Admixtures And Special Concretes

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Lecture

Chemical Admixtures: Water reducers - Part 1

Normal Water Reducers:

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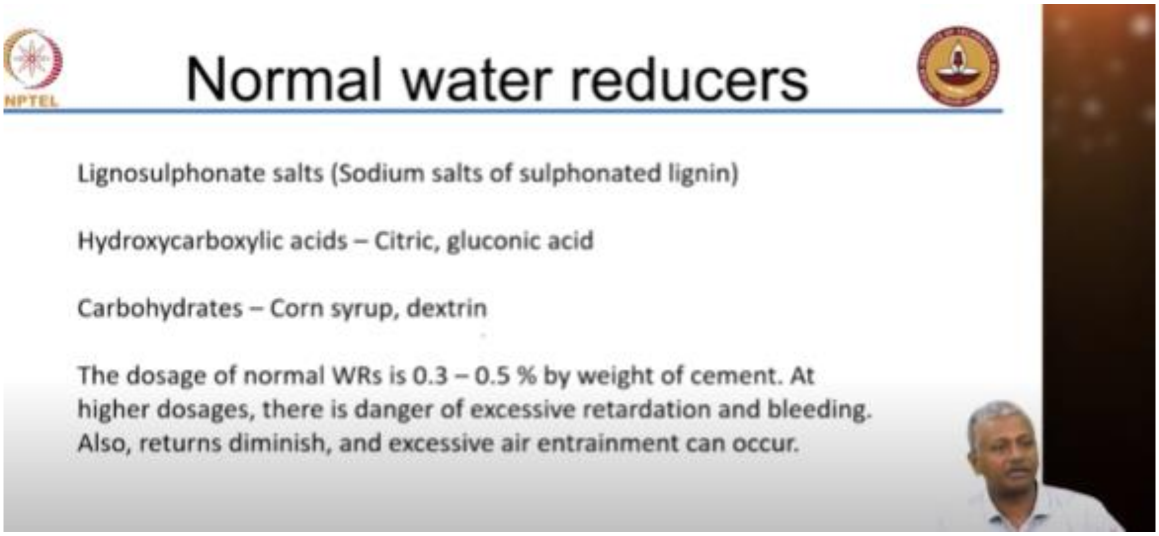

Normal water reducers

Lignosulphonate salts (Sodium 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.

Now what are these chemicals and where do we get these from?

As I said, most of the chemicals that we used in the past in the early generation usage of chemical admixtures or super plasticizers were all based on technologies or chemicals that were derived from other processing facilities. For instance lignin based chemicals, lignosulphonates. Where is lignin obtained from? From wood right, lignin is obtained from wood and we use wood for processing paper. From paper industries you get lignin, lignin itself is not water soluble so you have to make it sulphonated to make it water soluble. So sodium salts of sulphonated lignin or sometimes even calcium salts could be used as water reducing chemicals.

Typical hydroxycarboxylic acids like citric acid or gluconic acid which may be found in several of your day to day usage ingredients like sugar for instance or even lime, all of these can also lead to water reduction.

Corn syrup, dextrin; these are all sugar containing compounds and sugar is a very effective water reducer. It also turns out that many of these chemicals are also effective retarders, they also retard the setting of your concrete significantly and the reason for that will become apparent when we start looking at the mechanism of action of these water reducers.

Typically we use about 0.3 to 0.5 % of these chemicals by weight of cement. So if you have 100 kg of cement you use 300 to 500 g of the chemicals. So you can imagine we are using very little quantities to produce the effect that we want but nevertheless normal water reducers are only capable of giving you up to about 8 % water reduction. So they are not really producing concrete that is either extremely workable or extremely low in terms of its water content.

Now the problem with excessive usage of this kind of a chemical is that it may lead to excessive retardation and bleeding and also air entrainment. Now please remember many of these water soluble polymers are like surfactants like a detergent that you add in water. If you mix the water after adding detergent what happens you produce air. Same kind of thing can happen with the water reducing chemicals also because they lower surface tension of the water and it promotes the formation of bubbles. So if you overdose just like medical overdose, overdose of chemical admixtures in concrete is not good.

