Concrete Technology
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Lecture - 10
Chemical Admixtures

Welcome to concrete technology – module three, lecture two. We shall be continuing with chemical admixtures. If you recall, last class, we talked about water reducing agent and then we said you can use the water reducing agent to minimize the cement consumption at a given workability; increase the workability at a given level of strength; and, use the water reducing agent simply to increase the workability alone.

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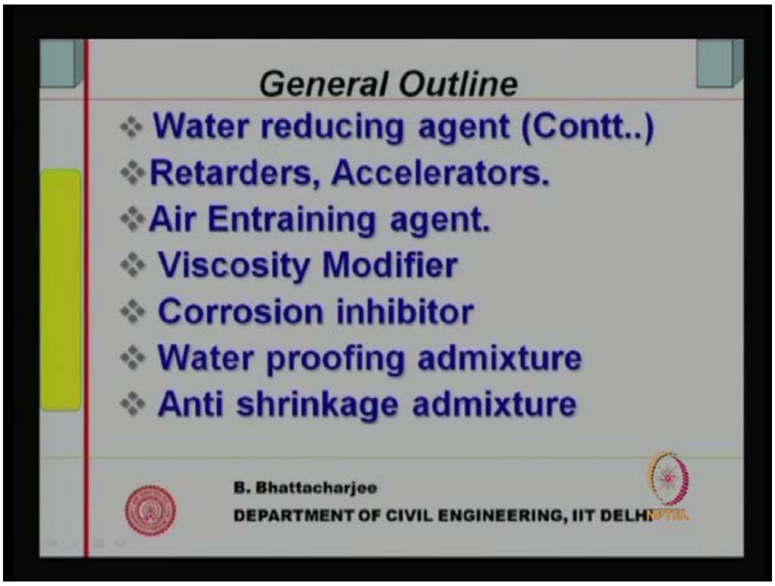

General Outline

- Water reducing agent (Contt..)
- Retarders, Accelerators.
- Air Entraining agent.
- Viscosity Modifier
- Corrosion inhibitor
- Water proofing admixture
- Anti shrinkage admixture

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So, we continue with that. Then, we shall look into retarders and accelerators, air-entraining agent, viscosity modifier, corrosion inhibitors, water proofing admixtures and anti shrinkage admixtures.

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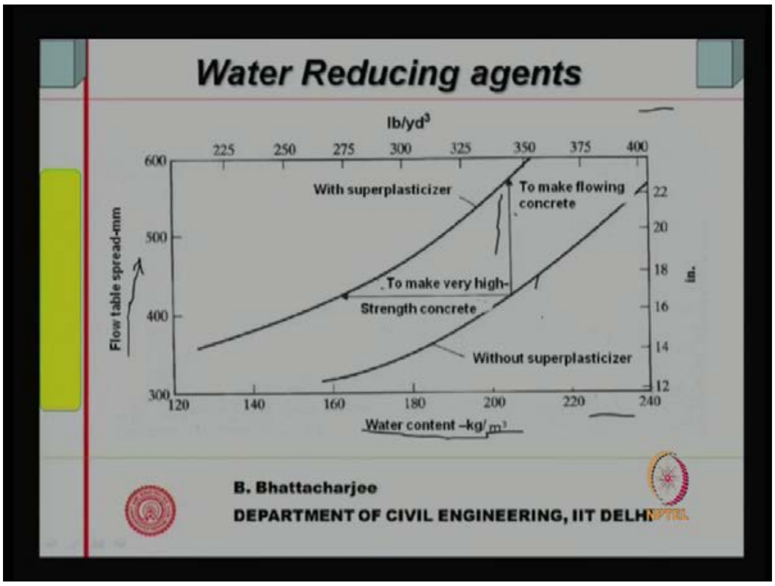

Water Reducing agents

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So, continue from the last class. If you recall, we looked into a diagram; we showed that we can use it in different way. For example, this is somewhat repeated in a slightly different manner in this diagram. In this axis if you see, we have water content. And then, in this axis in flow table spread. Now, this is flow table spread. So, if you use without super plasticizer, you want to increase the flow table spread, that is, the workability. You shall be increasing the water content. So, you increase the water content; the flow table spread will increase like this. This is the curve. But, if you add super plasticizer; but, supposing at the same water content, you want to get higher flow; then, simply increase the… add super plasticizer. With super plasticizer, at same water content, you can get higher flow. But, supposing you want to maintain the flow same, then you can reduce the water. And, if you want to maintain the same strength, you can reduce down the cement also.

