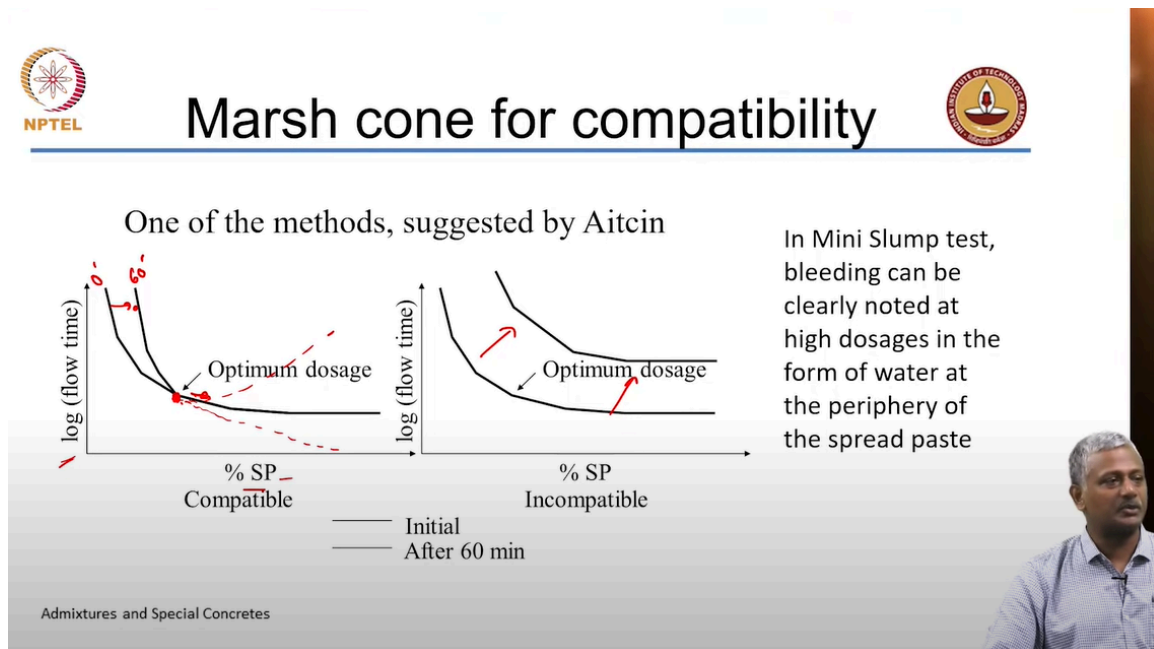
When you have other ingredients which can pose some issues because of their structure you need to be further careful about your compatibility. So here especially today there is a lot of interest in the use of calcined clay as a replacement of cement because people have estimated that worldwide resources of other supplementary materials are not as plentiful as calcined clay. So there is renewed interest in calcined clay but the structure of clay is such that it makes workability a difficult thing to achieve. So you know that surface adsorption will happen, clays have much greater surfaces because of their plate-like texture. So when you have the platelets you have the PCE molecules that can get adsorbed on the surface of the clay and in between the platelets. So there is some loss of the super plasticizer molecules in between the platelets of clay. So when clay based systems are used, not natural clay but calcined clay, we have to take the clay and calcined it only then becomes reactive. We will come to that when we talk about calcined clay based systems in the mineral admixtures chapter. So these admixtures can get between the clays. We call this process intercalation, loss of the super plasticizer molecules

between the plates of the calcined clay and this is happening because the clays or the interlayer space in the clays has a net charge and that is sort of attracting the super plasticizer inside. So here for instance the structure of the montmorillonite clay is given here, you have silanol groups of the clay layer and then the interlayer water that is present as bridging molecules between the plates of clay. So your poly glycol or your poly glycol that is coming from your poly carboxylic ether can have a tendency to get trapped inside here because of the charges that are present here.

So clays will cause a major problem with your workability, calcined clays. That is where you need to exercise judgment in choosing the right kind of super plasticizer that can make clay based systems work.

### Marsh cone for compatibility:

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So we talked about the use of marsh cones to check the saturation dosage of the super plasticizer. The same test can also be used to check the compatibility.