HRWR:

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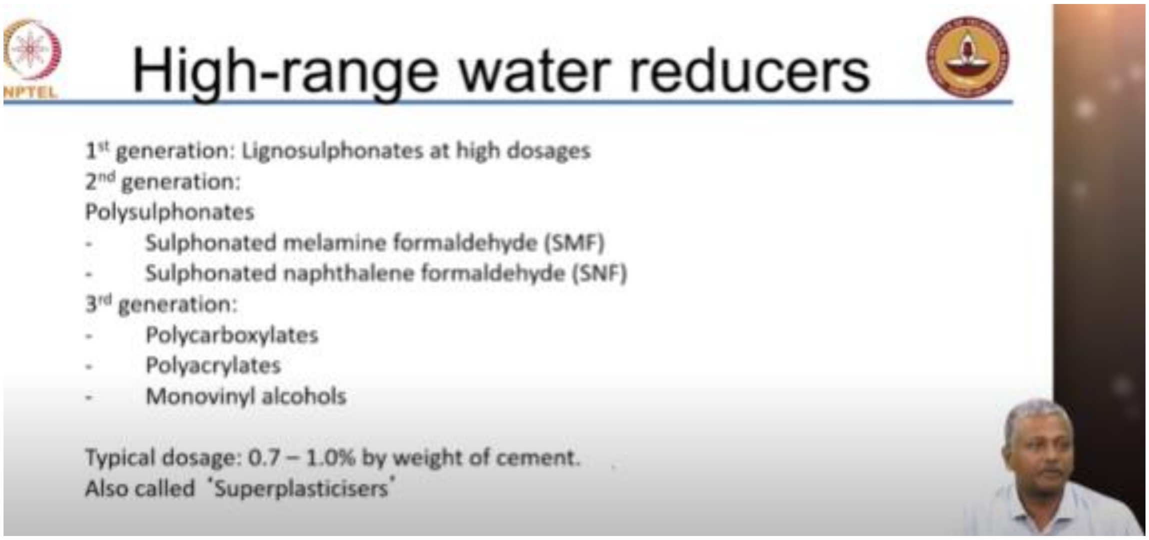

High-range water reducers

1st generation: Lignosulphonates at high dosages
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"

Now high range water reducing chemicals again people started obviously first experimenting with the normal water reducers and tried to use them at high dosages but they soon found out that these were not working. They produced retardation, they produced excessive air entrainment. Obviously when you entrain air it leads to drop in strength. More air in your system means less strength.

So second generation compounds again came through by accident. As I said polysulphonates, they were trying to experiment with these for dispersing carbon black and these kinds of chemicals again were from alternative industries. So these polysulphonates were initially from the leather industry. These are all used in tanning leather. These chemicals are used for tanning leather and that is where they were derived from initially.

Then of course we learnt to modify the molecule and make it more suitable for usage as a chemical admixture for concrete. So sulfonated melamine formaldehyde and sulfonated naphthalene formaldehyde came into being as the primary source of water reducers, high range water reducers for a long time. In fact even today if you look in the market sulfonated naphthalene formaldehyde is most commonly available in most markets because it is quite inexpensive, relatively inexpensive as compared to your other new generation chemicals that we talk about later. But even today you get a significantly large number of products which are manufactured with this technology of sulfonated naphthalene formaldehyde.

Then we come to the later generation which became quite interesting and popular after the advent of flowable concrete like self-compacting concrete. Here people started again polycarboxylates, these also were from other industries like the leather industry. Now when we start looking at polymer structures you will see that people could now understand how to manipulate this molecule best to get the most effective performance. So that is when they started really concentrating a lot more on specific additives for the purposes of construction chemicals. Now generally superplasticizers are used at higher doses generally because the kind of water reduction that we demand from these admixtures is much more than what we get with conventional water reducers. But if you want the same level of performance you can obviously work with much lesser dosages of these chemicals. But then since we wanted performance which is much greater than for water reducers we have to work with greater dosages. And of course they are also called superplasticizers as a result of their extremely high level of performance.

Process of production:

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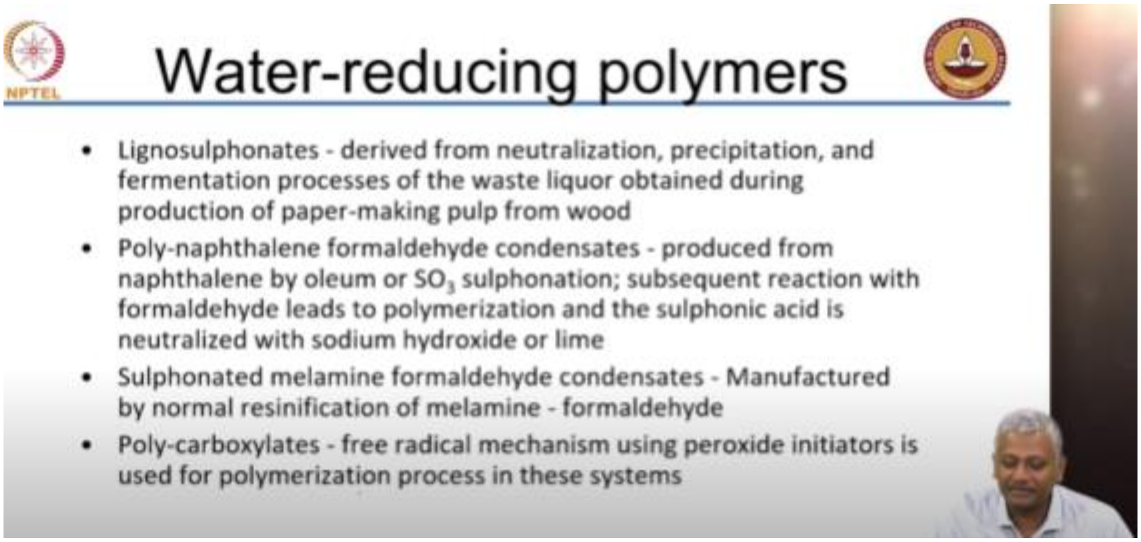

Water-reducing polymers

- 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

Lignosulphonates as I said, you are getting the lignite from the wood. It is basically the waste liquor that is obtained during the paper manufacturing process. Paper is basically you extract the cellulose out of the wood so lignin remains and you are leading to neutralization, precipitation, fermentation processes that lead to the ultimate production of lignosulphonate based chemicals.

Polynaphthalene formaldehyde condensates either melamine formaldehyde or naphthalene formaldehyde. Both have separate processes of manufacture. So naphthalene sulphoanates again as I said are obtained from leather industries and so on. So here the sulphonation leads to a charge on the naphthalene polymer structure and you subsequently react this with formaldehyde to lead to a polymerization reaction that produces long chains of these naphthalene sulfonates. So they cannot combine with each other but when you put formaldehyde inside you start concatenating the naphthalene sulfphonates and forming these long chains of polymers.

Often in the last procedure, in the last process of your admixture manufacture at least the older generation admixtures like lignosulphonates or naphthalene formaldehyde the last step involved neutralization with either sodium hydroxide or lime, because many a times you produce acidic materials so you neutralize with a base to make it more neutral. As a result most of the salts that you got are sodium salts or calcium salts.

Either lignosulphonate or naphthalene sulphonate you will get a sodium salt or a calcium salt depending upon the type of base that has been used to do the neutralization. In the case of malamine formaldehyde it is produced from normal resinification of malamine formaldehyde. Resinification means polymerization. You have malamine which is made to join together with the help of formaldehyde. Now the problem with formaldehyde is that it is a hazardous chemical. So when you polymerize naphthalene or melamine to make these structures you need to ensure that not too much free formaldehyde is left over in your chemical, otherwise it would not be allowed for use outside of laboratories.

I actually did work for an admixture manufacturer for about 2 and half years after my masters where we had to work with these formulations. It was very interesting to see the process of actual production of these polymers. The temperature and pH control were critical to get the right level of chain lengths and we will talk a little later about why these chain lengths are important from the point of view of effectiveness of the polymer. Now polycarboxylates are a little bit more complicated; they have a free radical mechanism using peroxide initiators and that is what initiates the polymerization which gets these vinyl monomers together to make the polymer structure.

Lignosulphontes:

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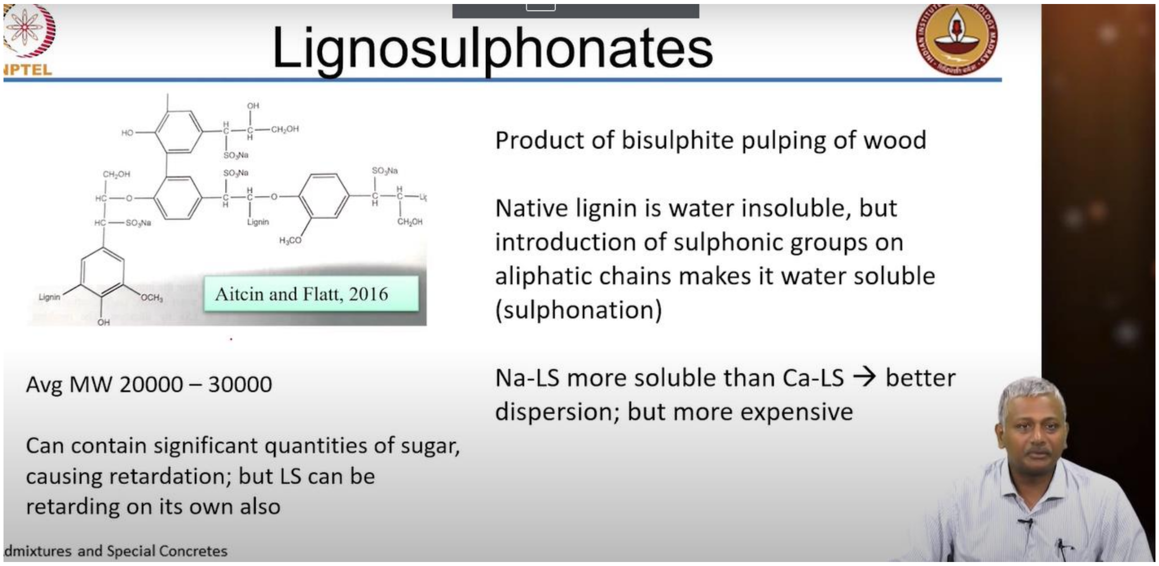

Lignosulphonates

Aitcin and Flatt, 2016

Product of bisulphite pulping of wood

Native lignin is water insoluble, but introduction of sulphonic groups on aliphatic chains makes it water soluble (sulphonation)

Avg MW 20000 – 30000

Na-LS more soluble than Ca-LS → better dispersion; but more expensive

Can contain significant quantities of sugar, causing retardation; but LS can be retarding on its own also

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So this is the structure of lignosulphonate so you can see it is fairly complicated but you can break it down into your sulphonate group which is SO_3Na sodium sulphonate and lignin. Lignosulphonate is a high molecular weight chemical so average molecular weight is about 20,000 to 30,000 g/mol. Of course the way that you do your polymerization will determine the molecular weight, the time, the temperature and the pH will determine the extent to which your chains become longer or shorter. One problem with these chemicals is that they may contain significant quantities of sugar.

Now sugar is an ingredient that causes retardation it also adds to water reduction but it can cause significant bit of retardation. Lignosulphonate can on its own also lead to retardation.

So as I said lignin is water insoluble but when you start introducing these sulphonic groups either calcium sulphonate or sodium sulphonate you make the lignin soluble or lignosulphonate becomes soluble. It turns out that sodium lignosulphonate is more soluble than calcium lignosulphonate. Which means what? It means that it will increase the effectiveness of the chemical but the problem there is it is more expensive as compared to calcium lignosulphonate. So depending upon the processes, availability of raw materials you may choose one over the other.

An interesting thing about this is because sugars are present and these kinds of chemicals also attract bacteria. So when you store these for a long time in drums and if you notice the drums from outside you will find after a long period of storage in the heat, these drums start bulging because the bacterial action on these sugars leads to the generation of gas and that gas starts bulging the drums. So very often in the formulations of these chemicals we also add what is called a biocide, something that can stop the growth of bacteria in the system.

Polynaphthalene sulphonates:

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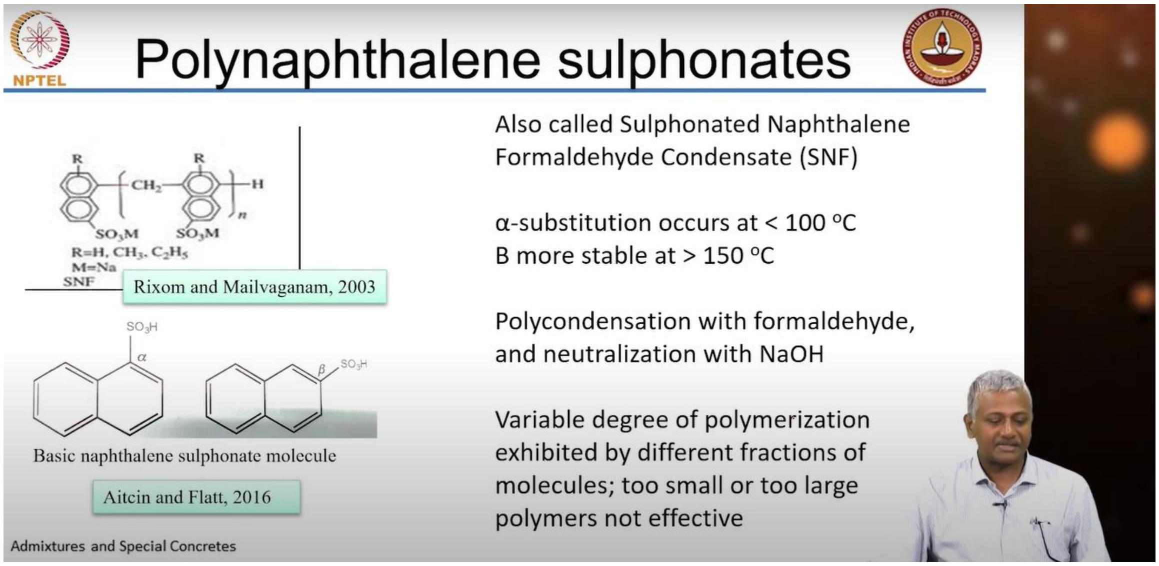

