

## Admixtures and Special Concretes

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### Lecture 11 Chemical Admixtures: Water reducers - Part 4

So, in today's session we will continue our discussion on the influence of super plasticizers on early age behavior of concrete. Primarily we will take a look at what aspects affect the compatibility between cement and super plasticizer.

#### Summary:


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## Summary of Part 2

- Nature of surface charges on cement particles
- Adsorption of chemical admixture on cement surface, and factors affecting
- Principal mechanisms of action – electrostatic repulsion and steric hindrance
- Relative performance and cost of SPs

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Let us look at what we learned in the last class. We talked about what type of surface charges are present in cement as a result of the processing, that is grinding primarily, and how that affects the overall adsorption of chemical admixtures on the surface. As we discussed, chemical admixtures are long chain polymers, the long chain gets adsorbed onto the surface of the cement particles, and depending upon the nature of the polymer either a surface charge is imparted to the cement particle which causes electrostatic repulsion. Alternatively bulky side chains that are present in these super plasticizer molecules prevent the coalescing of cement particles and that leads to long term maintenance of the workability. So, that is called steric hindrance. And towards the end of the last chapter we talked about what would be the impact of super plasticizers on cost.

And one very important lesson that we ought to learn is that it is not the material cost that is important, but it is the cost of producing concrete of a given quality. The cost should be calculated based on attaining the right characteristics in concrete. It is not just a question of choosing something cheaper or something more expensive. It is how they actually impact the properties of concrete that is important.

### Compatibility issues:

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The slide features the NPTEL logo on the left and the Indian Institute of Technology Bombay logo on the right. The title 'Compatibility Issues' is centered at the top. Below the title, a bulleted list defines incompatibility and lists performance indicators. A speaker is visible in the bottom right corner of the slide frame.

- Incompatibility may be defined as the lack of expected level of performance when a given combination of cement and superplasticizer is used
- Performance indicators:
  - Poor slump retention
  - Retardation
  - Bleeding / segregation
  - Low early strengths

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We have been talking on and off about compatibility. So, we are obviously dealing with the system that has several different chemical species. There could be complex interactions between these chemicals depending upon the composition of the chemical, the type of processing that each chemical undergoes, and the type of environment in which actually you are applying this material in concrete.


Cement is also a chemical obviously. It has got a chemical composition that often dictates the kind of behavior that cement exhibits. Super plasticizer is mostly an organic chemical. Of course, there are some inorganic chemicals also which we will talk about later. Of course, inorganic chemicals are not super plasticizers. Most super plasticizers are organic water soluble organic chemicals. So, when these chemical species are present together in the mixture, there can be instances when you do not get the kind of performance that you desire. So, this is what we call incompatibility. We are not really getting the right kind of performance from the concrete. So, it is a lack of expected level of performance when a given combination of cement and super plasticizer is used.

Now, what are these indicators of poor performance? Slump retention could be a major indicator. In today's world, we want the slump to be retained for a much longer period of time, and that retention of slump becomes quite critical to the way that concreting operations are carried out on site. So, retention of slump, lack of retention is an incompatibility problem. When you retain the slump as expected, then it is a compatible combination. Retardation is another example. You have excessive retardation that is happening because of some chemical interactions which does not permit a normal hydration to take place. Then you have bleeding or segregation. In some cases, the water becomes so freed up that it simply rises. Now, water is going to rise in concrete because it is the lightest ingredient and it has got the lowest specific gravity amongst all concrete ingredients. So, in a mixture where you have dissimilar weights, obviously the lowest weight has to come at top. You have to decide or design your concrete mixture appropriately to avoid this effect. This effect could be exacerbated when you have a chemical admixture in the mix.


Low early strengths is another issue. We often design concrete to obtain high early strengths. We want to open up the structure early. We want to carry out the work in a fast track manner. For that, attainment of early strengths is very important. So, when you do not get early strength, that is basically a sign of something wrong in the chemical system.

