

Advanced Concrete Technology
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Lecture – 13
Chemical admixtures – Part 1

This chapter is about the chemical admixtures used in construction industry. We will also talk about some issues that may not be there in the textbook which are deriving more from the experience that we have had working with different types of chemical admixtures in our laboratory,.

So, the purpose of this segment is to introduce you to the different types of construction chemicals that are typically used in concrete technology and look at what kind of interactions they have on a micron level, just to try and understand how well they can interact with the cementitious materials and what kind of properties are borne out of that interaction.

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What is a chemical admixture?

- Any chemical additive to the concrete mixture that enhances the properties of concrete in the fresh or hardened state
- Does not typically include paints and protective coatings (for steel or concrete)
- ACI 116R defines the term admixture as “a material other than water, aggregates, hydraulic cement, and fiber reinforcement, used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing”.



The term admixtures is not an English term, it is a concrete technology term and it simply means anything that you add to the mixture, right concrete mixture, so it is a chemical additive that is added to the concrete mixture and enhances the properties of concrete in the fresh or hardened state, so that is the simple definition of a construction chemical or a chemical admixture.

But a larger family of construction chemicals also includes protective coatings and paints which are not covered within the chemical admixtures. So admixture is something which you add integrally to the concrete mixture during the time of mixing, right so that distinction you need to make. If you look at the official ACI; 'American concrete institute' definition from committee 116R; it says that the term admixtures is a material other than water, aggregates, hydraulic cement and fibre reinforcement which is used as an ingredient of concrete or mortar and added to the batch immediately or before or during its mixing, okay, either you added before the mixing or doing the mixing process of the concrete or mortar and that is called an admixture.

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Classification

- Water reducers
- Set-controlling chemicals
- Air entrainers
- Specialty admixtures
 - Viscosity modifiers
 - Corrosion inhibitors
 - Shrinkage reducing admixtures
 - SBR latexes
 - Others

So, what are the different types of chemical admixture that are popularly used? we all know very well that the most popular type of chemical admixture includes water reducers, set controlling chemicals which can affect the initial of final setting time of the concrete and air entraining agents which are used very specifically for resistance to freezing and thawing.

These 3 types are the more commonly used types all around the world but apart from these, there may be other speciality admixtures that are used in very specific circumstances. So it will be mentioned about the different types of speciality admixtures including viscosity modifiers, corrosion inhibitors, shrinkage reducing admixtures, SBR latexes and also some other minor types of speciality admixtures which are very specific purposes.

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Water Reducers

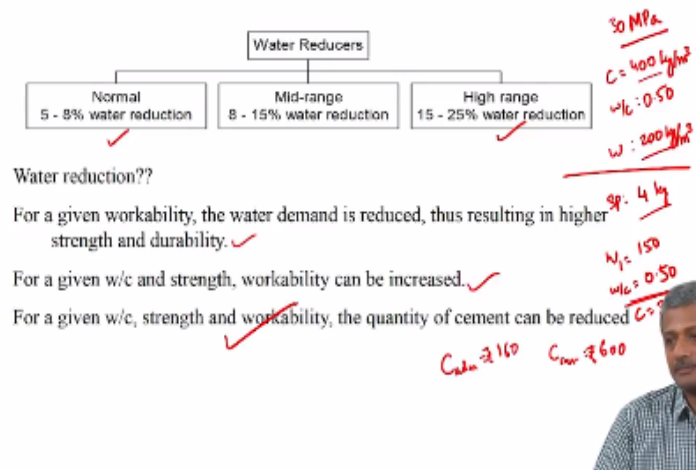
- Normal (plasticizers)
- High-range (Superplasticizers)

They are not added to the concrete all the time, unlike the top 3 which are possibly used all over the world, okay, so let us look at some aspects of water reducing chemicals. Now, water reducers are further classified into 2 types; one is called normal water reducer, the others are high range water reducer. The common terminology in the market for water reducers is plasticizer and for high range water reducers, is super plasticizer given that kind of performance you can actually expect from high range water reducers.

Water reduction means the water required for a certain workability in concrete can be reduced by the use of these chemicals and as a result what happens; the strength and durability will go up because the water to cement ratio is reduced and you can keep the same water cement ratio.

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Broad classification



And then you add the super plasticizer, you are going to increase the flow ability of the concrete or workability of the concrete. So you can use these chemicals in different ways, so for a given workability, the water demand can be reduced and that increases strength and durability, for a given water cement ratio and strength, if you simply add the plasticizer, you increase the workability, so obviously that results in improvement in your construction methodology because you can actually now place a concrete at higher workability, so lesser energy input is actually required to compact and finish the concrete. But a third more important manner in which super plasticizers can help in concrete technology is that since you are reducing water, you can reduce also an equal amount of cement and achieve the same level of workability and strength that you are setting out to originally.

Let us say, we have a 30 MPA concrete, in the field generally, it is around 400 kg is used and to have a slump of 100 to 150mm, around 0.5 water cement ratio can be used. Around 0.5, means a water content of 200kg/m³. Now let us see we add this super plasticizer, typically the super plasticizers are plasticizers are added in terms of percentage by weight of the cement, and generally the amount that is added varies between 0.5 and 1.5% by weight of the cement. Let us say we use at 1% by weight of cement, so super plasticizers let us say we are using 1% by weight that is 4 kilograms. Keeping the same cement content, water is reduced by using up to 4 kilograms of super plasticizers. Depending upon the type of chemical, the range of water that can be reduced can vary.