Polynaphthalene sulphonates

Rixom and Mailvaganam, 2003

Basic naphthalene sulphonate molecule

Aitcin and Flatt, 2016

Also called Sulphonated Naphthalene Formaldehyde Condensate (SNF)

α-substitution occurs at < 100 °C
Β more stable at > 150 °C

Polycondensation with formaldehyde, and neutralization with NaOH

Variable degree of polymerization exhibited by different fractions of molecules; too small or too large polymers not effective

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Polynaphthalene sulphonates again as I said the structure involves the naphthalene compound which is much simpler than that of lignin and then you have the formaldehyde which is helping the joining of these things together. So formaldehyde basically comes between the naphthalene monomers and ensures that there is condensation happening to form this naphthalene sulphonate. Now what happens is depending on where your sulphonation happens at what location (alpha or beta). Depending on where your sulphonation happens the effectiveness of the admixture also changes. So it turns out that when your naphthalene sulphonate has the beta location where sulphonation actually is happening it is much better as a water reducer.

Now how do you get that? Obviously you get that by control of temperatures during the polymerization process. So it turns out that when you take it to temperatures more than 150°C you make the beta location more stable. Alpha substitution is stable at less than 100°C. At higher temperatures the beta substitution is better and that leads to more effective performance of the polymer.

But again if you know this why do not you always produce it like this? Because there is always that balance that you need to give between economy and process and the effectiveness. More temperature obviously means more energy has been spent in actually making the molecule more costly, all that has to be balanced carefully. So as I said polycondensation happens with formaldehyde and because you produce an acidic material you have to neutralize with sodium hydroxide that is why sulphonate chains or sulphonate groups actually get attached to the naphthalene SO_3Na that is the sodium sulphonate group that gets attached.

Polymelamine sulphonates:

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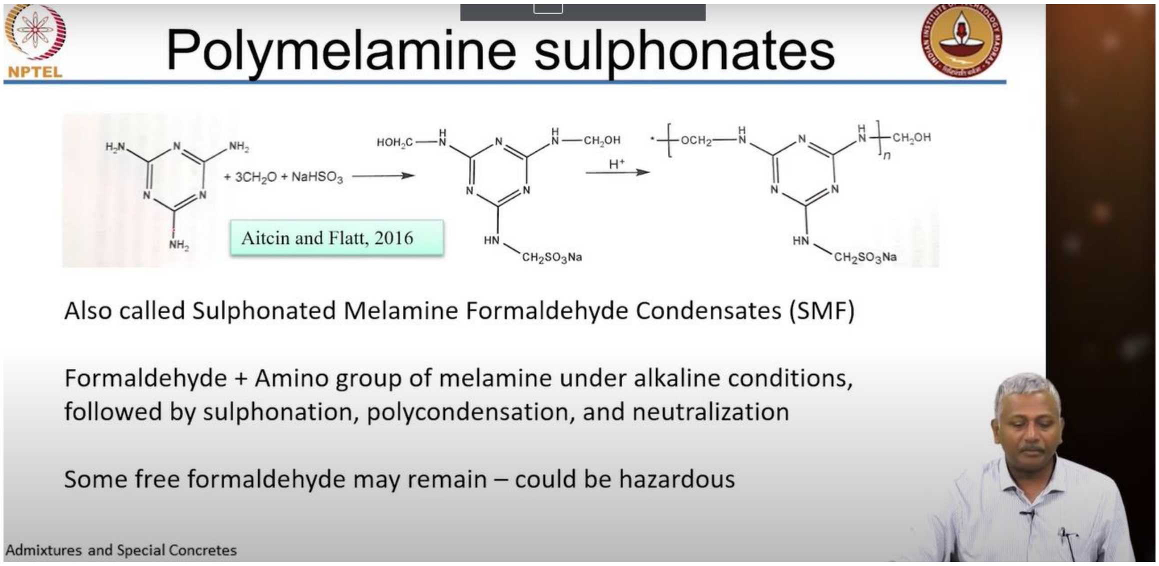

