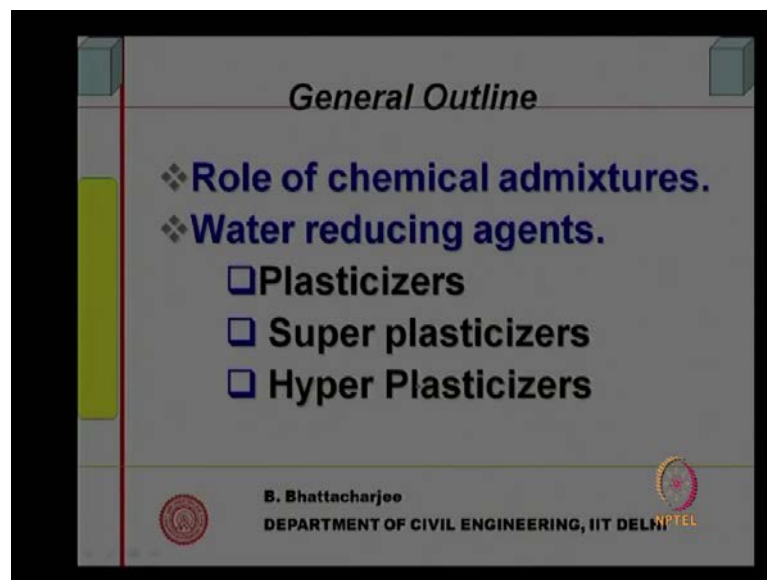


Concrete Technology
Prof. B. Bhattacharjee
Department of Civil Engineering
Indian Institute of Technology, Delhi

Lecture - 9
Chemical Admixtures

Welcome to concrete technology – module three, lecture one. In module three, we shall be looking into admixtures in concrete. First lecture – we look into chemical admixtures; and, the second lecture – also, we look into chemical admixtures. And, the subsequent lectures will be on mineral mixtures. Recall the (()) we are talking about concrete being six components, which include cement, water, fine aggregate, coarse aggregate; and, the other two are the two different types of admixtures, that is, chemical admixtures and mineral admixtures. So, these are must in modern engineered concrete. You cannot think of a concrete – a modern engineered concrete, which is without chemical admixtures or mineral admixtures. So, let us look into module three, lecture one.

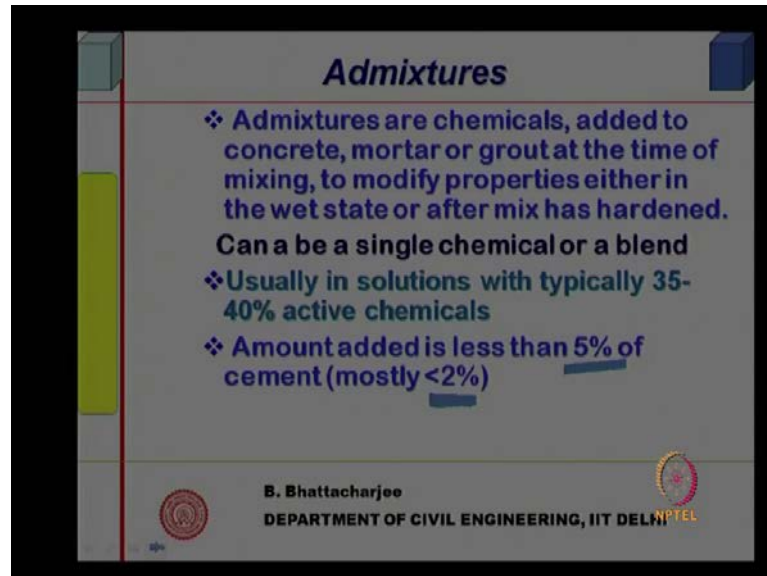
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Our discussion today will follow. First, we look into role of chemical admixtures; and, largely, we will be concentrating ourselves on water reducing agents today, which are called plasticizers, super plasticizers and hyper plasticizers. The nomenclatures of course vary. Some cases, people call them plasticizers, super plasticizers and hyper plasticizers. Some other people call them as water reducing agent, high range water reducing agent

and very high range water reducing agent. So, our discussions would be focused to us that today...

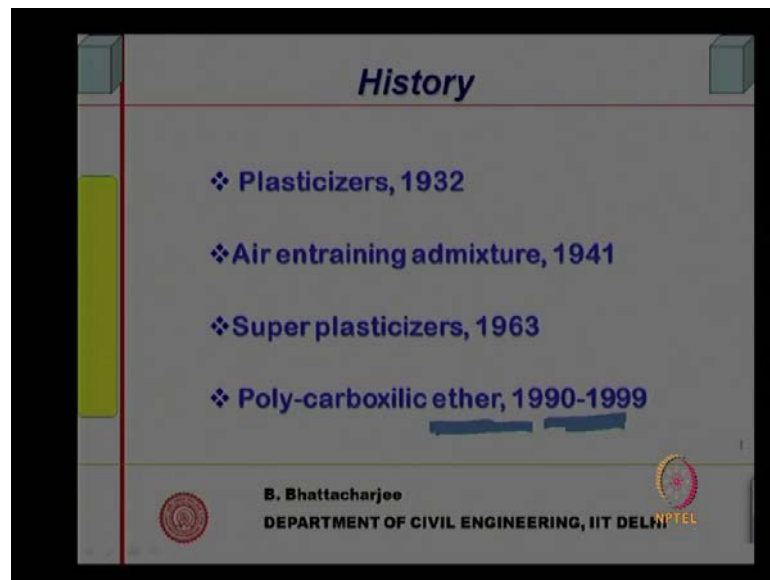
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But, before that, we must look into the definition of admixtures. Admixtures are chemicals, added to concrete during the time of its production; or, it is also added to mortar or grout essentially at the time of mixing, to modify properties either in wet state or after the mix has hardened. So, admixtures are essentially added to the conventional concrete I will say, which are cement, water, fine aggregate, coarse aggregate to modify the property as we desire. Property can be... Properties during the setting stage or infra-state or after it has hardened. Can be a single chemical or number of chemicals.

It can be a single chemical or composition of mixture of number of chemicals. So, generally, in solution form, typically 30 to 35 percent would be solid, active chemicals and rest all are solvent. So, it is a solution form typically 35 to 40 percent except active chemicals; rest all are solvent. And, generally, amount added is very very small. That is why... Amount added is very very small; less than 5 percent; quite often less than 2 percent. So, generally, less than 5 percent; quite often it is less than 2 percent. So, that is why you call them as admixtures.

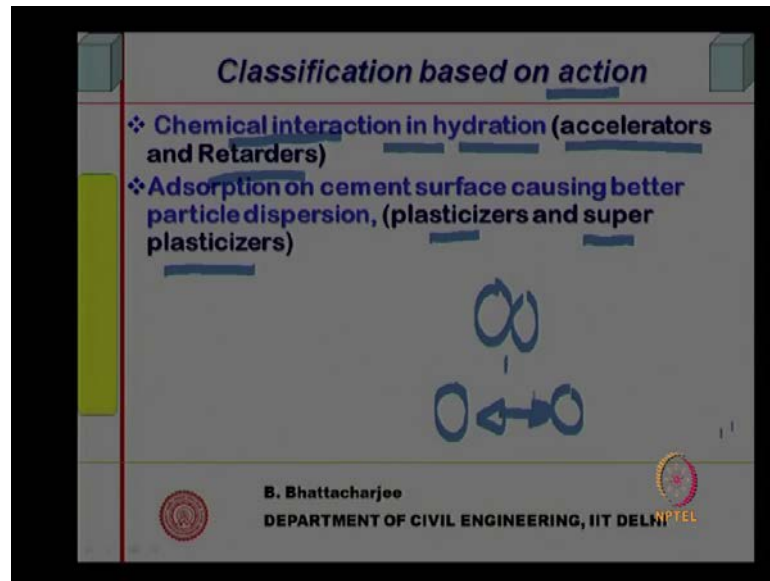
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Now, historically if you see it, the plasticizers or water reducing agents as we shall be seeing them, they came in 1932. And, more effective plasticizers, which are called super plasticizers – they came in 1963. Air entraining agent is an admixture, which is used mostly in cold countries, came in 1940s. And, very high range water reducing agents came in 1980s and 90s. So, plasticizer – 1932; air entraining agent – 1941; super plasticizers – 1963; and, these are very highly effective, high range water reducing agent – poly-carboxylic ether – they came in 1990 to 1999.

Now, although it came quite early, their usage... They were not so popular in the beginning. So, practically, they started becoming popular much later perhaps in 60s, 70s. And, if you see country like India, it is in 1990s in large infrastructure. But, most of the concrete today, manufactured in India or possibly many other developing countries like ours, large quantity of admixtures not used in non-mechanized concrete. So, in India, large quantity of concrete is not mechanized and there hardly any admixture is used. So, that is the history of their use.

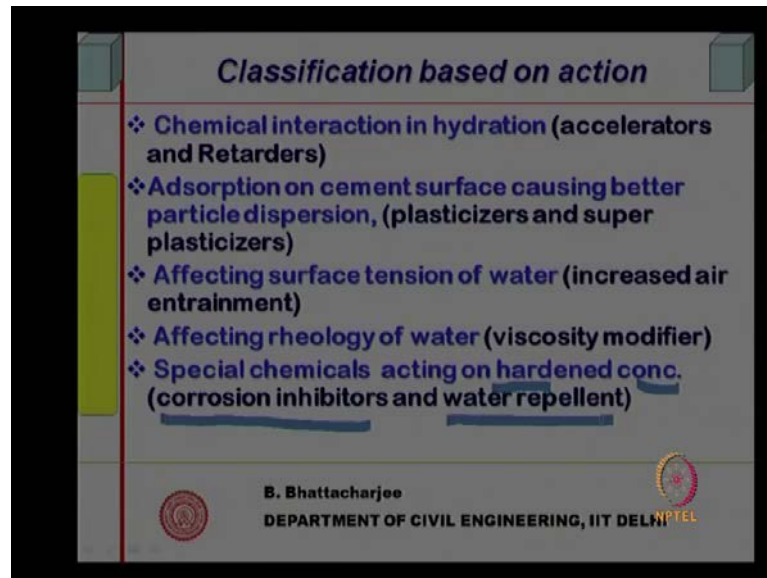
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But, we classify these admixtures depending upon their action. For example, those who chemically interact during the hydration process, their essential purpose would be to accelerate the setting or hardening process or both. And, retarders are the ones, which actually reduce down the pace of hydration. Therefore, retarders retard the setting process. So, retarders and accelerators – they actually interact during the hydration period and they cause either acceleration of the hydration process; some cause retardation of the hydration process.