As mentioned in the table, for a normal water reducer, you can obtain up to 5 to 8% water reduction, for a high rate water reducer, you can go 15 to 25% water reduction. So at 1% substitution, you can easily attain that 25% water reduction, so let us say we reduce 25% water, so new water content 150kg.

Let us say I want to keep the same water cement ratio. So, now cement content will be 300kg, so now I have 2 mixes assuming that we have the same slump requirement from both, let us say, 100 to 150 millimetres at the time of placing, in the first mix, I had 400kg of cement and 200kg of water and no admixtures. The second makes I have 300kg cement, 150kg of water and 1% by weight of cement as the super plasticizer.

The strength of concrete would not be much different because my water cement ratio is still the same, may be some aspect of the filler effect of cement may reduce, but then I do not know how much of often impact it have on strength which is already at the lower end, like M30 concrete.

So, now what I have done is; I have reduced my cement content by 100 kilograms, I have reduced my water content by 50 kilograms, so the benefits are the cost of this concrete is reducing but will the chemical increase the cost? Let's see. In the first case, I have 400kg cement and in second case I have 300kg cement. So, cement savings is 100kg. With approximate cost of Rs.6/kg of cement, 600 rupees is savings in cement. Now, the admixtures if we use 4 kilograms of and most typically, the kind of admixtures that provide the support 25% water reduction will be available to you nearly at about 40 rupees per kilogram. so cost of admixture is 40×4 that is Rs.160

Cement saving is Rs.600 but the cost of the admixtures is only Rs.160, so economically you have made a sound decision by using this super plasticizer. Environmentally also you made a sound decision because you have reduced cement by 100 implying that your overall CO₂ emissions that you expect from the concrete has also come down because cement production leads to a large proportion of CO₂ emissions around the world.

You must have seen the figures that 6 to 8% of CO₂ emissions around the world are because of cement production. So if you reduce the quantity of cement used in concrete, you already give a very good picture environmentally right but another important environmental benefit is that you are using the less amount of water for this concrete mixture. Now, in today's world you will increasingly realise when you actually go in to practice that water is getting to be a very scarce commodity especially water for concreting purposes.

You know that it is got to be of a quality that is almost equal to drinking water. That level of water is not easily available today, so if you can come up with strategies to reduce the water impact in concrete, those will go a long way in helping us preserve the water resources for the future. So again sustainability is easily achieved when you are talking about super plasticizers because you are reducing cement, you are reducing water and you can maintain the same level of concrete properties. This does not mean that I can do this ad infinitum, for example I cannot reduce 400 to 200 just by the use of a chemical admixture that may not be possible, when I am reducing my cement content by so much, I am totally going to be losing the filler effect. So I may want to add some additional fillers which are of the same fineness of cement and that may also incur some additional cost.

But to some extent, this reduction in cement can be effectively done for concretes, which are made with low grade. You must have seen that even for low grade concrete, people are using 7 to 8 bags of cement for M 20 concrete in the site that is because there are not allowed to use of any admixture, so they need enough water content in the concrete mixer to get workability.

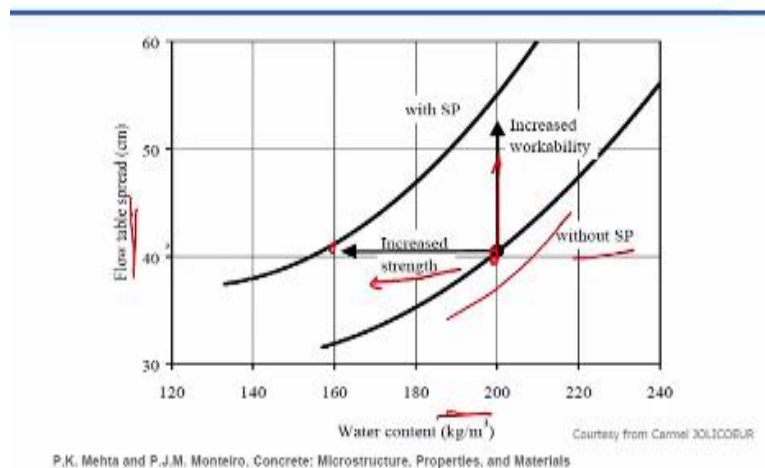
So, instead of water if you have the option of using an admixture, you can then cut down your cement content because effectively, you can work with your concrete with lower water content, so there is distinct benefits of using chemical admixtures. In the past, we used to think the chemical admixtures only necessary for high grade concretes, where we need very low water cement ratios. But today, because of this third characteristic of the water reducers are super plasticizers, we should ensure that chemical admixtures are used in every concrete, not just high grade but also low grade concrete. Of course this does not apply to volume batching, you know

that a lot of concrete in our country is still produced by volume batching. In volume batching, there is no control in the extent of water that you are adding in the system.

So, of course as concrete technologist, we really have to ensure that there should not be any volume batching, we have to engage only in weigh batching to produce our concrete because the weigh batching can control the design of the concrete accurately and help us to get the right amount of proportions of all the ingredients including water. So the days of 1:1:3, 1:2:4 that is in the past, we should not be looking at those at all.

And in fact today, very interestingly, I have also seen that many people have the habit of still putting proportions together after even of a way batching base mixed design has been done. People find out the weights in kg/m^3 and then represent the weights in terms of proportions of cement to find a coarse aggregate. That is not the correct practice because it can easily be misinterpreted as a volume batching.