There are different methods suggested, not all of these have the same technique but there are different methods suggested you can use either one of these. So when you plot the flow time versus SP dosage as we understand that as the dosage increases the flow time will keep on reducing but beyond a certain point there will not be a significant reduction in the flow time. That means we have already saturated the cement surfaces with respect to the admixture adsorption, no further adsorption is taking place. So when you do this test at 0 minutes and repeat the same test at 60 minutes, after 60 minutes of mixing you

repeat the same test what you will see obviously is that your curve will shift to the right, which means to produce the same flow you have the need for a higher SP dosage. But what will happen is if you are beyond optimum dosage the two curves at 0 and 60 minutes start coinciding. This will obviously happen in a system that does not have an accelerated setting, those effects are going to be quite different. Here in a system that is compatible you will see that the two curves start coinciding. For an incompatible combination the entire curve will be shifted upwards, you will not have any coincidence in the curves beyond the optimum dosage.

The other possibility is that we talked about this when we discussed the marsh cone test that if the adsorption is simply not getting completed this will keep on going down. Of course it cannot come to 0, but it will keep on going down that means you are not able to saturate your system. Alternatively if the superplasticizer starts causing bleeding the curve may start moving up. So that is also the sign of an incompatible combination. A compatible combination will achieve saturation and they will not see a major effect in the workability after that. Mind you when you do this test you are adding more and more dosages of superplasticizer and we discussed that the superplasticizer formulations that are available are partly solids, partly water 40% solids typically right 40 or 30%. That means the remaining 60 to 70% is just water. So you have to do this experiment keeping in mind that you are adding this extra water from the SP also. So that has to be subtracted from the mix water to get the same water to cement ratio. For that, what do you need to do? You need to test the solid content of the SP first. When you get the superplasticizer for testing you should check the solids content.

How will you check the solids content? Take some mass of the superplasticizer and put it in the oven at 100°C you remove the water only the polymer gets left behind. So the only problem is some polymers also start degrading before 100°C. So you have to be a little careful in adopting the right strategy for determining solids content. But you have to have an idea about that before you do this test. Again not sophisticated, you just need an oven. So any site lab can also have an oven. Any way you have ovens for measuring moisture content of the aggregate. And all you need for this test is that flow cone which can be fabricated. You do not even need to buy it; any workshop can produce it. And you also need a stopwatch to measure the time that it takes for the thing to flow out graduated cylinders are anyway there in most site labs.

## Range of action of common SP's:

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## Range of action of common SPs



The 1<sup>st</sup> generation HRWRs need a slump of around 75 mm for action ( $\sim 0.45$  w/c). The slump is increased up to 150 – 200 mm.

The 2<sup>nd</sup> generation admixtures can work at reasonably low slumps (25 – 50 mm, corresponding to w/c of 0.35 – 0.40) to increase the slump to  $\sim 250$  mm.

The 3<sup>rd</sup> generation HRWRs, on the other hand, can even be used with no slump concrete (0.29 – 0.31 w/c), and the slump is increased to more than 250 mm.

Admixtures and Special Concretes



Now it is also important as a practical concrete engineer to be aware of the extent of possibility of using these materials. How far can I go? Can I use any chemical in any concrete mixture? I should not do that because I am just wasting my time if I start off my mix design with all possible combinations. I have to know what the limitations are.

So first generation high range water reducers like lignosulphonates they already need your concrete to be somewhat wet. They need an initial workability of about 75mm to be able to act further. So this level of workability in most concrete you will achieve is around 0.45 to 0.5 water to cement ratio. So the slump has increased up to 150 to 200 mm. More than water cement ratio you should probably take a look at a typical water content. So generally let us assume a cement content of  $400 \text{ kg/m}^3$ . In this case then 0.45 becomes  $180 \text{ kg/m}^3$  water content. That is the extent of water that should be there in your mix for the lignosulphonates super plasticizer to be effective.

The sulphonated naphthalene formaldehyde or melamine formaldehyde can work with reasonably low slump concrete about 25 to 50 mm slump corresponding to water cement ratio 0.35 to 0.4 to increase the slump to about 250 mm. In fact I would not really consider 140 as effective for SNF. It will be very difficult to get much effectiveness out of this. I would rather go with about  $160$  to  $180 \text{ kg/m}^3$ .  $160$  to  $180 \text{ kg/m}^3$  is something that you need for SNF to be effective. If you are anywhere less than  $160 \text{ kg/m}^3$  I mean I am not saying there are formulae there are concretes where SNF cannot be used if it is water content of less than  $160 \text{ kg/m}^3$  people have used it is possible but it becomes more and


more of a stretch you need to keep on adding more admixture which is not really good because you get retardation you have other problems of low strength and so on.