Plasticizers and super plasticizers I was just mentioning. These are adsorbed – they get adsorbed on the cement surface and they cause better particle dispersion. So, in a way, they are dispersion – particle dispersion – cement particle dispersion causes dispersion of the cement particle; separate them out from one from... If it was the original situation, plasticizer will separate them out. So, that is what particle dispersion center. Second class – they get adsorbed on the surface and disperse the particles. So, plasticizer, super plasticizer, hyper plasticizers – they belong to this group.

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Air entraining agent – essentially, physically, they allow air to be entrained into the concrete. But, their action is – they change the surface tension properties of water. So, they affect the surface tension properties of water, because bubble formation – air bubble formation is dependent on the surface tension properties of the air, I mean liquid, because it is a liquid-air interface. So, surface tension – if you want to make the water to entrap or entrain more air; then, surface tension properties of water has to be modified. And, that is what the air entraining agent does. So, classification based on action is the one that affects the surface tension. Actually, air entraining agent belongs to that category.

Some can affect the rheology of concrete; for example, viscosity modifier. Viscosity modifier affects the rheology of concrete; that is, change the viscosity at the plastic state during the plastic stage; and, largely used in self-compacting concrete or even in underwater concreting, one can use those. They are similar to empty washout admixtures. So, they actually affect the rheology of water – viscosity property of water. They can modify the viscosity of water. In other words, it can thicken the water.

We will look into that when we will discuss in details. Then, there are special chemicals; they act on hardened concrete like corrosion inhibitors and water repellent – corrosion inhibitors, water repellent, etcetera. So, this is the classification based on their action. But, simultaneous classification or simultaneous name is also given side by side. They

can be classified as accelerators, retarders, plasticizers, super plasticizers, then air entraining agent, viscosity modifier, corrosion inhibitors and water repellent. And, based on their action... This classification is actually based on their action. Accelerator and retarder interacts during hydration process.

Plasticizers and super plasticizers actually get adsorbed on to the surface of the particle and cause particle dispersion. Air entraining agent modifies the surface tension properties of the water. Viscosity modifier will modify the viscosity of the water; so, change the rheological properties. Corrosion inhibitors would of course stop the corrosion process, the chemical, electrochemical reactions. Somewhere it will stop either anodically or cathodically. So, this is the classification of admixtures.

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Dispersing admixtures

- ❖ 60% of admixture used are dispersing admixtures, plasticizers, super plasticizer and hyper plasticizers etc.
- ❖ Plasticizer: 12% > Water reduction > 5%
- ❖ Dosage low 0.2-0.6% on cement.

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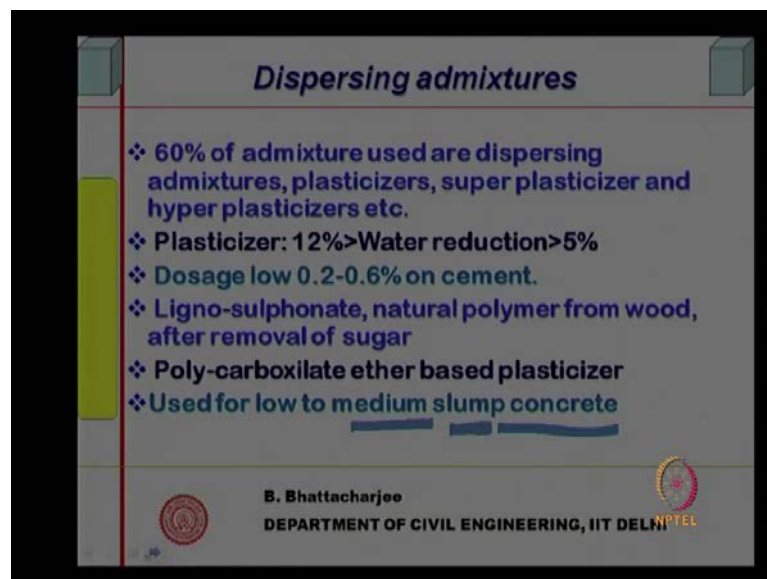
But, first, we will concentrate on dispersing admixtures, that is, the plasticizer, super plasticizer, etcetera. 60 percent of the admixture used worldwide, are dispersing admixtures. The name plasticizer, super plasticizer and hyper plasticizers, etcetera. So, most of the admixtures used in concrete belong to this category, that is, dispersing admixture. So, first one is the plasticizer. As we said, that came pretty early. And, this can reduce actually water; they plasticize the concrete. So, essentially reduce the water – water demand in concrete. You can make it plastic with less water; that is the idea. So, they plasticize the concrete. So, if you add them into the concrete, they will make it more plastic, more flowable. Therefore, for same plasticity, you can reduce the water required.

So, plasticizer – if you add them, they improve the plasticity of concrete; make them more plastic. And, therefore, they are water reducing as well for the same kind of plasticity or cohesiveness or similar sort of... Rather plasticity is the terminology I will use. For same kind of fresh concrete property, they can reduce the water. Therefore, we will call them as water reducing agent as well.

Essentially, nomenclature differs in ASTM classification; largely, they will call them as water reducing agent; whereas, some other nomenclature, they will be called as plasticizer. Now, this plasticizer can reduce water requirement by 12 percent to 5 percent. So, it will be more than 5 percent, less than 12 percent. So, water quantity for same effect – plasticizing effect, it will reduce the water by this amount.

The dosage generally – the amount you add is only 0.2 to 0.6 percent of the cement; or, that is on cement. So, if you have 300 kg of cement, 0.2 percent of that would be 0.6 kg in a meter cube. So, you see 0.2 percent to 0.6 percent. So, it will be about 1.8 kg. 3 kg is 1 percent; 0.3 is 0.1 percent. So, this is 0.2 to 0.6 percent. So, this much you will be adding in 1 meter cube of concrete. You can see that quantity is very very small. This quantity is very very small; this quantity is very (()) So, dosage is low – 0.2 to 0.6 percent.

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Dispersing admixtures

- ❖ 60% of admixture used are dispersing admixtures, plasticizers, super plasticizer and hyper plasticizers etc.
- ❖ Plasticizer: 12% > Water reduction > 5%
- ❖ Dosage low 0.2-0.6% on cement.
- ❖ Ligno-sulphonate, natural polymer from wood, after removal of sugar
- ❖ Poly-carboxylate ether based plasticizer
- ❖ Used for low to medium slump concrete

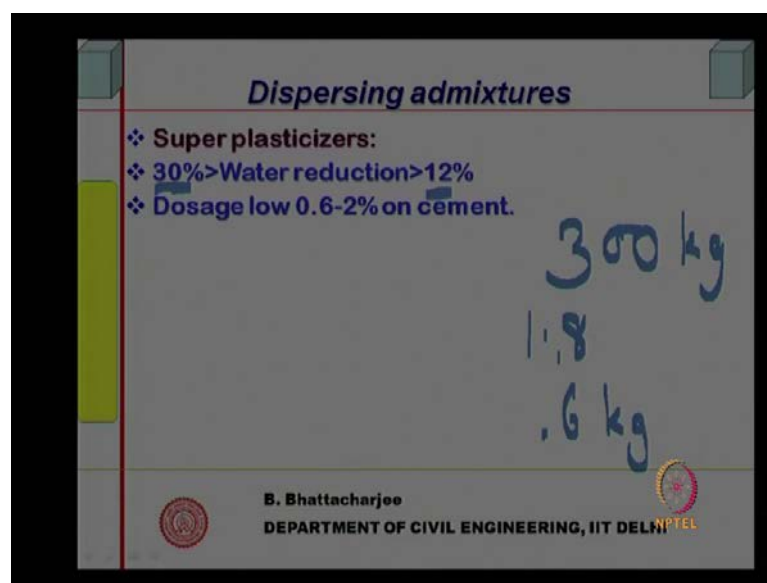
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And, the material that has been used are lingo-sulphonate. Ligno-sulphonates are natural polymer from wood. That is obtained after removal of sugar and carbohydrates – various

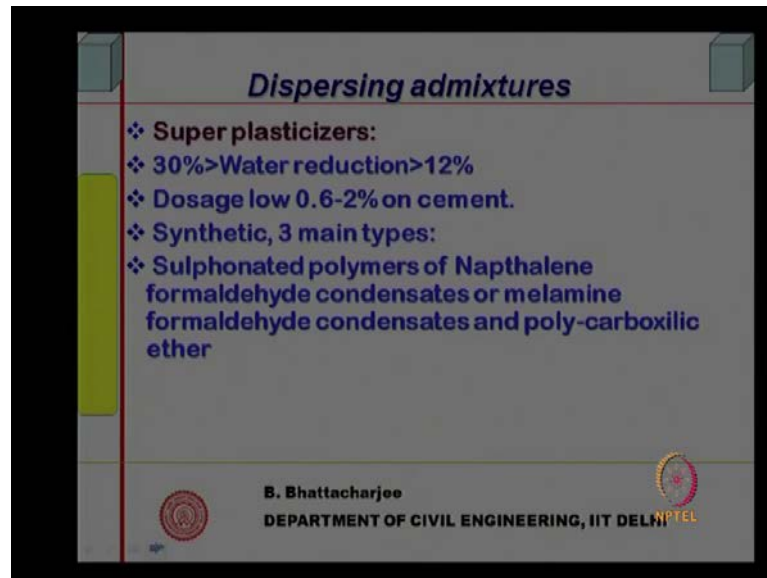
carbohydrates and then sulphonated. We will come to this process anyway a little bit more. So, lingo-sulphonates are the natural polymers; that is obtained from wood; the source is wood. Then, there are others like poly-carboxilate ether based plasticizer. So, there the plasticizer could be either poly-carboxilate or lingo-sulphonate. We will discuss this – the chemistry a little bit more. Their use is usually for low to medium slump concrete. Now, slump is a terminology we have not introduced to you at the moment. It is a terminology related to moldability or working on fresh concrete. So, we will discuss this sometime later on. So, generally useful for low to moderate slump concrete.