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So here you see that without the super plasticizer, the curve that is there to attain a given level of flow that means a given level of workability with respect to the water content in the mix is presented. So let us take any particular water content, say 200kg.

Let us say I want to simply increase the flow here, so what I am trying to do is; simply moving up this access, so I am keeping the same water content and I am adding the super plasticizer that leads to a shift in my flow or increase in my flow. Alternatively, I am still at 200 water content, I want to reduce my water to increase my strength and durability, so I add the admixture, I maintain the same flow level to obtain the concrete with lower water cement ratio.

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Normal water reducers

Lignosulphonate salts (Sodium ^{or Ca} salts of sulphonated lignin)

Hydroxycarboxylic acids – Citric, gluconic acid

Carbohydrates – Corn syrup, dextrin

The dosage of normal WRs is 0.3 – 0.5 % by weight of cement. At higher dosages, there is danger of excessive retardation and bleeding. Also, returns diminish, and excessive air entrainment can occur.

Water soluble polymer

So, there are distinct benefits obviously, we are using super plasticizer and that is simply conveyed by the help of this curve, just to prove this point further. The most chemical admixtures that are used in concrete technology are water soluble polymers.

So, normal water reduces that means, the ones which give you about 5 to 8% may be maximum of up to 10% water reduction are most commonly based on lignosulphonates, these sodium or calcium salts of sulphonated lignin. Lignin is obtained from wood; wood has cellulose fibres which are embedded in a matrix of lignin. You extract the lignin from wood and what type of an industry will lignin be extracted? Paper processing industry actually extract the lignin and it undergoes sulphonation process that produces the formation of calcium or sodium lignosulphonate. That is an excellent water reducing chemical. The other common water reducing chemicals include hydroxycarboxylic acids like citric or gluconic acid.

You can also use carbohydrates, corn syrup, dextrin, even sugar is a good water reducer. Normally these are used at a dosage of about 3.5% by weight of cement, you cannot use too much because when you increase the dosage, there is air entrainment in the system. You will see later that the type of chemicals that we are looking at us as far as water reduces the concern are similar to the class of chemicals called surfactants like your detergents for instance. So, they are going to be increasing the extent of air that entrain in concrete mix. You can also have excessive retardation, if you go too high in the dosage with these chemical admixtures. So you need to ensure that you keep the dosage fixed to between 0.3 and 0.5% because beyond that effectiveness, these admixtures can be reduced significantly.

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High-range water reducers

1st generation: Lignosulphonates at high dosages → *high retardation*

2nd generation:
Polysulphonates

- Sulphonated melamine formaldehyde (SMF) ✓
- Sulphonated naphthalene formaldehyde (SNF) ✓


3rd generation:

- Polycarboxylates
- Polyacrylates
- Monovinyl alcohols

Typical dosage: 0.7 – 1.0% by weight of cement.
Also called 'Superplasticisers'

Handwritten notes:

- 40% WR (next to 3rd generation)
- BASE (next to SMF, SNF)
- Fosroc (next to SMF, SNF)
- Sika (next to SMF, SNF)
- Corz Chem (next to SMF, SNF)
- Dow (next to SMF, SNF)
- Grace (next to Polycarboxylates)
- MC Bauhinia (next to Polyacrylates)
- Whitaker (next to Polyacrylates)
- Mapei (next to Polyacrylates)



High range water reducers; so what people started off with is trying to use the lignosulphonates at high dosages but then they found that this was leading to high retardation and air entrainment and because of that we are not very successful in using high range water reducers in the form of lignosulphonates, so later the second generation admixtures came into being. These were poly sulphonates, the most common one all around the world is the sulphonated naphthalene formaldehyde, especially in India that is a very good admixtures because it works very well in the warm climate that most of India has. Sulphonated naphthalene formaldehyde or sulphonated melamine formaldehyde, again are poly sulphonates and these were the second generation admixtures that probably started coming or becoming popular in around 1970's.

Those of you are interested to attract the history of how super plasticizers were developed or started getting used extensively in concrete also should look at the history of the rise of skyscrapers in the United States and that is principally, where people started developing these chemicals to ensure that they were able to work with higher and higher strengths of concrete. So in the early 70's people were trying to come up with very high strength concretes in those days, very high strength over 40MPa, people were routinely working with 20MPa, 30MPa and for them 40 was a difficult target to achieve.

Because they had to reduce water significantly and could not increase cement to a large extent because that was producing all kinds of negative impacts like cracking, thermal issues and so on. So because of that the research in chemical admixtures really picked up during that late 60's, early 70's period and especially, if you read the history, you will see that many of the skyscrapers that came up in Chicago in the United States that those were amongst the first ones to come up with very high strength concrete to be used in the construction.

So, anyway, if you go through that in more detail, I am sure that there are several sources that will actually give you the information. But later towards the middle 1980's and late 1980's in Japan there was a lot of work being done on self-compacting concrete and that led to the research on even more effective chemical admixtures, effective super plasticizers that led to the development of the third generation, which includes mainly polycarboxylates.

Today, polycarboxylates are most commonly used but you also have poly acrylates or monovinyl alcohols, so these were the third generation admixtures. Today, if you use these you can actually get up to 40% water reduction, that means you can practically turn a zero slump concrete into a flowing concrete that is the extent of impact that the super plasticizers can actually have.