**Factors affecting Compatibility:**

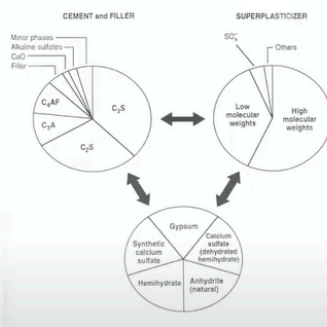
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## Factors affecting compatibility



- Type and amount of superplasticizer
- Composition and physical properties of cement and additive minerals
- Mixture proportioning of concrete
- Batching and mixing of concrete ingredients



(Aitcin, 1998)



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So, we have talked about some of these aspects, but let us take an entire look at the factors that can affect compatibility of the cement and super plasticizer. Of course, the type of super plasticizer, whether it is a sulphonate or a polycarboxylate, all of that could

have an effect on the compatibility. That is one thing. The composition and physical properties of the cement and the additive materials. These days, concrete is not just plain cement. We often have additives, mineral additives, which could have some effect on the overall composition of the cementitious blend. Then, you have other aspects other than chemistry like the mixture proportioning of the concrete, how much cement you have, how much water you have, batching and mixing of concrete ingredients. The order in which we put in, like in the last class we discussed, is to improve the effectiveness of sulphonated naphthalene formaldehyde, and you may want to add it slightly after the water has already come in contact with the cement. So, such strategies need to be worked out very clearly to make the concrete produce the right blend of properties.

Just to put this in a nutshell, if you look at the cement and filler, of course, you know that cement is composed of all of these four major compounds. It has other minor oxides including free lime sometimes, free calcium oxide. It has also got what is the most critical component: the alkali sulphates, sodium sulphates, potassium sulphates and the likes. Again, these are sulphates and these are highly soluble sulphates. So, you have to take that into account also while deciding on your early age chemical constituent of your pore solution. You then have the super plasticizer. We discussed that in the formulation of the super plasticizer, you want to have a particular chain length which is appropriate. You do not want too short a chain length or may be too long a chain length is not really worth the effort of going through. So, you have high molecular weight chains and low molecular weight chains within the super plasticizer. You may have sulfonate or you may have other functional groups that are actually associated with the super plasticizer. All of these will have an influence on the way that it interacts with the particular cement. And interestingly, the calcium sulphates that you add to the cement can have a major influence on the way that your system behaves. So, you have gypsum which is  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , two molecules of water associated with gypsum. Then you have hemihydrate that is  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ , what do we otherwise call this as POP or Plaster of Paris. If you further dry this, you get anhydrite synthetic calcium sulphates ( $\text{CaSO}_4$ ), which is what you get if you further dry the Plaster of Paris. You may also get natural anhydrite that means calcium sulphates which is naturally found that is another possibility. It turns out that when you use one or the other of these sulphates species in cement, the rate at which the sulphates become available for reaction can vary.



The solubility of the sulphates is different as you move from gypsum to hemihydrate or rather synthetic hemihydrate or Plaster of Paris to synthetic calcium sulphates, your solubility increases. As you go from gypsum to hemihydrate to synthetic calcium sulphates, your solubility goes up. That means the sulphates are available faster in solution to react with  $\text{C}_3\text{A}$  to lead to a normal setting process.

Now you do not want sulphates to come in too early, you do not want a quick set unless the condition really demands it, you want a controlled set. So generally what you will see

is in most cements, there will be a judicious blend of the different types of sulphates. Now what happens is when you grind the cement, the heat generated because of grinding, if it is excessive, can also have a tendency to convert gypsum into other hydrated forms of calcium sulphates, but you want some sort of a combination of these. Now it turns out if you use natural anhydride, naturally occurring calcium sulphates, the solubility is very low. It is even lower than that of gypsum. Interestingly synthetic anhydride can have high solubility, natural anhydride has a low solubility. So when you start using these systems in your cement, you need to be very careful as to what rate they are actually coming in. We will touch upon this again later.