Polymelamine sulphonates

Aitcin and Flatt, 2016

Also called Sulphonated Melamine Formaldehyde Condensates (SMF)

Formaldehyde + Amino group of melamine under alkaline conditions, followed by sulphonation, polycondensation, and neutralization

Some free formaldehyde may remain – could be hazardous

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Polymelamine sulphonates again melamine structure formed by formaldehyde and neutralized with sulphonates to actually form this polymelamine sulphonate structure. So again as I said free formaldehyde may be hazardous so you have to ensure that your process leads to almost a complete utilization of the formaldehyde. If you look at the material safety data sheets that come with chemical admixtures it will tell you about all the hazardous chemicals that are actually present inside and what quantity is present there. So when you handle these chemicals you obviously need to be careful on site.

Vinyl copolymers:

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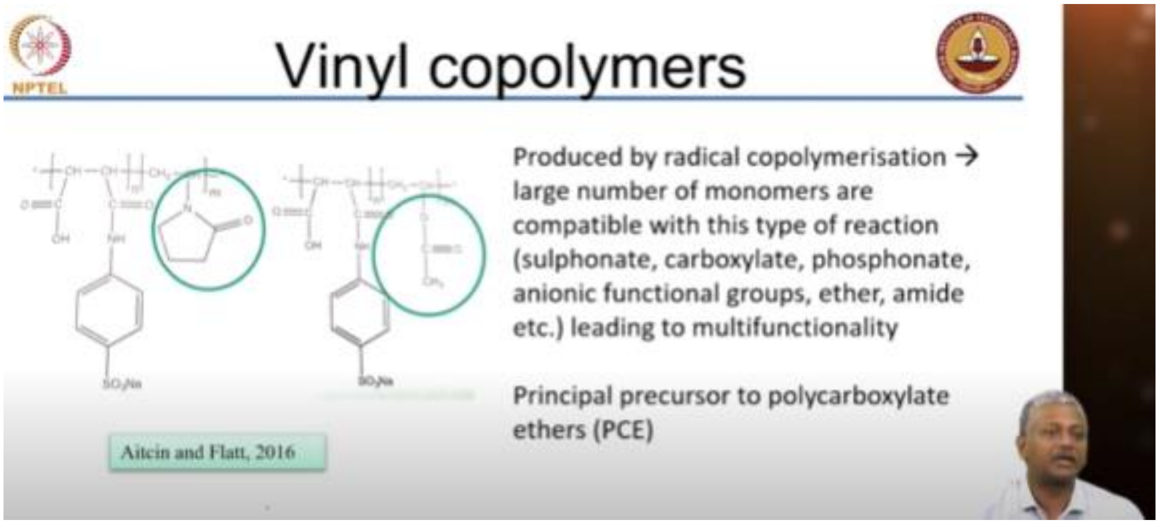

Vinyl copolymers

Produced by radical copolymerisation → large number of monomers are compatible with this type of reaction (sulphonate, carboxylate, phosphonate, anionic functional groups, ether, amide etc.) leading to multifunctionality

Principal precursor to polycarboxylate ethers (PCE)

Aitcin and Flatt, 2016

Now the interest in super plasticizers really picked up after people started using these polycarboxylates and vinyl copolymers. So here as I said the process is a little bit more complex as compared to your lignosulphonates or naphthalene sulphonates it involves radical copolymerization. Now what happens is because of the process and the choice of manufacture of these kinds of molecules it turns out that many different types of monomers are compatible with the type of reaction. So because of this we can actually get polymer chains here which have multiple functionalities. You can get sulphonates, carboxylates, phosphonates, anionic functional groups, ether, and amide and so on. Multifunctionality is the greatest contribution of the polycarboxylates or vinyl copolymers.