The chemicals that are used as super plasticisers are derived from other industries, so lignosulphonates we talked about derived from the paper manufacturing, the polysulphonates and the polycarboxylates are coming of leather processing industries. So there are several industries which actually have these chemicals that come out as by products in certain other processes but

now, of course chemical admixture manufacturing has directly taken up the polymerisation and production of these polymers directly by construction chemical industries.

There are several large construction chemical industries around the world like BASF , Fosroc, sika, Grace etc. Only few of the companies make the polymer of their own. Other companies actually purchase the polymer from manufacturers and then modify these formulations to produce their own admixtures.

Typically the dosage of these admixtures is at the rate of about 0.7 to 1%. That does not mean that you cannot use above that. You will have to be careful when use very high dosages because again it is just like a drug; you are giving concrete a drug and if you overdose the drug, you are going to cause problems. So, in this case also, if you over dose chemical admixtures, you may end up with problems with the concrete, most probably the problems are going to be dealing with excessive retardation, lack of early strength.

So, what do you think, we should do, if the concrete has been overdose with the admixture? Can we remove the concrete from the place it has been cast? Probably not. What do you do then? Adding the accelerator will be difficult to disperse it in the concrete. External heating to speed up the reaction is one option. This may not be applicable in all sites. Do you just have to wait until the concrete sets and hardens, it will happen eventually you would not completely lose the concrete but it will probably take a little bit longer to set and hardened.

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Water-reducing polymers

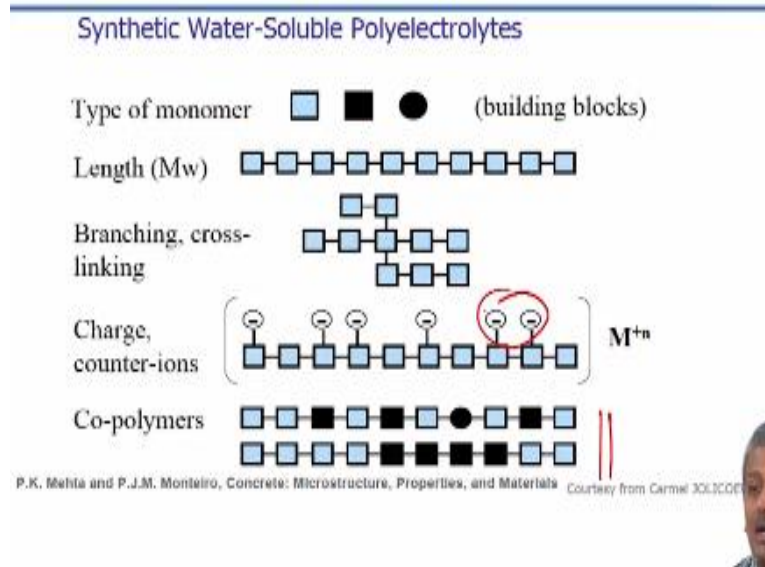
- Lignosulphonates - derived from neutralization, precipitation, and fermentation processes of the waste liquor obtained during production of paper-making pulp from wood
- Poly-naphthalene formaldehyde condensates - produced from naphthalene by oleum or SO_3 sulphonation; subsequent reaction with formaldehyde leads to polymerization and the sulphonic acid is neutralized with sodium hydroxide or lime
- Sulphonated melamine formaldehyde condensates - Manufactured by normal resinification of melamine - formaldehyde
- Poly-carboxylates - free radical mechanism using peroxide initiators is used for polymerization process in these systems

Let us look briefly at where these chemicals are derived from. Lignosulphonates are directly expected or coming from the paper processing industry. The waste liquor obtained during production of paper making pulp from wood that has lot of lignin and that is where we get these lignosulphonates. Then there are reactions where you change the structure of the lignin by sulphonating. Poly naphthalene formaldehyde condensates are produced from naphthalene by oleum or sulphate sulphonation and what you do is react them subsequently with formaldehyde and that leads to polymerisation. You have heard in chemistry about condensation polymerisation, when there are 2 different components, when they are added together they start forming links and longer chains and in the end process, you need to actually neutralise the chemical with either sodium hydroxide or calcium hydroxide that leads to either a calcium bearing polymer or a sodium bearing polymer. You can have sulphonated melamine formaldehyde that is manufactured by resinification of melamine formaldehyde condensates.

Polycarboxylates are little bit more complex but the end of producing polymers that can be suitably modified depending upon the kind of application that you are looking at. So, today many construction chemical manufacturers actually come up with very interesting variants of polycarboxylates, which can which can have another functionality also for example, some of these polycarboxylates can be modified their structure to also be accelerating, some can be retarding, some can actually have an additional component of shrinkage reduction. So lot of

functionalities can actually be given to the kind of polymers that are produced for this polycarboxylates ether based admixtures.