### Compatibility issues:

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## Compatibility Issues

Influence of :

- 1)  $C_3A$
- 2)  $C_3A/CaSO_4$  ratio
- 3) Alkali content
- 4) Fineness of cement

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So the important aspects that really affect compatibility, if you want to break down chemically and physically,  $C_3A$  is obviously very important because that is the one which participates in the early part of the reaction. It turns out more than  $C_3A$ , it is the calcium aluminate to calcium sulphates ratio or sulphates ratio, not calcium sulphates because the extent to which sulphates is available is governed by the solubility of the calcium sulphates.

The alkali content can also affect the compatibility. We will take a look at how this happens and the fineness of the cement. Why should the fineness of cement affect compatibility? The finer the cement, the more the surface area, so there will be greater adsorption. So your admixture effectiveness will be good in the beginning, but it may get lost quite quickly just like the effect of temperature.

## Influence of $C_3A$ :


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# Influence of $C_3A$

- Competition between sulphonates from admixture (particularly SNF) and sulphates from gypsum for aluminate sites (positively charged)
- SNF can also inhibit gypsum nucleation
- Relative amounts and types of  $C_3A$  and gypsum have pronounced effect on compatibility (Cubic  $C_3A$  less reactive; solubility of gypsum increases from dihydrate → hemihydrate → anhydrite; natural anhydrite v. low solubility!

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So we talked briefly about this previously that the sulfonate that is available from the SNF or lignosulfonate may have a tendency to start getting attracted to the  $C_3A$  sites. So it is competing with the sulphates from the gypsum and this competition can produce a very contradictory effect. So your sulfonate from the admixture when it is going and attracting to the surface of  $C_3A$ , it is preventing the reaction of gypsum with  $C_3A$ . But at the same time, the effectiveness of the admixture is also getting lost. So you are losing the admixture quickly, you are losing your slump, but you are also getting retarded set because your  $C_3A$  is not available to react with the gypsum anymore. So contradictory effects, we do not expect two of them to be together, but yes that happens in this case.

Now interestingly, SNF can also inhibit gypsum nucleation. Now what do I mean by that? In some mixes you may have seen that when you start mixing them, when you put all the ingredients in the concrete mixer and start mixing, there is some stiffening that happens in the mix. But when you continue to mix, the stiffening basically breaks down. It does not stiffen that much. We call this phenomenon a false set. Now why is this false set happening? It is happening because if there are other forms of gypsum, when they immediately come in contact with water, they convert back to gypsum. When you use gypsum boards, how are gypsum boards prepared? We use plaster of paris with fibers or with meshes and this plaster of paris converts to gypsum. So the hardening or stiffening happens when gypsum is formed. Similarly, in a concrete mixture, if the cement has too much of the anhydrite or hemihydrate, it will convert to gypsum as soon as it meets the water. So that is early stiffening, but that can be simply broken by continuing to mix


further. That is why we call it a false set. But if an admixture is present like SNF, it is going to prevent that false set because it inhibits gypsum nucleation and does not allow gypsum to nucleate to form as a crystal which leads to the stiffening. Interestingly the form of the  $C_3A$ , we talked briefly about this in the overview of cement chemistry that the compounds that are present in cement, silicates and aluminates are crystalline compounds and they may have different polymorphs. So type of polymorph can also affect the rate at which  $C_3A$  becomes soluble. So cubic  $C_3A$  is less reactive whereas orthogonal  $C_3A$  is much more reactive. So solubility of gypsum increases. That is the other reason, from dihydrate, hemihydrate to anhydrite. So as I said, natural anhydrite has very low solubility.

So  $C_3A$  crystal form affects the rate at which it dissolves. Sulphates availability is determined by the type of gypsum that is present in your system. Now just to take a step backwards, in cement chemistry all the reactions happen because the ingredients of cement start dissolving in the water around and recombining to form the hydrated phases. So obviously the dissolution of the cement compounds is a very important step. So anything that prevents a dissolution will retard, anything that accelerates a dissolution or speeds up the dissolution will accelerate.


So here what is actually happening is, the inherent solubility or reactivity of the material is responsible for its availability in solution to do the reaction. So  $C_3A$  in one form is more reactive than  $C_3A$  in another form.