So, you can have a cement saving. But, you want to get higher strength; keep the cement same. So, recall from the previous diagram, it is something similar. So, super plasticizer can be used to increase the workability at a given strength without adding anymore water. You can increase the strength for the same workability by reducing the water content and keeping the same cement same; and also, you can keep the water content same. You can reduce down the water… You can save on cement content by reducing down the water content and reducing down the cement as well. So, you can save on cement at the same strength and workability if you like. You can get highest strength at same workability; or, at same strength, you can get higher workability. So, this is the way one can use super plasticizer.

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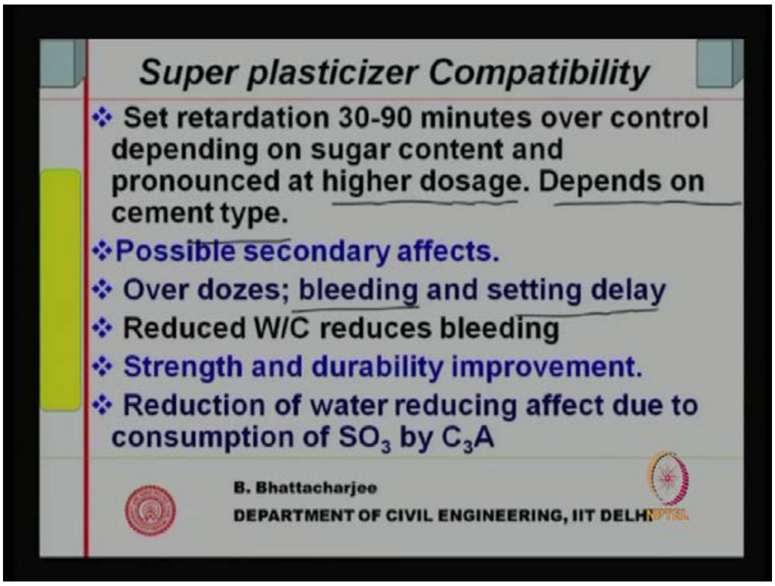

Super plasticizer Compatibility

- Set retardation 30-90 minutes over control depending on sugar content and pronounced at higher dosage. Depends on cement type.
- Possible secondary affects.
- Over dozes; bleeding and setting delay
- Reduced W/C reduces bleeding
- Strength and durability improvement.
- Reduction of water reducing affect due to consumption of SO_3 by C_3A

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It is important to look into super plasticizer compatibility; that means it must give the super plasticizing effect. The super plasticizer must give the super plasticizing effect. Set retardation could be some issues; that means depending upon the sugar content of the super plasticizer. And, at higher dosage, it may be pronounced. Of course, it depends upon cement type, because interaction of the cement is very, very important. It depends upon the cement type. There can be some secondary effects. For example, if you do over dozing, this can result in bleeding and setting delay. It can result in high bleeding. Lot of excess water might come out of the system and result in bleeding. And, setting delay can also be there.

So, one needs to look into those; no over dozing and that kind of competitive should be seen. In fact, if you go on increasing the dosage of the super plasticizer; beyond a point, it would not show any further plasticizing effect. There is a point of diminishing return. So, maximum dosage is added such that beyond that, if you increase further, you would not get any further plasticizing effect. So, that is the maximum. And, you should not have any kind of negative effect.

Water-cement ratio less means bleeding will be reduced and you will get strength improvement as well. So, that is right. And, reduction of water reducing effect due to consumption of SO 3 by C 3 – this can be an effect. For example, sulphonated super plasticizer or plasticizer – sulphonated compounds – they might react with high C 3 A in case of high C 3 A cement. And, water reducing effect may be reduced. So, because of this sulphonated compound, if you recall; that SO 3 – sulphonation was done; you will have sodium plus and SO 3. So, sodium goes into solution SO 3 and shows that it is negatively charged. Super plasticizer is negatively charged and it can get adsorbed. But, supposing the SO 3 is consumed by C 3 A, excess C 3 A being present in the cement; then, reduction of water reducing effect could be there. So, type of cement also matters.