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Super plasticizer is the next variety, which reduces the water from 12 percent to about 30 percent. So, 12 percent to about 30 percent reduction; water reduction is 12 percent to 30 percent. And, dosage of course is now higher. So, it can... Cement takes more of it – more of this material; it can absorb, because we said that, they get adsorbed at the surface of the particle, that is, cement particle. And, this... (()) More quantity can be adsorbed in the surface of the cement particle; and, dosage is usually 0.6 to 2 percent of the cement; that means if it was 300 kg of cement earlier; and, maximum you would have added is 1.8 kg of plasticizer. But, super plasticizer – you might (()) from 1.8 to about 6 kg. So, that is, the dosage is generally higher. But, their action is also higher; note that their action is also higher; they are more effective. And, that is why the name. That is why the name super plasticizer; plasticizer, then super plasticizer.

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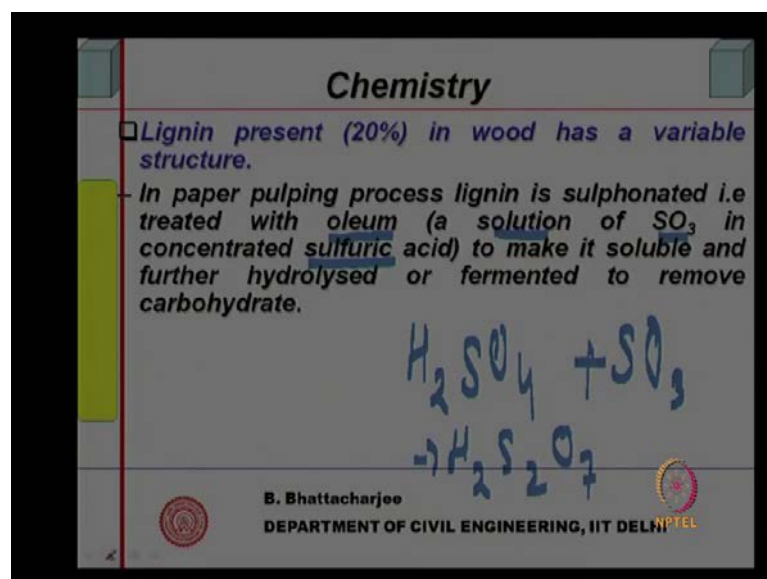
Dispersing admixtures

- ❖ Super plasticizers:
- ❖ 30% > Water reduction > 12%
- ❖ Dosage low 0.6-2% on cement.
- ❖ Synthetic, 3 main types:
- ❖ Sulphonated polymers of Naphthalene formaldehyde condensates or melamine formaldehyde condensates and poly-carboxylic ether

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The hyper plasticizer is also built in this; we have not made separate list here – separate classification. So, super plasticizer or high range water reducing agent and very high range water reducing agent; that is, hyper plasticizers – they are all included here. Now, they are synthetic and three types. First is sulphonated polymers of naphthalene formaldehyde condensates. So, sulphonated polymers of naphthalene formaldehyde condensates or sulphonated polymers of melamine formaldehyde condensates; they are the two varieties; second variety.

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Chemistry

□ Lignin present (20%) in wood has a variable structure.

— In paper pulping process lignin is sulphonated i.e treated with oleum (a solution of SO_3 in concentrated sulfuric acid) to make it soluble and further hydrolysed or fermented to remove carbohydrate.

$$\text{H}_2\text{SO}_4 + \text{SO}_3 \rightarrow \text{H}_2\text{S}_2\text{O}_7$$

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So, sulphonated polymers of naphthalene formaldehyde condensates or melamine formaldehyde condensates. And, third variety is poly-carboxylic ether. So, these are the three varieties of super plasticizer. And, that includes the hyper plasticizer as well. Chemically, they are this kind. If you look at the chemistry of the plasticizers, wood is made up of lignin and cellulose. Now, 20 percent lignin is present in wood; and of course, it has got variable structure depending upon the type of wood, the season it is taken from wood and so on and so forth. So, it has got a variable structure.

And, about 20 percent is present in the wood. Now, paper industries – they make pulp out of the wood. Paper industries make pulp out of the wood. So, in this pulping process, lignin is sulphonated. know, what is sulphonation? This is treated with oleum, which is nothing but a solution of SO_3 in concentrated sulfuric acid. In fact you will write it is as... So, lignin is treated with this. That is called sulphonation.

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Chemistry

- Lignin present (20%) in wood has a variable structure.
- In paper pulping process lignin is sulphonated i.e treated with oleum (a solution of SO_3 in concentrated sulfuric acid) to make it soluble and further hydrolysed or fermented to remove carbohydrate.
- The key part in ligno-sulphonate is phenyl propane units that can link up to form polymer.

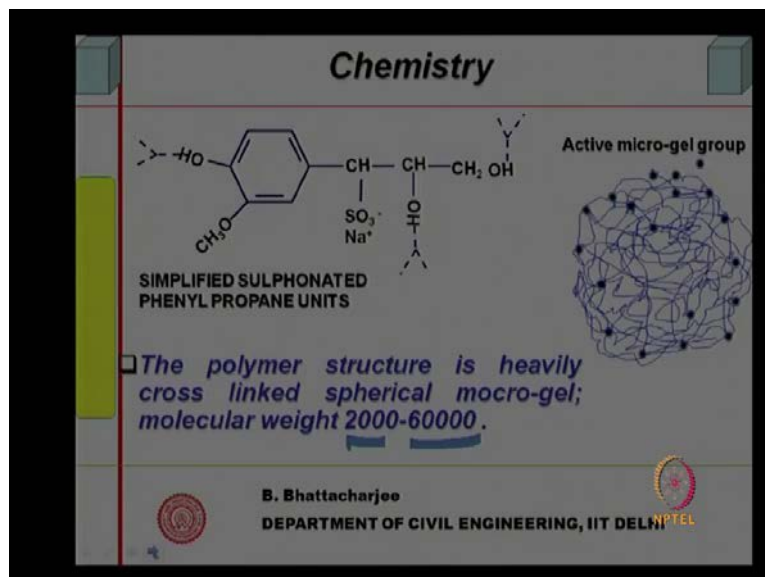
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So, lignin is treated with this; it is sulphonated. That is treated with oleum to make it soluble; and then, it is further hydrolysed or fermented to remove carbohydrate. So, paper – it is actually a product from paper industry. In the pulping process, lignin is sulphonated. It is treated with oleum in the process of sulphonation. And then, further hydrolysed or fermented to remove carbohydrate. The key part in this one is – in ligno-sulphonate of course is phenyl propane units that can link up to form polymer. So, in this

one, chemically phenyl propane is a unit, which can polymer. And, that polymer is a key part, which is responsible for plasticizing effect.

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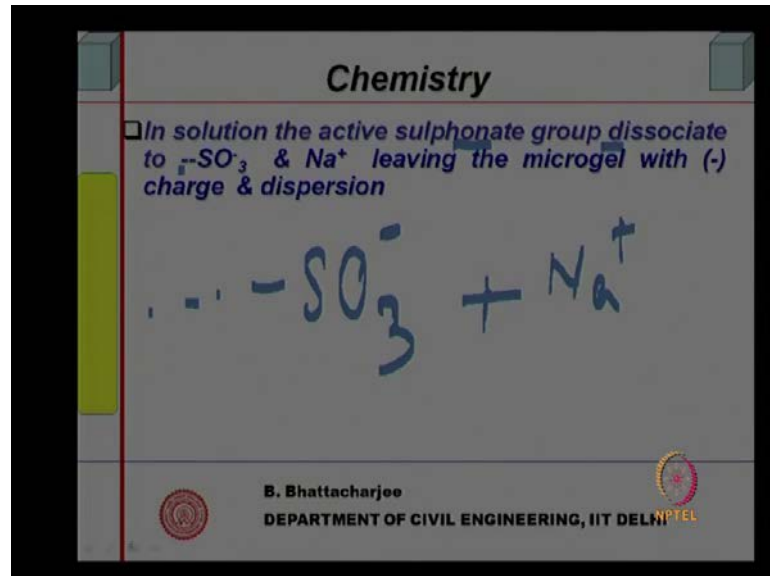
Now, the phenyl propane looks like this. This is phenyl with hydroxyl ion. So, this is phenyl. And, the SO₃⁻ - suphonated SO₃⁻ - that this is sulphonated. This is the simplified sulphonated phenyl propane units. And, it has got sodium - SO₃⁻ with sodium; that is, linked with sodium. You can see this. And, this is the unit; it gets polymerized. So, this is essentially the structure of the phenyl propane unit, which is the chemical, which is responsible for plasticizing effect.