### Influence of $C_3A$ /Gypsum ratio:

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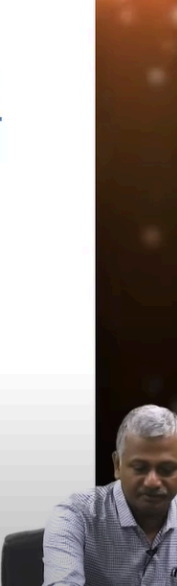
## Influence of $C_3A$ /Gypsum ratio



Reactivity of $C_3A$	Availability of sulfate ion	Setting time	In the presence of SNF?
Low	Low	Normal (2-4 h)	Not much affected
High	High	Normal (1-2 h)	Setting may get delayed slightly; slump loss
High	Low	Quick set (10-45 minutes)	Setting normal; slump loss
High	Nil	Flash set (<10 minutes)	-
Low	High	False set (<10 minutes)	No false set; normal setting

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Based on Mehta and Monteiro, 2003



So if you take a look at this book, Mehta and Montiro, we have this very interesting table which consists of the first three columns. They talk about normal hydration process of cement, they talk about the fact that if  $C_3A$  is present in one form which is more reactive, one form which is less reactive, combined with sulphates that is available very quickly or not at all available or very slowly available, what happens in a normal hydration process? What I have done is, I have introduced a fourth column to see what happens in the presence of a sulphonated naphthalene formaldehyde. So let us take a look at these in close detail.

So here, reactivity of  $C_3A$  is low, that means it is in the cubic form, it becomes available slowly. You have sulphate possibly in the gypsum form, where solubility is a little bit low as compared to anhydrite or hemihydrate. So in this case, you get what is known as a normal set, but the setting time is between 2 to 4 hours. So slightly more, but still it sets in the normal set.

What is the set which is retarded, which is not normal? As per the code, 10 hours is the limit placed on initial setting time, cement should set within 10 hours.

So here, you have 2 to 4 hours, it is still a normal set. When both are high, that means  $C_3A$  is very reactive and sulphate is also available very fast, you get a normal set. But then the normal set here is 1 to 2 hours, it is less than the previous one, because your initial reactions between the sulphate and the aluminate to form sulpho aluminates like ettringite that happens quickly.

So what happens when in such cases, which are seemingly normal for normal concrete, what happens in the presence of SNF? In the first case, SNF does not affect the overall setting time. Why would the setting time not be much affected with the help of SNF, in the presence of SNF?  $C_3A$  is less reactive, so we may not lose the sulphate from the SNF very quickly to the  $C_3A$ . So, the effectiveness of the admixture will be maintained. At the same time, there is sulphate from the gypsum or gypsum sources that could still react with the  $C_3A$  in a normal fashion. So, SNF may not have a major influence there.

But when the  $C_3A$  is highly reactive in the second case, in such a case, the SNF will now start getting attracted to the high reactivity  $C_3A$ . Now in this case, you want to avoid this from happening that is the reason you go for a delayed addition. You add SNF later, so that this reaction can happen first and then the SNF comes into play. So, it is very important to understand your system from the perspective of the cement composition and then realize in what stage you need to have this delayed addition made possible. But more interestingly, when  $C_3A$  is responsible or very highly soluble, but sulphate ion availability is low, what is going to happen? Some of your  $C_3A$  is available to directly react with water. It may form a quick set, but at the same time, your admixture effectiveness is going to go, because it is getting attracted to the highly soluble  $C_3A$  and it is causing some slump loss.



Well, why should the presence of SNF convert it from a quick set to a normal set? Why do I say that setting becomes normal in this case? Because now your sulphate is not combining with the  $C_3A$  very early, just like what is happening in a normal case without the SNF. It is combining with the  $C_3A$  in a manner which is similar to the first case, because the admixture went and adsorbed itself on the  $C_3A$ , it is not available for reaction immediately. So, it is slowly available for reaction. So in other words, the presence of the SNF makes this high into low reactivity and converts into a normal setting time. So, from a quick set, you get a normal set, but you also get slump loss, because your effectiveness of the admixture goes down.