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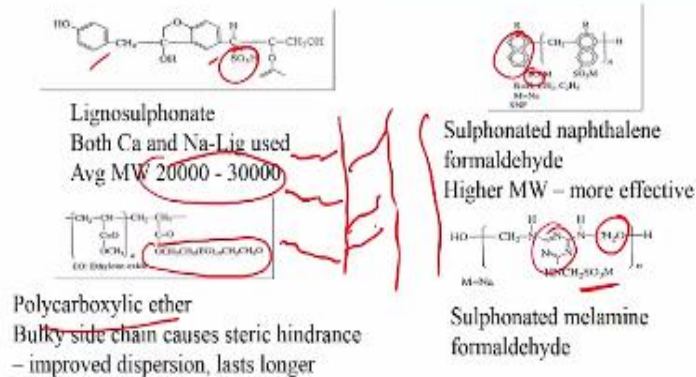


And that essentially, happens because of the polymer structure . Some polymers can be having single monomeric units or it can have an coupled monomeric unit that happens because of condensation. So you form these copolymers and in most cases, all your chemical admixtures are copolymers and in several cases, what happens is; there are counter ions present on the structure of the polymers itself, that leads to some sort of a surface charge that these polymers can have.

And this surface charge only leads to very interesting characteristics to some of the polymers. We will come back to that when we look at how these polymers are actually effective in providing water reduction in concrete.

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Molecular structures



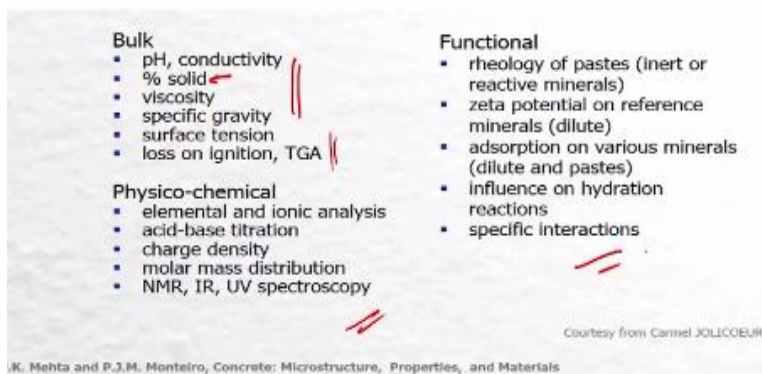
The molecular structure is defining the structure of the monomeric unit. So in lignosulphonates, you see that there are several benzene rings and then you have the sulphonate group which is attached to the long chain and in terms of the molecular weight, the average molecular weight is about 20,000 to 30,000, so higher the molecular weight, the more the effectiveness of the admixture.

In terms of the sulphonated naphthalene formaldehyde you have the basic naphthalene structure and you have the sulphonate attached to a certain position in the naphthalene structure and sulphonated melamine formaldehyde again, has this basic melamine unit and which has been sulphonated and there is also formaldehyde attached in this chain which produces the monomeric unit.

Now, the interesting part about this polycarboxylic ether is that you have a side chain that is extremely bulky. So that means you have a main chain which is long. In all the other polymers, you have a long chain structure for the polymer. But in the polycarboxylic ether and the third generation admixtures, you have very bulky side chains coming from the long chain. So bulky side chains are coming out from the long chain polymers and this bulky side chain is what gives the new generation admixtures are slightly different mechanism of action.

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How are SPs characterized?



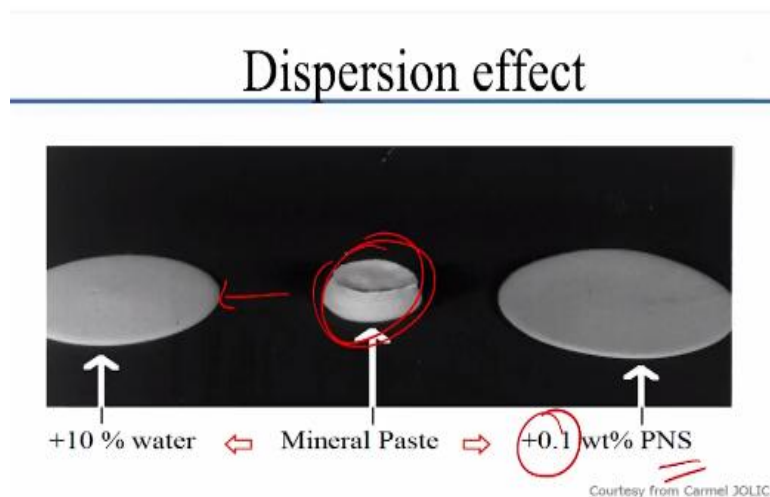
But before that there are several methodologies which are applied to characterise the super plasticizer to try and understand their properties. There are several properties that are important as far as their effectiveness is concerned. The primary ones which civil engineers are most concerned with quality control specialists in concrete manufacturing industries like RMC industries, should essentially at least determine the percentage solids that are there in the admixture. Admixtures are mostly sold as liquid formulations and the solid component is the active ingredient in the admixture, the remaining part is water. So the solids are dispersed in water because they are water soluble and it is an easy way of dispersing them within the concrete.

If you put the solid material into concrete dispersing becomes difficult. So that is why most super plasticizers are sold in terms of liquid formulations. So it is very important to understand what the solids content of the liquid is. How do you determine solids content? Just take it to a temperature more than 105 degree Celsius in most cases that will drive off all the free water that is present and you will get the solid ingredient remaining. So, mostly that what is done and can be easily done in a QC lab because you are routinely checking the moisture of the aggregate, so you can easily do the extent of liquid present in the admixture. Sometimes problem is when you heat to 105°C, some of the polymer structures may also get affected which may change the solid content. So there may be some other methodologies by which you can actually determine solid contents.

So when a new batch of SP comes, we need to ensure that the solids content is maintained at the same level otherwise, we will get a major distinction in the performance. So QC labs on site should do solids content determination for chemical admixtures. There are several other things which we do not do all the time as far as civil engineering is concerned.