This structure is heavily cross linked. So, the polymer that is found out of this is heavily cross-linked; that means a cross link is... These are the linear chain. For example, there could be a linear another one, another this of molecule and another of this molecule; they will form chains. And, when there are several chains, which are cross-linked in 3-D let us say - 2-D, 3-D; that is cross-linked. So, we say that, cross-linked. Several such chains are connected in between. This is cross-linked. So, the polymer structure is heavily cross-linked. And, they form actually a spherical micro gel like this.

So, active micro gel group. So, it forms a spherical micro gel. It forms a spherical micro gel like this. So, these are the active micro gel groups. And, you can see they are all linked up; cross linked 3-D structure. So, it is almost like a heavily cross linked spherical micro gel. So, that is what this structure forms. And, its molecular weight - of course, if

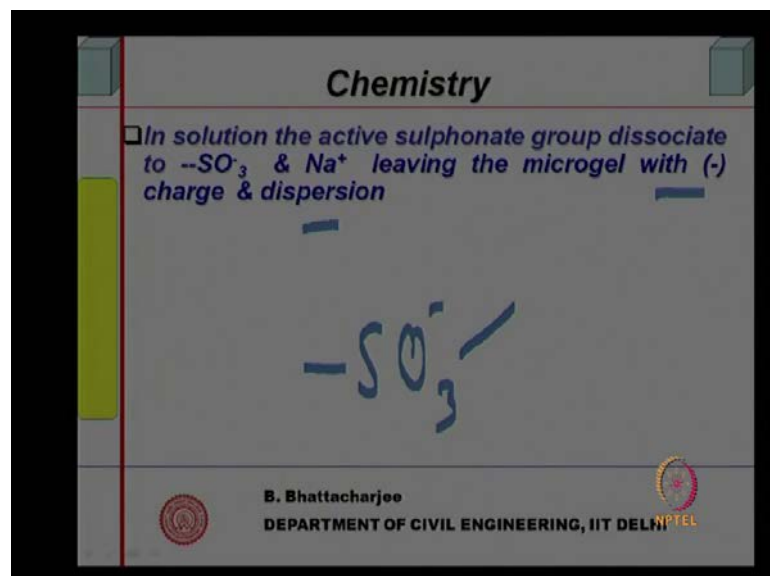
you look at it, it varies from 2000 to 60000; that is the molecular weight in normal carbon 12 scale.

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And, in the solution, what happens is; the active sulphonate group dissociate to SO_3^- . There are something more on this side and SO_3^- , which will be negative plus the sodium. So, sodium plus separates out; sodium ion separates out leaving this portion negatively charged. Therefore, microgel, which is there in the microgel structure of the phenyl propane.

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And, it leaves it with negative charge. Now, this negatively charged molecule with each other... If they are all negatively charged molecule, they will push the particle apart. So, that is how the whole idea. The mechanism of course we will understand better. So, it is the negative charge. This negative charge ensure its attachment to the cement particle as well, because SO_3^- – sodium dissociate leaves with SO_3^- and negative charge. This can get attached to the cement particle and induce a kind of negative charge on to the cement particle itself and thereby cause dispersion. So, we will look into this slightly more in detail as we follow through.

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Chemistry

- In solution the active sulphonate group dissociate to $-\text{SO}_3^-$ & Na^+ leaving the microgel with (-) charge & dispersion
- Sulphonated naphthalene formaldehyde condensates (SNF) or poly naphthalene sulphonate (PNS) is obtained by sulphonating petroleum or coal tar naphthalene at high temperature.
- The product is polymerized with formaldehyde and neutralized with Na, Ca salts. Molecular weight is 500-2500.

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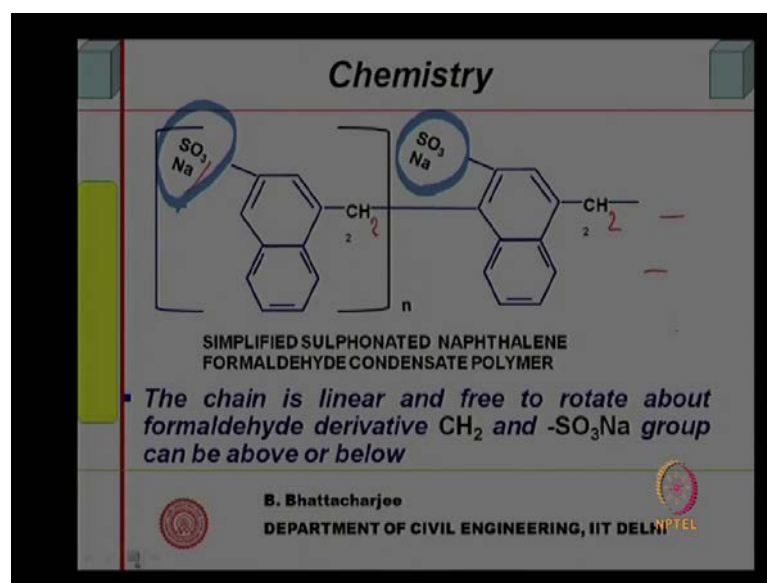
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The second one is super plasticizer, which is sulphonated naphthalene formaldehyde condensates. And, we call it SNF. So, this sulphonated naphthalene formaldehyde condensates or poly naphthalene sulphonate – it is also another nomenclature there – poly naphthalene sulphonate – PNS. More commonly used is SNF, that is, sulphonated naphthalene condensates formaldehyde. So, SNF. Some people call it for poly naphthalene sulphonate as well – PNS. And, this is obtained by sulphonating petroleum or coal tar naphthalene at high temperature. So, this is also sulphonated in the same manner as the lignin. And, this is done at high temperature.

Naphthalene is now sulphonated at high temperature to obtain this material. The product is then polymerized with formaldehyde and neutralized with sodium, calcium or some other material; usually sodium, calcium salts. And, molecular weight is small. That is

why the quantity adsorbed on to the cement surface is more. And therefore, more possibly negative charge; therefore, more action compared to plasticizer. So, less molecular weight, more negative charge, because more it can be adsorbed onto the surface of the particle; more negative charge. And therefore, more dispersion; that is the idea.

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Let us see the chemical structure of it. Naphthalene structure is this. This is the naphthalene structure. And, this is the sulphonated SO_3 in the sodium with it; and then, this is polymerized with n number of them; it will repeat. N number of them it will repeat. This is actually CH_2 ; this is... 2 has gone there; this is CH_2 ; this is CH_2 ; the 2 has gone there. So, that (()) a small correction actually. This needs a small correction. The 2 has gone down; 2 is here actually. So, this CH_2 , CH_2 . So, this is the polymer.

So, it is the naphthalene. Naphthalene is 2 benzene ring combined together. And, in one of its arm would be SO_3Na . And, this when polymerized, this is actually simplified formula shown – sulphonated polymer formaldehyde condensates; sulphonated naphthalene formaldehyde condensate polymer. So, simplified structure is shown. And, this chain is linear. So, it is a linear chain will be formed; several of them linear chain will formed. And, it is free to rotate about formaldehyde derivative CH_2 and SO_3Na group can be above or below. So, it is above... And, this axis it can rotate. And

therefore, this can be above or below; this can be above or below; this can be above or below.

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Chemistry

□ In solution the SO_3Na group dissociate to $-\text{SO}_3^-$ & Na^+ leaving the molecule with (-) charge effecting dispersion.

$-\text{SO}_3^- + \text{Na}^+$

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Chemistry

□ In solution the SO_3Na group dissociate to $-\text{SO}_3^-$ & Na^+ leaving the molecule with (-) charge effecting dispersion.

- Sulphonated melamine formaldehyde condensates (SMF) are similar in structure as SNF, except that melamine ring replaces Naphthalene
- The SMF is available only as Na salts. Molecular weight is higher than SNF.

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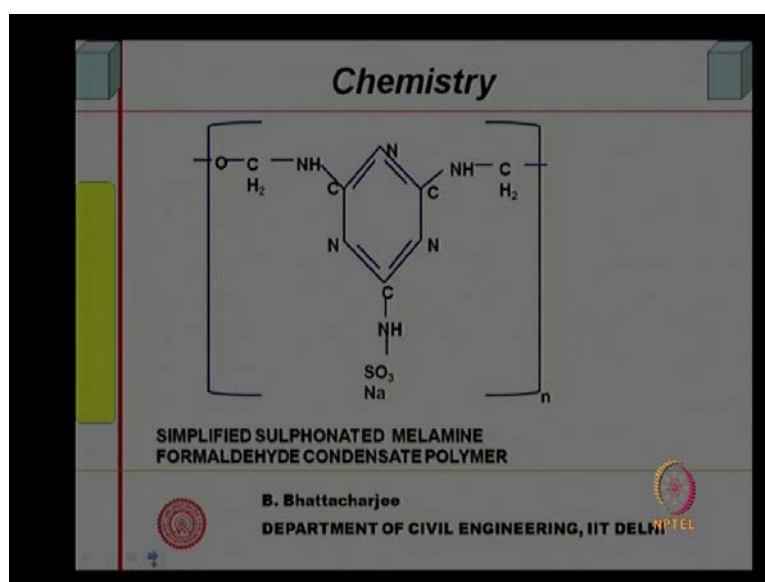
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Anyway, the main important issue is, on dissociation, if you put in water, this component will dissociate into something; all other components – SO_3 with negative charge plus sodium positive charge like the ligno sulphonate. And, this will now affect the dispersion in the same manner, because this being negative, it can get attached to the surface of the

cement, which has got cationic surface charges. And, there it can get attached and induce negative charge on to the cement particle itself.

So, similar action as the ligno sulphonate; only difference being more quantity can be adsorbed and its action is more prominent. The next one is sulphonated melamine formaldehyde condensates. And, this is similar as SNF; that is, the earlier one that we looked at – sulphonated naphthlene formaldehyde, except that melamine ring replaces the naphthalene double ring. So, melamine ring will replace the naphthalene double ring. This is available only as sodium salts, not a calcium salts; molecular weight is higher than SNF; so, slightly higher than SNF.