So if it is less than 160 kg/m<sup>3</sup> today the ideal choice is to go with a polycarboxylic ether or third generation super plasticizer. So all your self-compacting concrete where you need extremely high flow in such cases you need to control the water content also to ensure that you have a suitable material of the right kind of strengths. In such cases you have to achieve it by using the third generation admixtures.


Now it does not always work this way. There are sites where people will tell you that you have to use only SNF. Why is that? Because it is cheaper the product is cheaper, because people are still not taking a look at how effective it is in concrete before they decide on the cost they look at the overall initial product cost. So that you need to be a bit wary of the guys who make the decisions in most construction companies are the people who have no idea about civil engineering. So you need to contend with these people and get them to understand that technically things have to be sound only then things work. It is a difficult battle. I can tell you that having been involved in many of these projects is a very difficult battle. Even civil engineers who become upper management seem to cloud themselves when it comes to technical aspects and only worry about the economy. But you cannot achieve everything with just the economy. You have to ensure that the technically sound solution is used ultimately it will become economically more favorable also. So that is something that the responsibility is up to you to really convince your boss to ensure that they make the technically sound judgment.

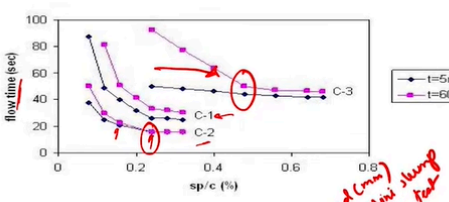
### Paste tests with different cement:

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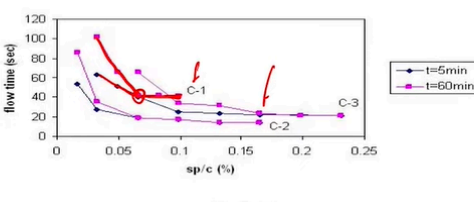


## Paste tests with different cement – SP combinations






**SNF**



**PCE**

	C-1	C-2	C-3
PCE	0.066, 162	0.066, 155	0.165, 175
LS	0.266, 114	0.228, 80	0.760, 125
SNF	0.240, 150	0.240, 139	0.640, 158
SMF	0.266, 153	0.228, 138	0.456, 129

PCE more compatible than SNF  
Optimum dosages for PCE lowest among four families of SPs



Admixtures and Special Concretes

Now I am just showing you some results from IIT Madras studies. So we had done several different types of cements to try and understand whether this concept of saturation, does it really work, or does the concept of compatibility does it really work.

So here there are three cements C1, C2 and C3 they have very different chemical compositions. I will show you that a little bit later but what you see is entirely different effects produced by sulphonated naphthalene formaldehyde and poly-carboxyl ether. So we looked at one definition of compatibility where when the test marsh cone test was done at 60 minutes the curves should start coinciding after the optimal dosage.

So in the case of let us say C1 with SNF admixture is that compatible or not compatible? It is mostly incompatible because the curves are not coinciding by that definition of compatibility.

C2 it is compatible the curves are coinciding.

What about C3? It is a little bit interesting. It seems to be a part but more or less similar because this is actually actual flow time not the log. So the difference is not that great. We can consider it to be compatible but what is happening is your optimal dosage is or saturation dosage is shifted way to the right. What could be the reasons for this? The C3 cement has an optimum or saturation dosage which is shifted far to the right? Fineness could be one reason. In fact in this case that was the reason C3 was much finer as compared to C1 and C2, it required much greater SP dosage and the same effect you can see here also in PCE also the extent of fineness of C3 cause the saturation dosage to be much higher.

But what do you notice as the difference between SNF and PCE? In all cases PCE produced compatible combinations with all three cements. You had the same issue of higher dosage required for C3 but none of the things were incompatible. If you compare C1, here this is C1, you see this curve at 0 minutes and the curve at 60 minutes coinciding after the saturation dosage. So yes this concept of compatibility is clearly indicated here.