But the chemical admixture manufacturers use several different methodologies to actually characterise the type of super plasticizer and their interactions with the cement. So when a super plasticizer is produced, it is not only the chemical structure that is important, how the structure actually interacts with the cement that is also very important characteristic that needs to be addressed carefully.

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The dispersion effect is shown in the picture above. When you have a low workability for example the mineral paste, addition of 10% water is increasing that workability significantly and you get a larger spread but instead of that additional 10% water, if you simply add a small amount of this poly naphthalene sulphonate, we end up getting the same sort of workability as you would have got with additional water. So what is happening in the system causing dispersion? Water is the main ingredient contributing to workability. The more water you have, more workable your concrete will be of course, until the point of segregation. But here why is this water not providing workability? It may be not sufficient or it may be not able to move

around freely to provide flow characteristics to the paste. You need to free up the cement particles, separate the individual cement grains, so that the water can move between them freely to cause a dispersion of your cement paste.

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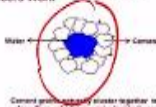
Mechanism of action - old

- Lowering of Zeta Potential (leading to electrostatic repulsion) after surface adsorption
- Substances with functional groups
 - Lignosulfonates
 - Sulfonated condensate of naphthalene formaldehyde
 - Sulfonated condensate of melamine formaldehyde
 - Sugar refined lignosulfonates



Adsorption

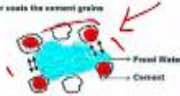
How Conventional Type A Water Reducers Work




flocs

Cement particles clump together in flocs, which may cause trouble later.

1. Water Reducer coats the cement grains
2. Water Reducer imparts negative charges to cement grains
3. Like charges repel cement grains from each other



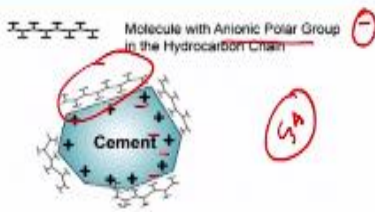
<http://www.carolinapumping.com/education/elementary/admixtures.html>



The old type of super plasticizers like lignosulphonates, the poly naphthalene sulphonates and so on, have their the polymer chain wrapping itself around the cement particle by adsorption and what it does is; after surface adsorption, it lowers what is called the zeta potential. What is this zeta potential? When we produce cement, we do grinding in the final stages of cement manufacture, which leave the material with some surface charge. Certain particles of cement may have a positive charge, certain types may have a negative charge. So what these super plasticizers molecules do; the naphthalene sulphonate or lignosulphonates; is that they go on wrap themselves around the cement particles and end up providing a like charge to all the cement particles, which is negative and these like charges will repel. So cement particles end up repelling each other and spread out into the paste. So, without the super plasticizer, the cement grains, will end up forming what we call as flocs, this is common to all fine powders that will be in suspension in water that they will tend to agglomerate and form flocs. Since they have surface charges; flocs will track the water inside and prevented from moving around freely which causes workability. So, what the adsorption does is that it creates like charges forcing the cement particles to repel each other and causes the water inside to get freed to mingle outside or to flow freely outside that leads to workability of the paste. So that is the mechanism of action of

substances which have functional groups like lignosulphonates, poly naphthalene sulphonates or sugar refined lignosulphonates. So, first process is surface adsorption, second is lowering of the zeta potential that means the charge on the surface becomes more and more negative, and third process is electrostatic repulsion.

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Molecule with Anionic Polar Group in the Hydrocarbon Chain

Cement

The polar chain is adsorbed alongside the cement particle; instead of directing a nonpolar end toward water, in this case the surfactant directs a polar end, lowering the surface tension of the water and making the cement particle hydrophilic.

P.K. Mehta and P.J.M. Monteiro, Concrete: Microstructure, Properties, and Materials

As depicted above, you have the cement grain here which is shown to have a positive charge; some grains of cement may have positive charge, for example, the aluminates and so on those are known to have a positive charge; whereas the silicates may have a negative charge. These are the polymer chains that are getting adsorbed on the cement particle and the polymer chains which have the anionic polar group end up giving the negative charge to the cement particles.

So, essentially the polar chain is adsorbed alongside the cement particles instead of directing nonpolar end towards water. In this case the surfactant is the polar end, which are directing the polar end towards water reduces surface tension, that means the water becomes more easily flowable and the cement particles become hydrophilic as a result of this polar chain getting oriented towards water.

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Surface Adsorption

- Negative charges on surface of fine powders
- Surface adsorption increases with molecular weight
- Calcium ions promote surface adsorption

So, surface adsorption leads to negative charges on the surface of fine powders. Generally, the higher the molecule weight of the chemical, the higher will be the surface adsorption and generally, if you have calcium bearing salts instead of sodium bearing salts, you get better surface adsorption on the cement particles. So again as an admixture, you are just getting the admixture, you do not know whether it has got calcium salt or sodium salt. But sometimes when the source of the admixture changes, if your performance is changing one of the reasons could be that you have switched to a different chemical which may be a sodium salt or a calcium salt. So as an engineer you do not necessarily have to tell the construction chemical manufacturers, how to formulate their products, they know that well. But when you get a problem in your concrete as a result of the application of the admixture, you should have an idea what may be the cause of this problem.