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And, that is how it will look like. This is the naphthlene double ring replaced by melamine, which has got three nitrogen in the ring instead of carbon. So, this is the melamine; everything else remain same. And, here is the SO 3 Na, which is the main important component. And, on addition to water, this sodium will dissociate out leaving everything else negative; which can get attached to the cement particle surface and cause dispersion. So, these are simplified sulphonated melamine formaldehyde condensates polymer with n number degree of polymerization. So, that is showing this – showing the same.

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Chemistry

- Polycarboxylate ethers (PCE) are also called PC or combed polymer.

$$\text{R-O-R-COOH}$$

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The last variety, that is, polycarboxylate ethers; these are also called polycarboxylate... PCE based; polycarboxylate simply or combed polymer. Carboxylates are nothing but derivatives from... They come from carboxylic acid having COOH group. This stage gets replaced. In case of salt, this will be replaced by carboxylic salt. This will be replaced by metal. And, in case of esters, they will be replaced by organic groups. Ethers are compounds, which have got oxygen of this kind of structure.

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Chemistry

- Polycarboxylate ethers (PCE) are also called PC or combed polymer.
- The backbone polymer is typically obtained from polymerization of acrylic acid but can be substituted by other groups.

$$\text{R-COOH}$$

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And, let us see how do they look in our case. The backbone polymer is typically obtained from polymerization of acrylic acid, but can be substituted by other group. So, essentially, carboxilates are obtained from carboxylic acids, which has got structure like this. So, typically, they are obtained from acrylic acid. But, you can substitute other groups. So, there is lot of possibility actually. That is why many groups can act here.

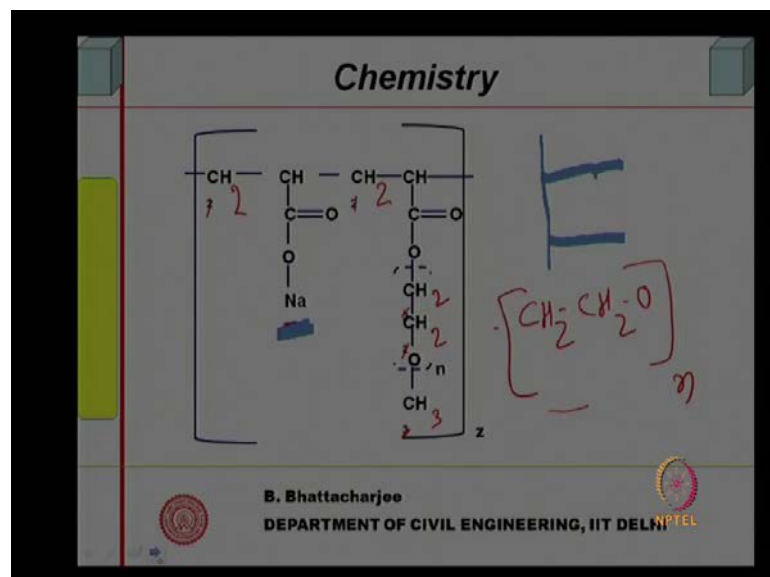
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Chemistry

- Polycarboxilate ethers (PCE) are also called PC or combed polymer.
- The backbone polymer is typically obtained from polymerization of acrylic acid but can be substituted by other groups.
- The carboxilate group is neutralized by Na^+ that dissociates in solution .

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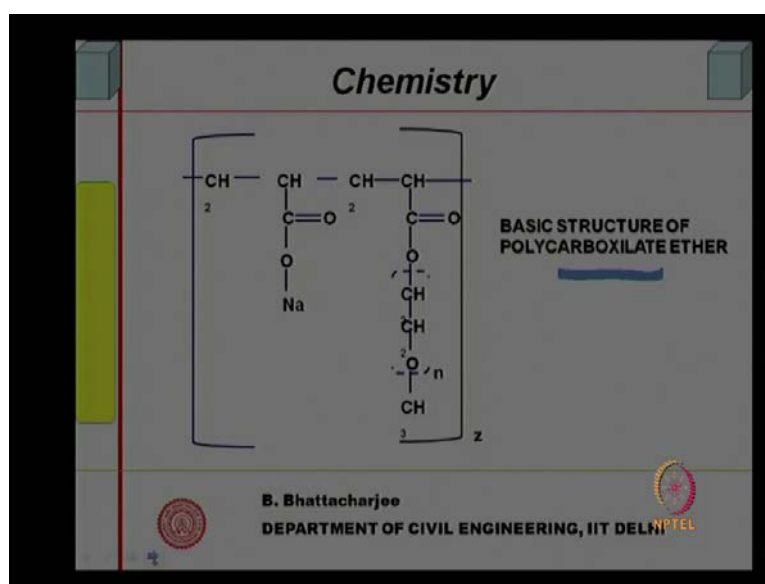


And, this group is finally then neutralized by sodium that dissociate into solution. So, caboxilate group is neutralized by sodium. And, in solution, sodium gets separated out leaving everything else negative, which can get attached to the cement particle.

The chemical structure will look something like this. So, this is CO; H is replaced by sodium; CH and this is CH₂. This should be CH₂; 2 should go up here actually. This 2 should go up here. It has got some or other distorted; some or other it has got distorted. 3 should be here, rather than here. CH₂, CH₂ here; this has got distorted. And, this is CH₂; this is also CH₂, etcetera, etcetera. So, this is not there; this is not there. This has got distorted. So, there is a polymer here. You can see this. This is CH₂-CH₂-O. And, that is ether; that is one ether. So, there is an ether here. This is the polycarboxilate; sodium carboxilate maybe (()) sodium whatever the... So, sodium is there in the (()) And, in this one, instead of sodium, there is another ether – polymer; co-polymer. So, there is a copolymer here.

So, there is a polymer here. So, you can see this is sodium; it does not get dissociated. This will attach to the cement particle; this will attach to the cement particle; this will attach to the cement particle. But, this one – these branches where there is a polymer – co-polymer, this will remain outside; in the sense that, this will remain attached to the branch. So, you have a comb structure.

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This is the branch, which is attached to the cement. And, something else is protruding out of it. So, this portion is protruding out of it. And, this is the co-polymer. More importantly, you can change this co-polymer. It need not be $\text{CH}_2\text{-CH}_2\text{-O}$ – ethylene glycol. As we shall see, this is the compound. You can have any polymer – co-polymer here – ether; co-polymer as any other ether here. Therefore, by changing this, you can actually tailor-make the property of this plasticizer. Let us see how it is done. So, this is the basic structure of polycarboxylate ether. So, the ether is here.

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Chemistry

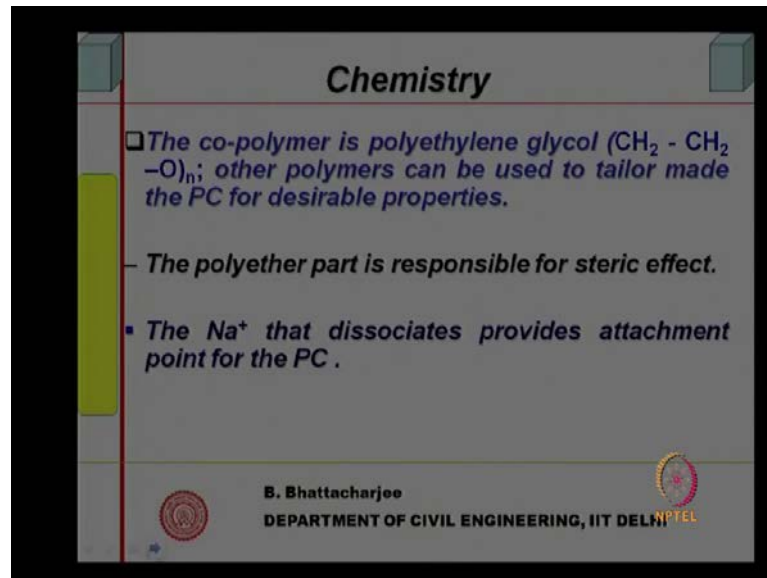
- The co-polymer is polyethylene glycol ($\text{CH}_2 - \text{CH}_2 - \text{O}$)_n; other polymers can be used to tailor made the PC for desirable properties.
- The polyether part is responsible for steric effect.

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And, idea is like this. The co-polymer here is polyethylene glycol – $\text{CH}_2\text{-CH}_2\text{-O}$ n. Other polymers can be used to tailor-made the PC for desirable properties. So, this is the biggest advantage. And, this development took place in 1990s – largely 1990s; let us say late 1980s and late 90s. Therefore, you can see that, there is an... We have a choice of actually designing various kind of or developing various kind of super plasticizer as they are called hyper plasticizer using this polycarboxylate ether type of formulation.

The polyether part is responsible for what is known as steric effect. I will come to steric effect, because it is now comb structure. Structure is comb. So, this is the main chain, which is the polycarboxylate chain. And, here is the ether. So, the ether group chain is here – polymer. Therefore, this honeycomb structure. And, this effectively increases the size of the particle and causes further dispersion by size effect, which is known as steric effect. We will come to that sometime later on again.