Of course, when  $C_3A$  is high and availability of sulphate is nil, that means no gypsum is added in the system, you get a flash setting. Now, there is no point in analyzing this, because it is not going to happen. We do not really have a system like this in any case. So, there is no need to mix SNF and a system where you know that there is no gypsum added.

Now, what about the other way?  $C_3A$  availability is low or reactivity is low, but sulphate is very highly available, that means you have other forms of sulphate than gypsum. So, as I said there will be a false set, because you have anhydrite and hemihydrate present in your system. As soon as water comes in contact with this gypsum, it starts forming gypsum. You continue to mix, break the set and then what happens is it undergoes normal set. In the presence of SNF, there is no false set. Why? Because you do not get any nucleation of gypsum, formation of gypsum crystals is not going to happen, because SNF will inhibit that. So, what this goes to show is that the cement composition in the way that the  $C_3A$  and  $C_4A$  and  $CaSO_4$  are present in your system, the addition of your charged super plasticizers the polymers that have a surface charge or sulphonated super plasticizers like lignosulphonate or naphthalene sulphonate, they may have an interaction which can change the nature of the initial chemistry. So, you have to look at this carefully. That is the reason why we want to do the compatibility tests in the lab before we start adding the admixture on site to do the concrete. So, it is important to do this to try and understand this.

## Effect of Alkalis:

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# Effect of Alkalies



- Modern cements have higher alkali contents – for early strength
- Soluble alkali (sulphate) content can work positively with SNF – reduce the competitive adsorption of SNF on aluminates; thus, when cement and SNF are incompatible, addition of alkali sulphate is a solution
- However, more alkalis in solution can also lead to acceleration – causing slump loss → competitive effects!

See paper by Grzeszczyk and Kucharska (1988)

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What about alkalis? Generally modern cements have opted for higher alkali contents and this is because we want to accelerate the strength development. In the presence of more alkali it turns out that our  $C_3S$  is able to react faster. We talked about the fact that  $C_3S$  is responsible for early strength development. We already have more  $C_3S$  in the system, if you have a higher alkali content you end up getting higher strengths.

Now, the form of the alkali is very important. If alkali is present in the form of alkali sulphates which are highly soluble, it can work very positively if you have sulphonated chemicals like SNF. Why is this? Because the sulphate from this alkali can be made available even before the gypsum starts dissolving to really interact with the  $C_3A$  to start the hydration process. Otherwise the sulphonate from the super plasticizer which is again highly soluble will start getting available and have a competitive adsorption with the  $C_3A$ .

So, alkali sulphate can be added in instances where you have an incompatible combination. Which one of these is an incompatible combination? First one incompatible? No. Second one? Possibly, because you get slump loss. So, it is incompatible. What about the third one? It is still incompatible, you get slump loss. So, in such cases having a sulphate source that is highly soluble like an alkali sulphate can help. But what happens is alkali is present in the solution and can lead to acceleration and that leads to slump loss. So, there is a competitive effect here. The sulphates from the alkalis are helping, but they alkalis themselves because they accelerate and lead to slump loss. So, you need to evaluate the situation carefully.

Most Indian cements seem to have alkali contents that are fairly on the lower side about 0.5, 0.6 %. How is alkali content represented in cements? As percentage equivalent sodium oxide alkalis in cement are represented as % eq NaO. Why? Because alkalis typically in cement are present in two forms sodium oxide and potassium oxide. We convert potassium oxide content to an equivalent sodium oxide content by taking a ratio of the molecular weights.

Now, as compared to Indian cements, if you go to Europe or the US their ordinary cements have much higher alkali contents somewhere close to even 1%. Why do they do this? Because they want their cement performance in terms of strength at early ages the demand is much more than what our cements actually produce. So, they have higher  $C_3S$ , higher alkali, and higher fineness as compared to Indian cements. So, maybe I have not really done an extensive study of the admixtures available in the European and American markets in terms of the compatibility issues. There the challenge of compatibility could be sometimes greater than what we see here, because our alkali contents are usually smaller.