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Electrostatic Repulsion

- SNF is effective for both positively and negatively charged particles
- Increased effectiveness with polymer charge
- Functional group (-HSO₃) should be in β position in SNF superplasticizer

If you have more and more charge on the polymer, then the effectiveness increases, in other words if you have SNF with a fairly high molecular weight, that means there are more links in the chain. So there will be greater charge on the surface of the polymer, so that will increase the effectiveness with which it provides the electrostatic repulsion and it is interesting that when you actually come back to the structure of this polymer, this sulphonated naphthalene formaldehyde structure; the sulphonate group if its present in a particular location; the beta position on the naphthalene ring, it leads to a higher degree of effectiveness in the super plasticizer. So this is a strategy used by construction chemical manufacturers to come up with more effective chemicals to ensure that the dispersion reproduce in cement paste is optimal.

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Inhibition of Reactive Sites

- Some low molecular wt organic materials cover reactive sites and inhibit reactions
- Examples: Starch, Glucose ← *lignosulphonate*
- With SNF, reactive sites may be inhibited by low molecular wt fractions, dimers and trimers
- This leads to excessive retardation
- Remove dimers and trimers from SNF *Centrifuging*



The problem is that when you are adsorbing the chemical on the cement particle, there is a possibility that you may also block some reactive sites and prevent the reaction of cement from happening fast enough. So some low molecular weight organic materials are responsible for doing that; they cover the reactive sites and inhibit the reactions. These low molecular weight ingredients which may be present in your admixture includes starch and glucose, or sugar.

So when the reactions are inhibited, the setting time will go up or retardation will happen. With sulphonated naphthalene formaldehyde, your reactive sites may be inhibited by low molecular weight fractions like dimers and trimers. Dimers means polymer with 2 monomeric units, trimer is 3 units, which may go on block the sites on the cement grain that are reactive and inhibit the chemical reactions that is going to lead to retardation.

So, what you need to do is; modify your process in such a way that it can remove the low molecular weight materials. This can be done by centrifuging, which is the process by which in which you spin the material at a very high speed and when you spin it the higher mass materials will come to one side and the lower mass materials will go to the other side. So this way you can actually extract the ones which have a longer chain length and use those more effectively for providing the best kind of dispersion without causing this inhibition that actually happens with SNF. The starch and glucose is mainly from lignosulphonate. So, sugars can be found in tree extract also, which may lead to this kind of a problem, and you will find later that this very aspect of lignosulphonates and of carbohydrates leads to them being quite effective as retarders also. So as retarders the same family of natural; normal water reducers that we saw earlier, those will also be acting as retarders in concrete.

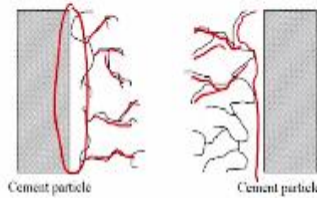
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Mechanism of action - new

- **Steric hindrance along with surface adsorption and repulsion**

- **Polymers with backbone and graft chains**

- Polycarboxylic ether (PCE)
- Carboxylic acrylic acid with acrylic ester
- Cross linked acrylic polymer



Up to 40% water reduction possible!!
Good slump retention



The polycarboxylic ether acid has a very interesting sort of a structure here with very bulky side chain. So again you have surface adsorption; the long chain polymer molecules attach themselves to the surface of the cement, thus orienting their bulky side chain outward. So what is happening now is; after you have the adsorption taking place, the structure of the polymer itself prevents the cement grains from getting together. In other words, flocculation is prevented by the bulkiness of the side chain of the chemical admixture and this process has got steric hindrance.

So, in the older generation admixtures, the repulsion was being caused because of charge. In this case the repulsion is being caused because of steric hindrance; that is the difference between old and new generation. Now, problem with the old generation is the charge will diminish after some time. So the effectiveness of the older generation admixtures in maintaining the slump would be low. Whereas the new generation admixtures tend to maintain slump for a longer time because they don't depend on surface charge, they depend on the availability of bulky side chains in the material. So, the hydrates basically, will start filling up the structure and then your charge will go down in case of old admixtures. When water starts reacting with the cement, your charge will diminish but in case of polycarboxylic ether, the effectiveness of the chemical will last for longer time because you are not relying on the charge.

Other kind of chemicals that will have this type of an action are cross linked acrylic polymers or carboxylic acid with acrylic ester. These chemicals can actually provide you up to 40% water

reduction and fairly good slump retention. You all know about world record for concrete pumping for self-compacting concrete is with Burj Khalifa; 600 metres vertically upwards and we can imagine that the time taken for pumping the concrete up and then applying the concrete on site in a self-compacting form would have been tremendously large and the slump had to be maintained for a long period of time and that was done effectively with the use of polycarboxylic ether based super plasticizer.

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Steric Hindrance

In cement systems:

- PC admixtures act by steric hindrance
- PC admixtures are effective in low w/c ratio
- PC admixtures – no compatibility problems

❖ With SNF steric hindrance is secondary

So, polycarboxylic ether admixture or PC admixtures act by steric hindrance because of which they are effective at low water cement ratios. Especially when you want to produce very high grades of concrete or ultra-high strength concrete, you have to rely on polycarboxylic ether admixture and generally they are not known to have compatibility problem. With sulphonated naphthalene formaldehyde, if you are providing a very high molecular weight chemical, you may still get some steric hindrance but it's secondary. The primary aspect there is the electrostatic repulsion and not the steric hindrance.