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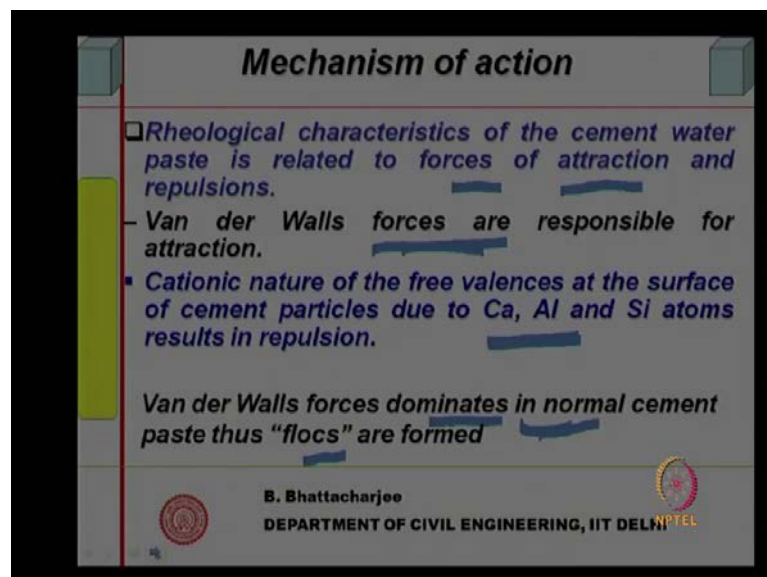
Chemistry

- The co-polymer is polyethylene glycol ($\text{CH}_2 - \text{CH}_2 - \text{O}$)_n; other polymers can be used to tailor made the PC for desirable properties.
- The polyether part is responsible for steric effect.
- The Na^+ that dissociates provides attachment point for the PC.

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The sodium that dissociates provides attachment point for PC. So, PC gets attached to the cement, because sodium will dissociate and that causes attachment to the PC. So, that is how the chemistry of plasticizers and super plasticizers are.

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Mechanism of action

- Rheological characteristics of the cement water paste is related to forces of attraction and repulsions.
- Van der Waals forces are responsible for attraction.
- Cationic nature of the free valences at the surface of cement particles due to Ca, Al and Si atoms results in repulsion.

Van der Waals forces dominates in normal cement paste thus "flocs" are formed

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Now, if you look into mechanism of actions; we can now look into the mechanism of actions, which more or less we understand from the chemistry. Basically, rheological properties of cement water paste is related to forces of attraction and repulsions. So, in the beginning when we add water, the viscosity of the paste that you form or how much

force is required to cause it to move or deform or reeled if I may say so; these are all functions of the forces of attraction and repulsion with the cement particle themselves. So, two types of forces of course we recognize. One is a Van der Waals forces, which are responsible for attractions. Van der Waals forces between the covalent compound in the cement as we have seen earlier when we looked into the chemistry of cement. They will cause attachment or they will try to bring them together.

So, they are attractive forces. Whereas, you see the free surface valences – they are essentially cationic in nature, because calcium ion, aluminum ion, aluminum – they are there and they are cationic in nature. That is why they can actually attach water also – get attached to the water to form water of crystallization; and, the reaction, that is, hydration do take place. So, they are positive in nature and they cause repulsion of this particle.

Now, the repulsion in the beginning is less compared to expansion. So, the Van der Waals forces dominates in normal cement paste; thus, flocs are formed. So, in the beginning, if you do not add any plasticizer, cement tend to floc together because of this force. Although this force is there, these forces are more dominant; and therefore, flocs formation do occur as it occurs in many other fine particles.

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Mechanism of action

- *Water reducers in water dissociate to negatively charged component and metal ions.*
- *The negatively charged component is attached to positively charged cationic surface, thus getting adsorbed irreversibly.*
- *Thus inducing negative charge on particles.*

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But, when you add this super plasticizer or water reducing agent, the super plasticizer – it forms negatively charged component and then the metal ion, that is, sodium or calcium that you have added. And, this negatively charged component is attached to positively

charged cationic surface that, they get adsorbed irreversibly. So, because of their negative charge and because the cationic surface – characteristics of the surface, because of calcium, aluminum, etcetera, this negatively charged sulphonated compounds or negatively charged compound after dissociation of the metal gets attached to the cement particle. Now, since they are negatively charged, they now induces negative charges into the cement particle itself; which can overcome the Van der Waals forces. Therefore, deflocculation occurs or dispersion occurs. So, they induce negative charge on the particle after adsorption and they cause dispersion.

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Mechanism of action

- Water reducers are surface acting agents (-ve)ly charged, adsorbed on the cement and fine particles, giving the particles negative charge leading to repulsion.
- The negative charge also causes development of sheath of oriented water molecules around particles.

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
So, water reducers are surface acting agents negatively charged as adsorbed on the cement particle or any other similar fine particles, giving the particles negative charge. And, this leads to repulsion. That is why they are dispersant. Now, negative charge also causes development of sheath of oriented water molecule around particles; that is, if this is the particle, now, everything is negatively charged and water is H_2O is polarized with this positive and negative charge not coinciding. Therefore, water will get oriented and it will give you a sheath of oriented water molecules for waiting purpose.

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Mechanism of action

- Water reducers are surface acting agents (-ve)ly charged, adsorbed on the cement and fine particles, giving the particles negative charge leading to repulsion.
- The negative charge also causes development of sheath of oriented water molecules around particles.
- Water is free from restraining mechanisms of flocculated system and available for lubrication.

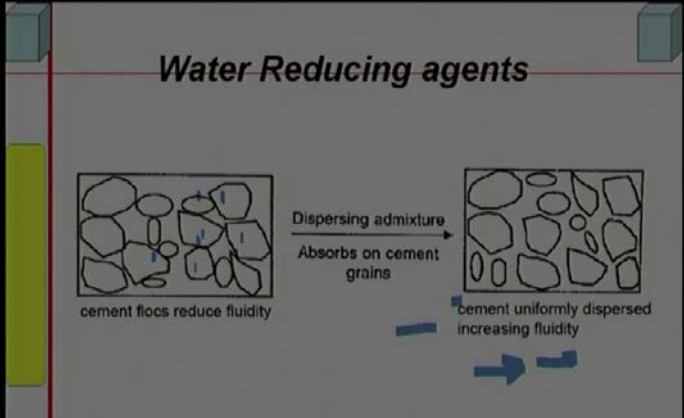
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And, this results in release of some water. Some water gets released from restraining mechanism of flocculated system. And therefore, more water is available for lubrication. Therefore, the plasticizing effect. So, two ways. First, it pushes. But, this is possibly true for ligno sulphonates, SNF and SMF. PC – we will see on the other hand, does something more. So, they essentially causes negative charge on to the particle, pushes them apart.

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Water-Reducing agents




cement flocs reduce fluidity

Dispersing admixture
Absorbs on cement grains

cement uniformly dispersed increasing fluidity

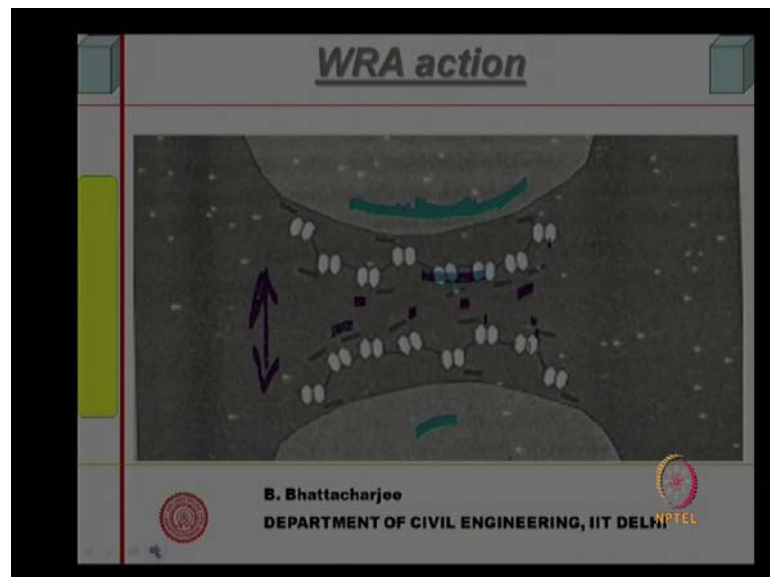
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Not only that, it creates a sheath of oriented water molecule around a particle and some water gets free, because now, it is easily weighted, because of the discipline, arrangement of the water, accumulation of water at the surface. Some water gets free. And, that is how this water is available for further lubrication.

So, they will look something like this. Water reducing agent will look something like this – dispersing admixtures. Cement flocs; and, initially, they are something like this; each of them are very close to each other if you see. They were flocs. But now, they got uniformly dispersed increasing fluidity. So, this increases the fluidity.

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This is how they will look. The particles are... This may be the particles; this may be the particles. The chain... Since SNFs are linear polymers, linear chain polymers, they are creating negative charges; and, this negative charges repel each other. This is another particle. These are the... This is showing for SNF. You can see the naphthalene – naphthalene rings – double rings; naphthalene (()) rings. So, this is actually SNF action shown. So, SNFs are double rings here, double rings here. So, these are SNFs and this is a polymer. So, long chain polymers with negative charge around. And, this negative charge causing – pushing the particles apart; pushing this particle apart. So, that is how causing effective dispersion.


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(H)WRA action SNF (surface charge)

zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.