Why are we interested in multifunctionality? So if you add one chemical it leads to water reduction, the same chemical can also help in waterproofing, the same chemical may also help in shrinkage reduction. So that is the kind of functionality we can get from vinyl copolymers which you cannot get from naphthalene sulphonates or lignosulphonates. So today the most common term that you hear in the admixture market is PCE, polycarboxylate ethers and that is what is most commonly used today as the super plasticizer as the go to super plasticizer for producing self-compacting concrete and for producing extremely high strength concrete. And today we cannot really live without using PCE for those purposes although there are still examples of use of SNF but we do not use SNF as much as PCE today.

PCE:

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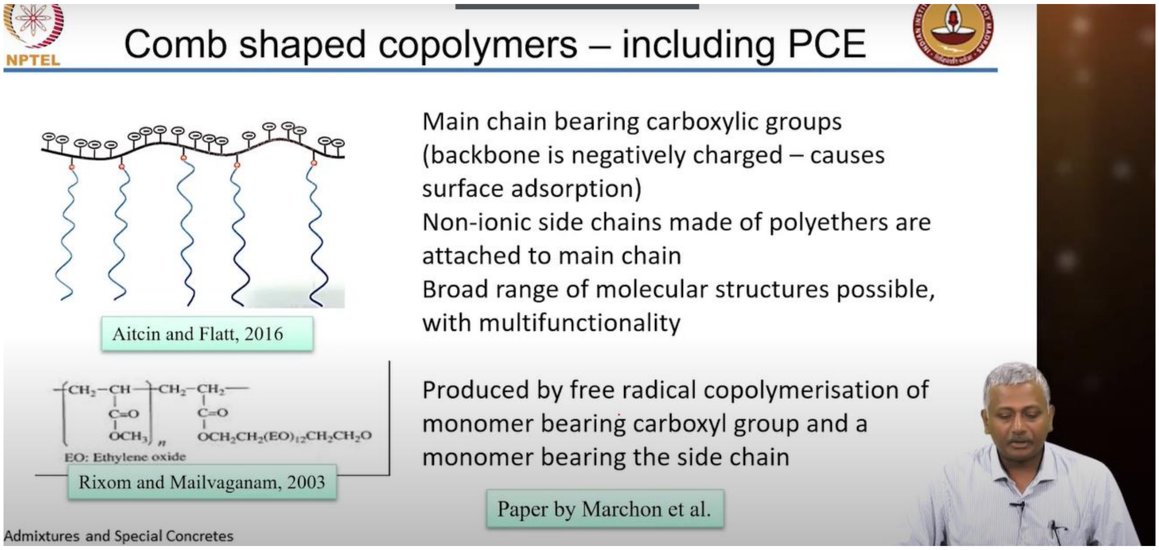

Comb shaped copolymers – including PCE

Main chain bearing carboxylic groups (backbone is negatively charged – causes surface adsorption)

Non-ionic side chains made of polyethers are attached to main chain

Broad range of molecular structures possible, with multifunctionality

Produced by free radical copolymerisation of monomer bearing carboxyl group and a monomer bearing the side chain

Aitcin and Flatt, 2016

$$-\!\left[CH_2-\underset{\underset{\underset{OCH_3}{|}}{C=O}}{\overset{}{CH}}\right]_n\!-CH_2-\underset{\underset{\underset{OCH_2CH_2(EO)_{12}CH_2CH_2O}{|}}{C=O}}{CH_2}-$$

EO: Ethylene oxide

Rixom and Mailvaganam, 2003

Paper by Marchon et al.

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Now this polymer structure was developed further to make these comb shaped polymers, so again you see here there is a main chain and then there are these side chains that come out of this. So you can see the structure here of polycorboxylate which is given, you have the main chain and the side chain itself is quite big and quite bulky. Now when we talk about the mechanism what you will see is these polymer chains go and wrap themselves around the cement particles and these side chains start projecting out. What will happen? The particles of cement will not be able to come together to flocculate, they will not be able to flocculate. So the side chains being bulky helps in non-flocculation and keeps the workability for a very long time and that is the major benefit of using these large side chain materials. So the main chain bearing carboxylic groups causes surface adsorption, it helps to wrap the polymer around the cement. The side chain basically leads to repulsion of the cement particles and causes this repulsion to last for a longer period of time. So again many of these mechanisms are described in one more paper by Marchon.