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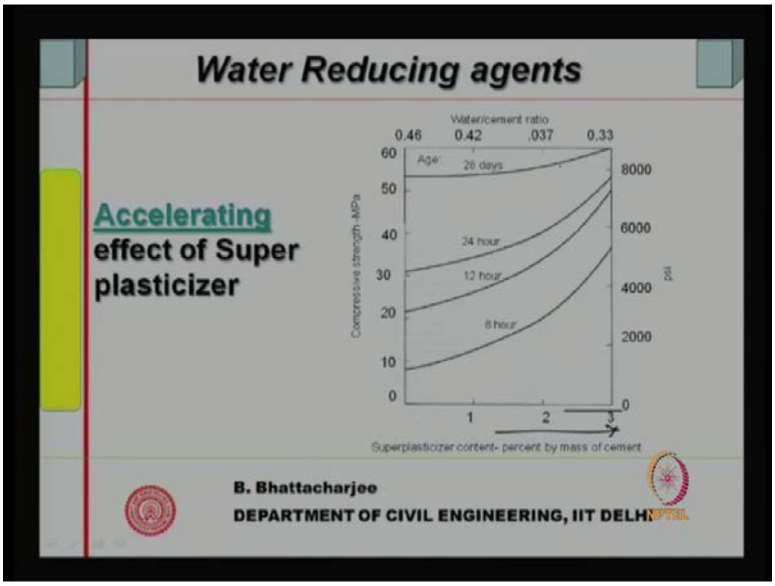

Water Reducing agents

Accelerating effect of Super plasticizer

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Some accelerating effect is seen from super plasticizer, because they can disperse the… Since they disperse the particle, you can see that, with super plasticizer dosage, higher the dosage… With higher super plasticizer dose, you have strength; no zero super plasticizer… If this was the compressive strength with higher dosage strength, early strength increases – 12 hour strength, 24 (( )) 28 days strength. There is of course much less influence. So, this is because, better dispersion of the system; that is because better dispersion of the system. So, it has got some or 10 accelerating effect, because hydration will get accelerated; more dispersion, more particles will come in contact with water and resulting in better hydration process, more uniform hydration product. That is why you have got somewhat accelerating effect of the super plasticizer.

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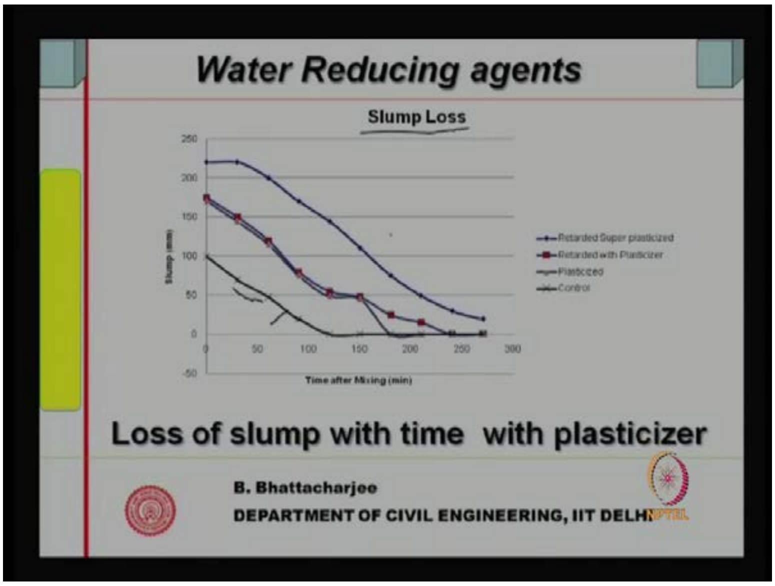

Water Reducing agents

Slump Loss

Loss of slump with time with plasticizer

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After time loss if you see this slump loss; or, in other words, if you look at slump retention of water reducing agent; now, this is important because of in case of ready mix concrete, you would like to deliver the concrete after may be certain period of time after mixing, because it will be there in the agitator track. So, in such situations, slump retention is an important parameter or factor; that means it should remain green or it should not set. So, setting time of the concrete here is important. And, supposing you have control; this is the control concrete without anything; control concrete is this. This is the control concrete. So, control concrete is here. So, here is a slump; and, this slump became practically zero after let us say sometime, say 100 minutes after mixing; 125 minutes or 20 minutes after mixing. Now, you have plasticized one; that is, this line; just plasticized. So, initially, it is high. Obviously, it is retained for also longer period of time. But, if you have a plasticizer cum retarder, it is still retained for a long period of time. So, it is nearly doubling of the time when slump becomes zero.