Water

15V bulk

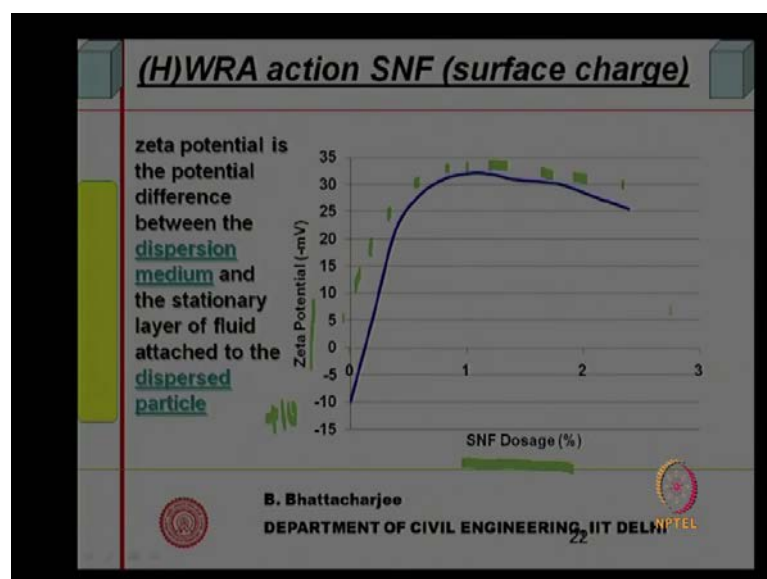


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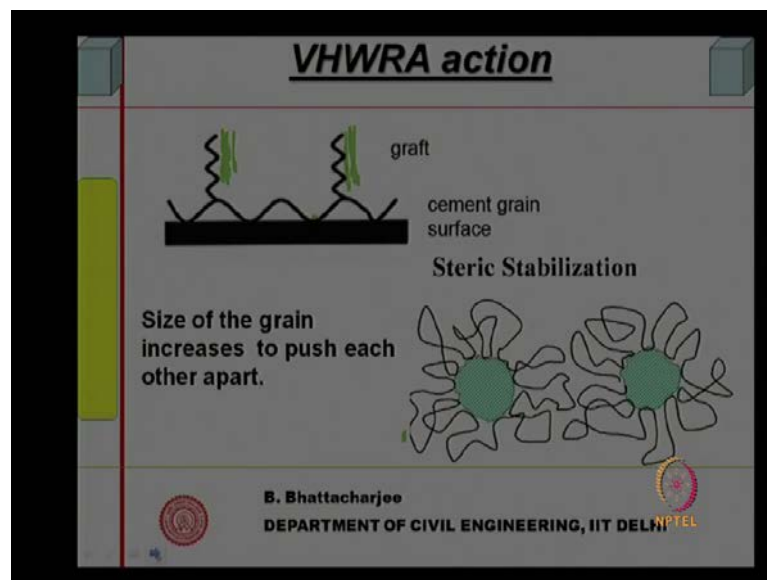
Now, this charge increase has been measured also; and, the potential... This charge increase is defined in terms of zeta potential. Zeta potential is a potential difference between the dispersion medium, that is, water; in our case, it is water; and, the stationary layer of fluid attached to the dispersed particle. So, if you have... These are the particles; and, if the surrounding water layer is somewhere here... So, this water layer and potential of the bulk water here – this difference is called zeta potential. So, zeta potential is the Δv across the bulk dispersion and the one layer attached here. That is how by definition this is zeta potential.

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And, this zeta potential if you measure, it is observed that, SNF dosage increases, zeta potential negative; remember this is negative, because potential is negative on the surface. So, minus 10, minus 10; minus millivolt this is; which means this is plus 10 volt; plus 10; and, these are all negative. Just for the sake of plotting, we are showing it this way. So, as you increase the SNF doses, the zeta potential, which is negative zeta potential; so, negative zeta potential increases. But, beyond a point of course it does not increase further; which tells us that possibly there is an optimal dosage beyond which there is no further improvement by adding SNF. This may be... This is also true for SMF or possibly even ligno sulphonates. So, negative potential has been confirmed by experimental studies through zeta potential studies. And, that is what this diagram shows.

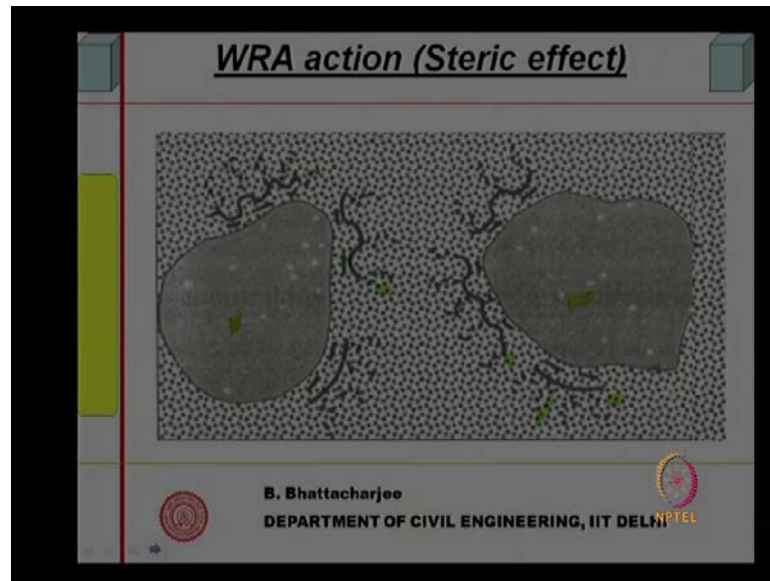
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If you look at very high range water reducing agent or PC-based super plasticizer action; now, you remember we said that, this will have combed structure. So, there is another – the co-polymer ether. So, co-polymer, which is an ether – this will be here; this is the main carboxylate group. So, long chain and this is the graft, where you can put in any desirable ether depending upon the properties you require. And, because of this, you find that, a long chain outside, which are again polymers; this particle gets dispersed more. In fact, it is attached here, because of the sodium dissociation. Sodium dissociation – it gets attached here. So, negatively charged – the whole thing; and then, the graft or the co-polymer; that is, the ether is somewhere here. And, that is what results in increase in effective size of the particle and pushes apart. So, this is called steric stabilization.

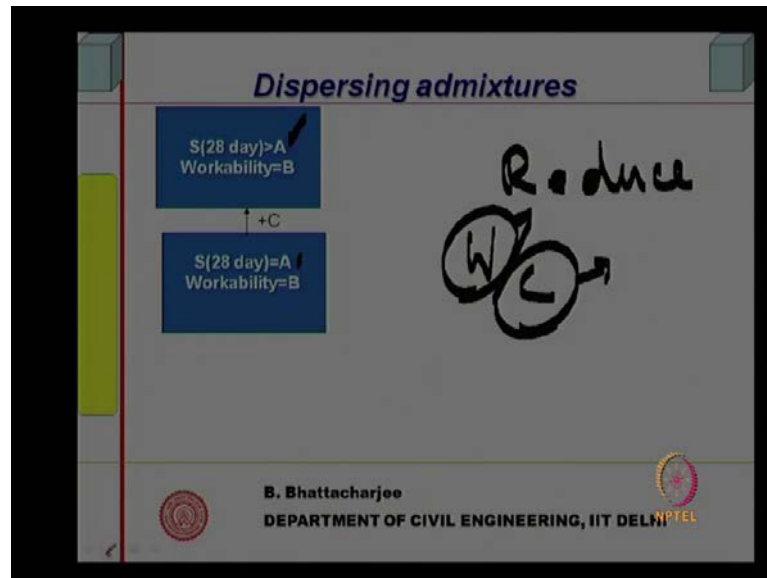
Therefore, the action of PC based admixtures are not the negative repulsion, rather largely it is the action of the co-polymer, which is grafted and effective size increase. Because of the sheer size, they push each other apart. And, they are quite more effective. In any case, this is a negative charge – sheath of negative charge here as well as the surface.

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So, the steric effect is visual here. For example, you can see that, main chain; and, the branches are here. So, main chain, the branches are on this side. These branches causes pushing apart. So, steric effect is because of the size. So, this is the cement particle; this is the cement particle. And, because of the size, they push each other more away from each other. So, push them away from each other.

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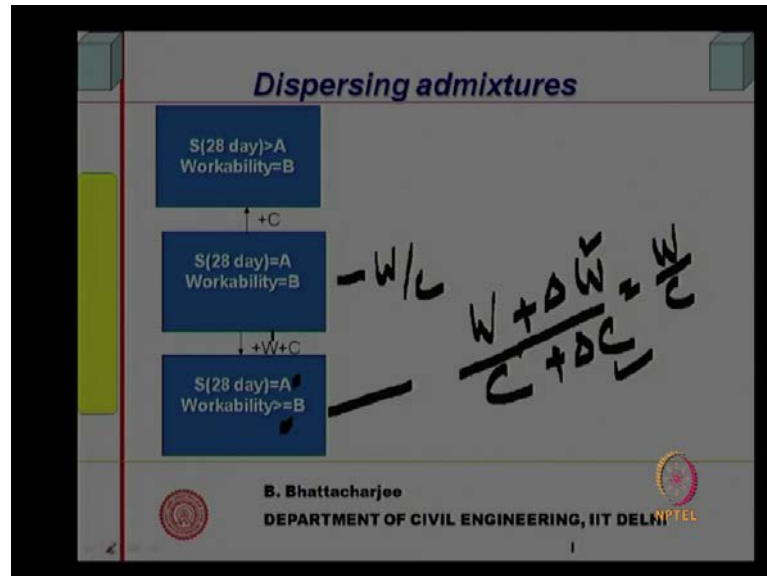


So, dispersing admixtures – continuing with that. Now, let us see some of their usage. How can you use them? You have understood the chemistry somewhat. And, we have also tried to understand the mechanism of the reaction. Now, how do you use them? You can use them beneficially. In fact, in my opinion or possibly opinion on most of the students of concrete and concrete technology, these are must, because this admixture is a must in engineered concrete, because it saves on cement. And, if you remember, we talked about cement clinker, is produced with the expense of energy and it also produces carbon dioxide – green house gas. And, we also said sometime in the very beginning; then, 1 tonne of cement is almost equivalent to 1 tonne of carbon dioxide production; cement in... clinker – OPC clinker here.

Now, if you can reduce the cement consumption; not only that you will make it cheaper; but, you will possibly reduce... If you can reduce the clinker consumption of course, it will help in reduction in green house gas emission. Now, admixtures of plasticizers or super plasticizers have some sort of beneficial effect on this also. Let us see how they are. Consider a concrete with 28 days strength A and workability B. And, I want to get a strength of 28 day greater than a workability B. When we study further, we see that, for doing that, what I need is to reduce the water to cement ratio; reduce. I want to keep the workability same. So, largely, the water – I will keep same. If I keep the water same and I want to reduce the water-cement ratio; then, I must increase the cement. So, I got to

increase the cement. So, you want to go. A concrete, which has got higher strength compared to this; this is A; this is greater than A; you would add cement.