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Influence of structural aspects of PCE

Parameter	Structural aspects		
	Relative chain length of backbone 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

The people; because they can play around now with this main chain and side chain of the PCE; have tried to impart a combination of different types of characteristics. So for example if you are in a precast application, you want very high flowability in the beginning, but your slump retention may not be large as the concreting gets done very fast.

On the other hand in a ready mix concrete application, you may not want very high initial workability but you want to maintain that for very long period of time. If you have low dispersibility and short dispersibility retention, you will be ending up with a backbone polymer which is long, the side chain length is short and a large number of side chains will be provided to have low dispersibility and short dispersibility retention. On the other hand, when you want high initial workability, you go with short backbone polymer, long relative side chain length and small number of side chains. If you want to maintain the same slump for a longer period of time, you may still go with shorter backbone length, longer relative side chain length and a large number of side chains to ensure that the polymer does not lose its effectiveness fast enough.

So, this process can be controlled to a large extent by the construction chemical manufacturers to provide formulations that are attuned to a particular job. So if you have precast application verses ready mix application or a long haul application, you can actually alter the structure of the chemical suitably to give you the desired characteristic.

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Types and properties of plasticizers

- a) Unrefined lignosulfonates ✓
- b) Melamine formaldehyde ✓
- c) Naphthalene formaldehyde ✓
- d) Polycarboxylate esters and acrylic copolymers

Now, we will go through some types and properties of super plasticizer. So we will talk first about unrefined lignosulfonates, then melamine formaldehyde, naphthalene and finally the new generation chemicals.

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Unrefined Lignosulfonates

- Wide variation in properties ✓
- Large molecular weight
- Sugar content causes retardation
- May entrain air ✓
- Inconsistent performance ✓

So, unrefined lignosulfonates, are borne from the first generation chemicals and because of that when we use them in high dosages, there is a wide variation in properties. You do not get effectiveness all the time. You may entrain air and get inconsistent performance primarily because of retardation that is caused by the high dosages of lignosulfonates; because of the sugars that are present inside the lignosulfonates. So you can try and do something which will

remove the sugar and to ensure that you always get consistently good performance, you should also keep the polymer chains long enough and you want to reduce the smaller chain lengths.

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Modified Lignosulfonates

- Sugars removed by fermentation
- Low molecular wt matter removed by ultra-centrifuging (less entrained air) ✓
- Modified lignosulfonates used as superplasticers
- Suitable for blending with SNF and PCE admixtures

So, you can use fermentation to remove the sugars to retain the basic polymer structure without any sugar. The smaller molecular weight components that are leading to air entrainment because they are acting as surfactants, can be removed by centrifuging. That may end up giving you modified lignosulfonates which are quite well used as super plasticizers and advantage with these is; they are suitable for blending with sulphonated naphthalene formaldehyde and PCE admixtures. Now, one of the problems that we encounter is that with use of SNF and PCE, you may get a very quick loss of slump especially in very warm climates. To induce some retardation into it, the construction companies typically add some lignosulfonates to prolong the setting time in warm climates.

So, you should have chemicals, that are miscible; only then this can be actually obtained. So lignosulfonates are quite nicely miscible with both SNF and PCE based chemicals. So essentially you are producing a concoction of different types of ingredients trying to get the desired characteristic for a particular application.

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Melamine Formaldehyde

- No slump retention
- Suitable for cold weather
- Suitable for precast concrete
- Unsuitable for ready mix concrete (long hauls)
- Unfavorable costs
- Not widely used in India

Melamine formaldehyde is difficult to use in India except in certain precast industries because it has got absolutely no slump retention in the warm climates. It is suitable only for cold weather. For precast concrete especially, when you have RMC and long hauls, you may not be wanting to work with melamine. The costs especially what you find in India could be highly unfavourable in terms of usage in concrete to a large extent.

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Naphthalene Formaldehyde

- Good slump retention
- Can be blended with lignosulfonate
- Suitable for hot tropical climates
- Favourable cost → 30-50/kg

Downside:

- Not compatible with PC admixtures
- Problems in concretes with low w/c ratios

Incompatibility

But naphthalene formaldehyde on the other hand, even in warm conditions it works quite well in terms of good slump retention. It can be blended with lignosulfonate to increase the setting time and the cost is also quite favourable. Typically, you will find that these are available at about 30

to 50 rupees per kg. Lignosulfonates will be much cheaper but generally, you will find that SNF is available probably around 30 to 50 rupees per kg.

The downside is; you cannot mix them with PCE admixtures. You want to keep mixing admixtures because PCE admixtures are expensive and so you want to bring down that cost a little bit by putting something cheaper inside which can still be effective. Unfortunately with SNF and PCE, there is no compatibility. Main issue with SNF is the problem in concrete with low water to cement ratios.

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Superplasticizers based on graft chain copolymers

- Works in low w/c ratio systems
- Good slump retention
- No compatibility problems
- Dilution with modified lignosulfonate is possible
- Cannot be diluted with naphthalene formaldehyde
- Limited experience
- Expensive

PCE based or those plasticizers that are based on these graft chain copolymers, they work quite well in low water cement ratio systems, they have good slump retention, they may not have any compatibility issues and dilution with lignosulfonate is possible but not with naphthalene formaldehyde. These are expensive of course, the experience is no longer limited people have been using these for nearly 20 years now and especially in the last 10 years, the usage has gone up by leaps and bounds.