But, anyway you might be requiring some fixed slump. So, it can retain for a longer period of time. Retarder with… This is with plasticizer. But, if you have super plasticizer; so, then, slump itself in the beginning, is very high and it is retained for longer period of time. Note that slopes in these cases are more or less similar. So, the fact that, you have high slump in the beginning; as the time passes, the loss of slump bread is same, but it can retain for longer period of time. So, it is a useful thing as far as ready mix concrete is concerned. You have now more time for placing; no adverse effect on concrete in any case. So, loss of slump with super plasticizer as we have seen is somewhat lower.

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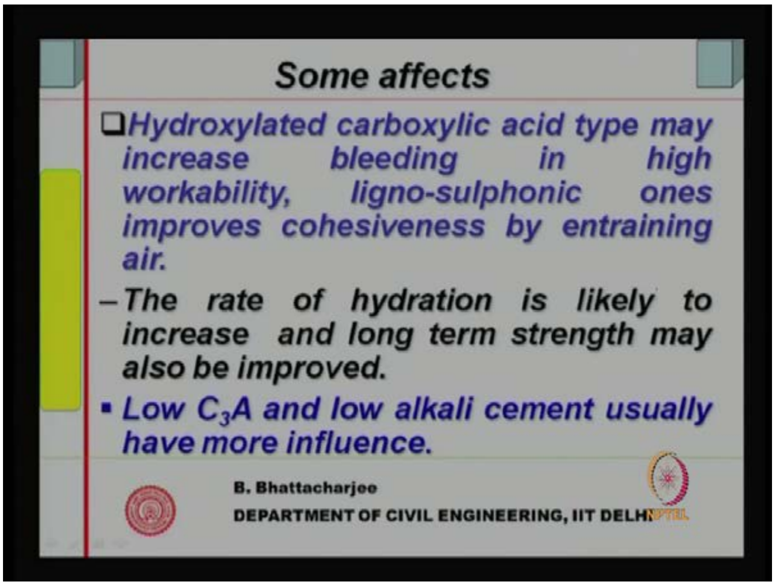

Some affects

- Hydroxylated carboxylic acid type may increase bleeding in high workability, ligno-sulphonic ones improves cohesiveness by entraining air.
  - The rate of hydration is likely to increase and long term strength may also be improved.
  - Low C_3A and low alkali cement usually have more influence.

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Hydroxylated carboxylic acid type may increase bleeding in high workability and lingo-sulphonic ones improves cohesiveness by entraining air. So, these are some secondary effects. Hydroxylated carboxylic acid type may increase bleeding in high workability. These are poly-carboxilate and similar ones. Bleeding in high workability can be seen in this kind of thing. And, ligno-sulphonic acid ones may improve the cohesiveness by entraining some amount of air. Rate of hydration is obviously likely to increase; and, long term strength also may be improved. Low C 3 A, low alkali cement usually have more influence. Low C 3 A and low alkali cement usually have more influence. So, C 3 A should be low, because as we have seen in many cases, alkalies and C 3 A – they can interfere with the super plasticizers action. And, thus, it is better that, you have low C 3 A and low alkali cement. So, this was water reducing agents – plasticizers, super plasticizers and hyper plasticizers.