Dispersion Effect:

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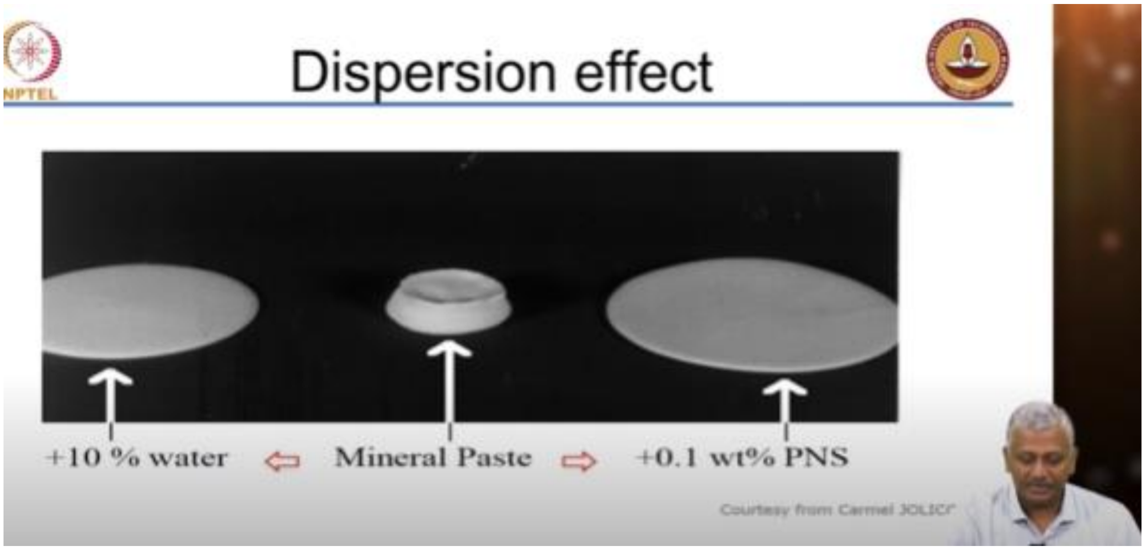

Dispersion effect

+10 % water ⇦ Mineral Paste ⇨ +0.1 wt% PNS

Courtesy from Carmel JOLICr

Now just to revisit the effect of dispersion in a very simple way, if this is a cement paste that is formed with just water and cement, if you add extra water you make it more flowable but you do not add extra water you just add the super plasticizer in this case poly naphthalene sulphonate only about 0.1% can make it more flowable than adding extra water.

Now poly naphthalene sulphonate is also written as SNF, sulphonated naphthalene formaldehyde. So PNS is not always used in India, the more common term is SNF. So in India you will always hear about SNF or PCE. In most of the cases in construction projects people will talk about SNF admixture or PCE admixtures.

Some of the references here are,

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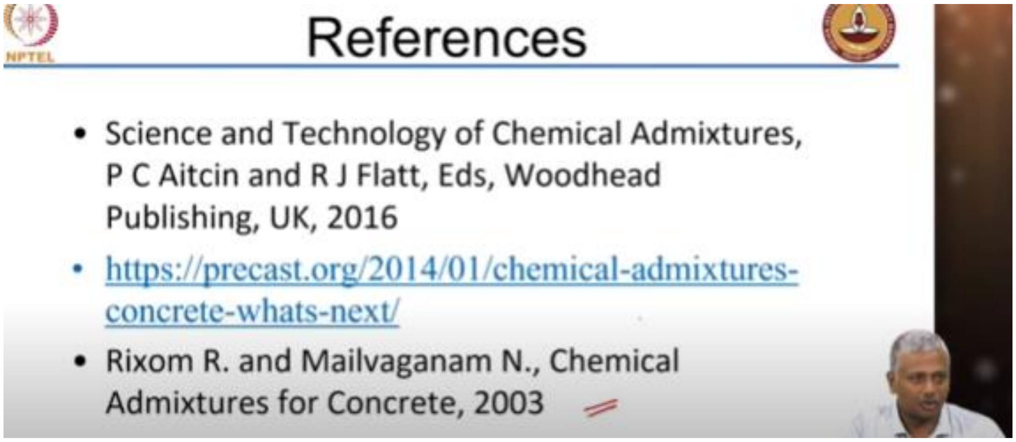

References

- Science and Technology of Chemical Admixtures, P C Aitcin and R J Flatt, Eds, Woodhead Publishing, UK, 2016
- https://precast.org/2014/01/chemical-admixtures-concrete-whats-next/
- Rixom R. and Mailvaganam N., Chemical Admixtures for Concrete, 2003