What you also see is the dosage required for saturation. With C1 PCE you require 0.066%, C2 - 0.066, C3 - 0.165 much greater dosage of PCE. But as compared to PCE if you look at SNF you need much higher dosages for saturation. Look at the workability produced. This is the spread in mini slump. What is presented here is the spread in millimeters from mini slump tests. What does this mean? That you are producing with SNF and PCE nearly similar workability. May be slightly higher with PCE but nearly similar but all this you are obtaining at a much lower dosage of PCE.



Saturation effectiveness is very important to understand. If you look at lignosulphonate saturation is obtained but look at the workability. It does not really have that ability to produce a highly workable material. Similarly melamine formaldehyde has similar



dosages but workability is not really good with C2 and C3. So you have to evaluate how effective your admixture is going to be with the type of cement.

### Lab investigations on concrete:

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## Lab investigations on concrete

	w/c	Slump values (mm)				Compressive strength (MPa)	
		0min	30min	60min	90min	3 days	7 days
<b>Control mix</b>	0.45						
C-1		170	70	10	0	20.0	25.3
C-2		180	70	10	0	20.3	26.0
C-3		120	40	0	0	27.5	28.5
<b>With PCE</b>	0.35						
C-1		180	140	80	20	34.0	36.9
C-2		190	140	80	20	36.0	39.0
C-3		180	130	60	20	40.4	40.7
<b>With LS</b>	0.35						
C-1		110	80	10	0	16.2	26.3
C-2		100	60	0	0	17.3	26.5
C-3		80	10	0	0	18.7	28.3
<b>With SNF</b>	0.35						
C-1		150	80	0	0	32.8	39.0
C-2		140	60	0	0	33.4	38.4
C-3		200	130	40	0	38.8	41.8
<b>With SMF</b>	0.35						
C-1		140	100	70	20	32.4	38.5
C-2		190	130	40	0	31.0	38.8
C-3		100	40	0	0	34.2	40.0

*Handwritten notes on the slide:*  
 - For Control mix:  $\% WR = \frac{0.1}{0.45} \times 100 = 22\%$   
 - Red circles highlight slump values at 0, 30, and 60 minutes for various mixes.  
 - Red circles highlight 3-day and 7-day compressive strengths for several mixes.  
 - A red arrow points from the 7-day strength of the LS C-1 mix to the text below.

Admixtures and Special Concretes

Now obviously you will be asking if this is all on cement paste. I want to see the effect in concrete. Do we get the same effect in concrete and that is what is being seen here.

So here we produce a control mix without any admixture at 0.45 water to cement ratio and with the four different super plasticizers at 0.35 water cement ratio that means my water reduction percentage water reduction is how much? About 22% let us say. So we all know that at this cement ratio your lignosulfonate is not going to be effective at all. So your control mix produced workability is of 170 to 180 for C1 and C2 and the lower slump for C3. Why? Because C3 was finer as you rightly said earlier. So finer material absorbs more moisture, water is not freely available to provide workability so you get lower workability and that slump was not getting retained much. You see that after 10-60 minutes almost 0 slump in all of these cases. With lignosulfonate you are not getting the effectiveness at all. That means that this water cement ratio is not working to produce a high slump and of course the initial slump itself is bad so workability retention is going to be bad.

What about sulphonated naphthalene formaldehyde? It is able to produce a fairly good initial workability but then it is losing workability quite quickly.

What about PCE? Better workability and better retention of workability at 60 minutes.

What about strengths? At 3 days the control mix is giving around 20 again the finer cement is given higher strength expected faster reaction, by 7 days that difference comes down that is also expected.

Now compared to this look at how much strength the PCE mixture is given nearly 1.5 times or more than 1.5 times but at 7 days that difference is not 1.5 but about 1.2-1.3 times. If you look at the codes I will talk about the codes later it seems to match with what is expected. Similarly the strengths produced with SNF and SMF at 7 days are still ok but you are not getting any strength with the lignosulfonate even though water cement ratio is 0.35 you are not getting a strength which is much greater why this happening is? We talked about this when first generation water reducers are used as super plasticizers you have to add too much of it to really make it effective and that causes strength retardation.

So of course I do not have data for 28 days . If I had done a comparison I may have had a slightly better improvement in the strength but by 7 days I didn't really get the strength because retardation was too much with the lignosulfonate.

So again what we are seeing with respect to paste studies is that our experience in concrete is also sort of matching the expectations. So this concept of saturation helps to reduce the extent of mixture proportioning trials that you have to do to get the required characteristics in terms of strength and workability.