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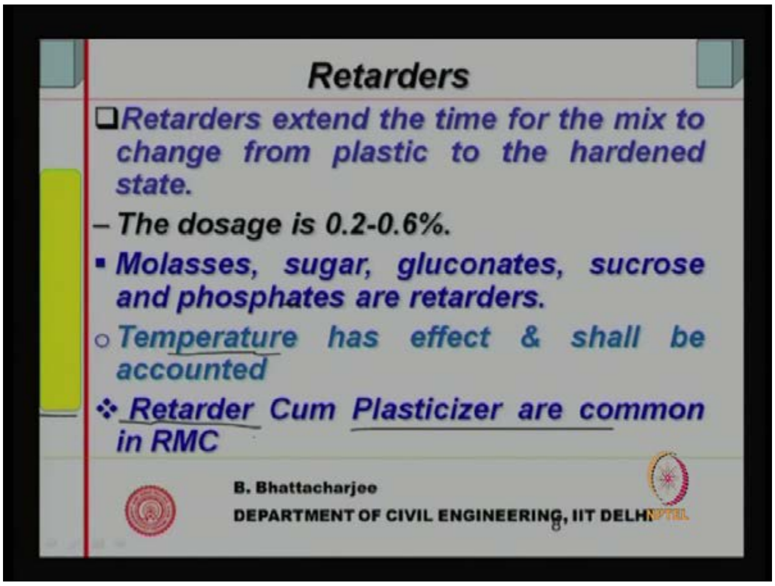

Retarders

- ❑ Retarders extend the time for the mix to change from plastic to the hardened state.
- – The dosage is 0.2-0.6%.
- ▪ Molasses, sugar, gluconates, sucrose and phosphates are retarders.
- ○ Temperature has effect & shall be accounted
- ❖ Retarder Cum Plasticizer are common in RMC

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Now, we can come to retarders – another kind of admixtures. And, we defined perhaps the one, which will retard the setting and hardening process. Let us see what they are. Essentially, retarders extend the time for the mix to change from plastic to the hardened state or hardened of course, solid state; first to solid and then hardened state. So, solid state is requires more time. Typical dosage would be 0.2 to 0.6 percent. And, examples are molasses, sugar, gluconates, sucrose, some phosphates. So, they are the retarders. In fact, sugar is a good example. Supposing the machine is stuck; you are not able to… The agitator truck is stuck in a traffic and you know that, you would not be able to reach the site in time. And, actually it will set by the time you reach, because it (( )) traffic jam or something like that. If you put some retarder like let us say sugar – sufficient amount; it will never set. So, it is called killing of concrete; concrete mix can be killed actually. So, it will never set. So, they are retarders.

Temperature do have some effect on the retarding action. And, this should be seen; this should be also considered. So, temperature has some effect and shall be accounted. Higher temperature – first reaction takes place; retarding action will be less. These are common in RMC I said, because plasticizer cum retarder – these are usually common in ready mix concrete. RMC stands for ready mix concrete, because we want long time – somewhat longer slump retention, because when you want to deliver the concrete at the site; the time required may be slightly higher. And, therefore, you would like the slump to be retained. And, that is why you use retarder cum obviously plasticizer to minimize the water content, water required; and, save on cement for the same strength.

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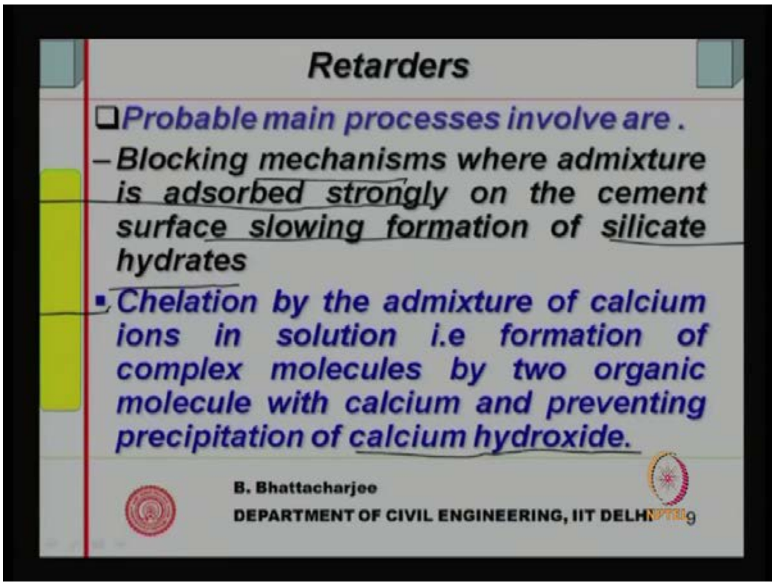

Retarders

❑ Probable main processes involve are .