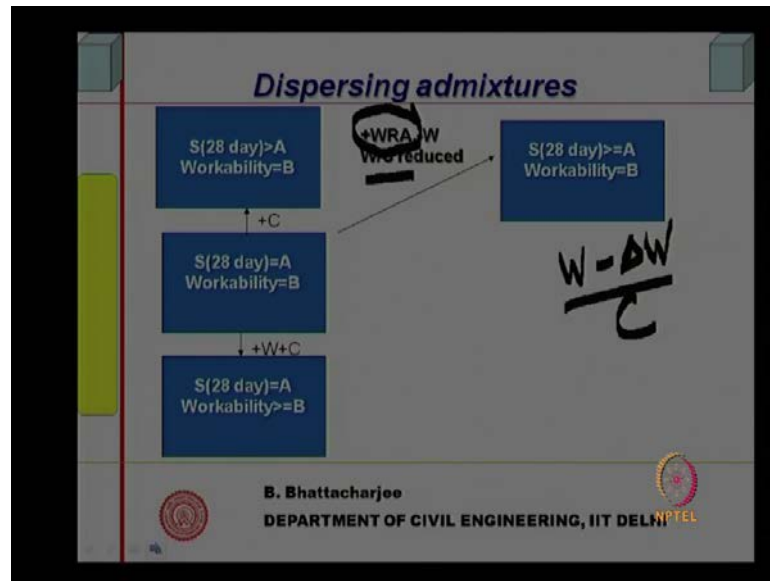
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But, same can be achieved through another route as well. We will come to that. But, let us see in another case, I do not want to increase the strength, but I want to make it easily moldable; workability is a terminology, which is related to moldability. It should be ease – ease of working on to it. In fact, include what I can say so. Now, you want to easily work on to it; you got to add water; you got to add water, because then it will be flowing and you can compact it easily. That is very commonsense, tells us. Its intricacy and details we will look into some time later on. But, at the moment, we will assume that, I have to add water. But then I want to keep the strength same.

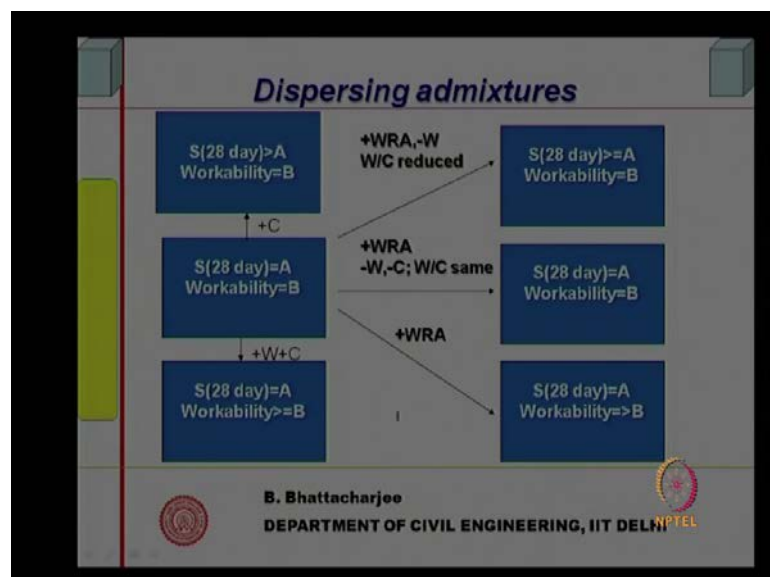
And, I said that, we will understand the strength is a function of water to cement ratio. Higher the water cement ratio, strength is lower. So, I have to maintain the water-cement ratio. Therefore, I got to add both water as well as cement, because I got to maintain water-cement ratio same as this. So, I got to... I will add delta w; and, proportionally, I will have to add delta C such that W by C remains same. So, if this was the W by C; this has to remain same here. So, I am adding water, adding cement as well. Here I did not want to increase the workability, but I want to increase the strength. Therefore, I was adding cement alone.

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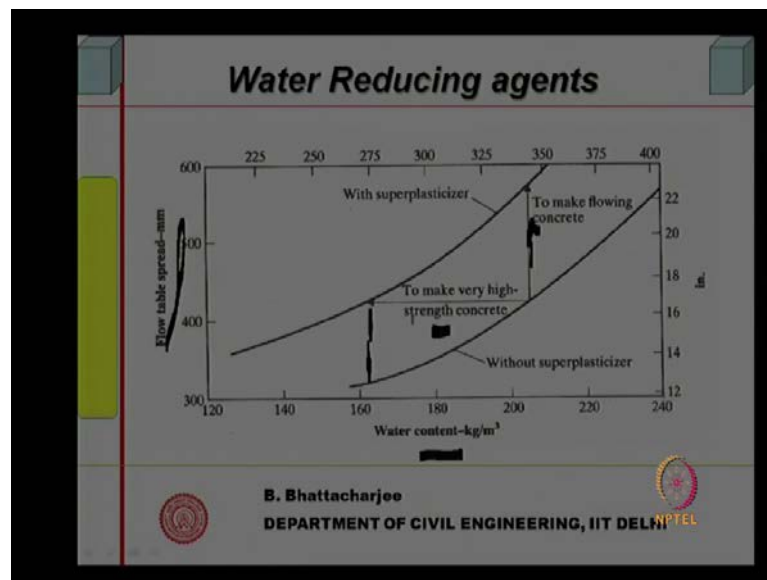
Now, same thing I can achieve by water reducing agent. What I do; I add water reducing agent; then, I will reduce the water. So, if I reduce the water, keep the cement same, water-cement ratio is reduced automatically. So, I am having ΔW divided by C . So, water-cement ratio is reduced; strength will be greater than A ; workability will be equal to same as what it was earlier. So, using WRA, I can achieve the same thing. Therefore, whichever root is cheaper, I will follow that. I will follow that whichever (()) This is cheaper root usually, because quantity added is very small. But, the secondary benefit you remember that, you are reducing the carbon dioxide emission as well.

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Want to keep the strength same and workability same. I will add some water reducing agent; reduce the water content; also, reduce the C same. So, the W by C will remain same. And therefore, I will get the same strength. So, I get the same strength by adding water reducing agent and with lower cement content. So, again it might be cheaper route to add water reducing agent rather than add cement. So, you will have to see whichever is cheaper. And, the last case – if I want to get this, I simply add water reducing agent. And, this will ensure that, I will get higher workability, but same strength. So, you can see that, by using water reducing agent, we can save on to cement. For same strength, if I add water reducing agent, I will reduce the water; I will reduce the water also correspondingly, cement also correspondingly. Therefore, there is a saving in cement and this might be a cheaper route. Similarly, if I want to increase the strength, use water reducing agent, water reduces, but cement will remain same. Therefore, strength may increase. And, if I want to simply increase the moldability, I add water reducing agent without adding cement. But, otherwise, I would have had to add water as well as cement. So, this is how we can use...

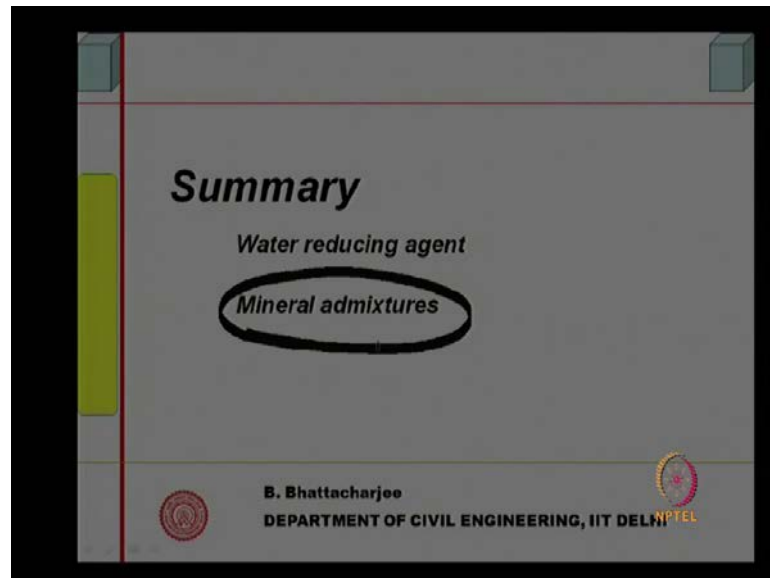
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In the next class, we will look into this again. Some more issues related this we will see. Same thing can be explained in different manner. For example, without plasticizer, water content is here, the workability is here. Now, you add plasticizer; then, the plasticizer, water reducing agent – just add them. It will be more flowing concrete. But, if you reduce the water, use a lower quantity of water; you will get higher, same strength, you

will get same workability. So, this will make higher strength concrete. So, you can increase the strength. We will repeat from this diagram in the next class. There are several other benefits. And, some effects we will study.

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We will now summarize. What we have looked into? We have looked into water reducing agent. And, some of their aspects we have looked into. This we did not look into today. In the next class, we will look into this. We have studied today in fact, what are the admixtures; how do you classify them; what are their purpose; define them. Followed by, we will look into plasticizers and super plasticizers; try to understand their chemistry, definition, some action, mechanism; and, how they are useful in concrete system. We will continue with the super plasticizer and hyper plasticizer and plasticizer a little bit including their other effects; what happens to the strength; what happens to durability and so on and so forth. They deduce the water for same plasticity. But, do they have any effect? Those aspects we will look into; then, look into other admixtures namely, the accelerators, retarders, etcetera, etcetera.

Thank you very much.