- Blocking mechanisms where admixture is adsorbed strongly on the cement surface slowing formation of silicate hydrates
- Chelation by the admixture of calcium ions in solution i.e formation of complex molecules by two organic molecule with calcium and preventing precipitation of calcium hydroxide.

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The retarders are processes involved or the mechanisms if you look at it; blocking mechanism, where actually admixtures is adsorbed on the surface strongly on the cement surface and slows down the formation of silicate hydrates. So, that is the thing. So, basically, they can be adsorbed on to the cement surface. And, therefore, formation of silicate hydrates is stopped, because they are adsorbed on the surface and strongly. And therefore, slows down the process of formation of silicate. A second mechanism could be chelation by admixture of calcium ions in solution. Basically, calcium ion – two organic molecules can form a complex with calcium ion. So, the retarders compounds, organic compounds in the retarder can form complex with the calcium; and therefore, prevent precipitation of calcium hydroxide. So, that is what it is. So, calcium hydroxide precipitation is prevented.

Now, if calcium hydroxide cannot precipitate; therefore, the reaction cannot go in, because calcium silicate hydration formation needs calcium hydroxide production. Reaction calcium as C 3 S and C 2 S forms calcium hydroxide and calcium silicate hydrate. If calcium is not precipitating, these two reactions cannot proceed. So, that could be another mechanism or both.

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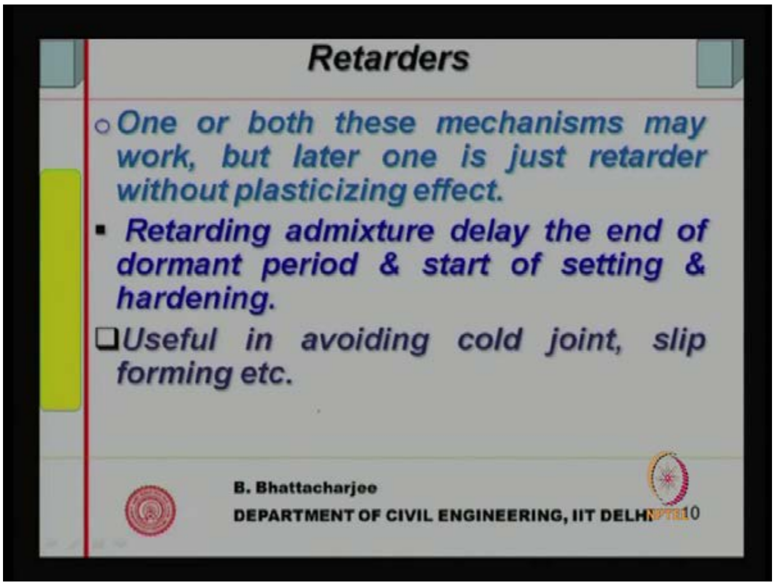

Retarders

- One or both these mechanisms may work, but later one is just retarder without plasticizing effect.
- Retarding admixture delay the end of dormant period & start of setting & hardening.
- ❑Useful in avoiding cold joint, slip forming etc.

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So, both these mechanisms may be at work, both later one is just retarder without plasticizing effect. First one is with plasticizing effect, that is, coating on top of the surface. So, this coating might also disperse the cement particles; while the second case will not have calcium ions forming complex; we will not have plasticizing effect. Retarding admixtures delay the end of dormant period. Dormant period – we saw it earlier sometime. Dormant period means the period during which ettringite is largely form. First 30 minutes, ettringite is formed right and CHS formation really do not start. So, this essentially ensures that, longer ettringite period, longer dormant period. And therefore, setting is delayed. And, after that, setting starts and followed by hardening. Good, useful in avoiding cold joints and slip form concrete, etcetera, etcetera. Slip form construction is continuous construction of vertical members – chimney or even buildings, walls and things like that; vertical members. So, continuous casting can… Casting goes on continuously.

Now, cold joint is formed between hardened concrete and fresh concrete, because they do not bond well. So, if you have longer setting period and you have put in a layer of concrete and you want to put in the next layer of concrete; it will be a longer setting period. You are putting fresh concrete over unset concrete; it will ensure that, there is no cold joint formation, because they will bond better. So, bonding is better if the setting time is longer. So, you are pouring the concrete – already unset concrete, not set concrete. So, there will be no cold joint formation.

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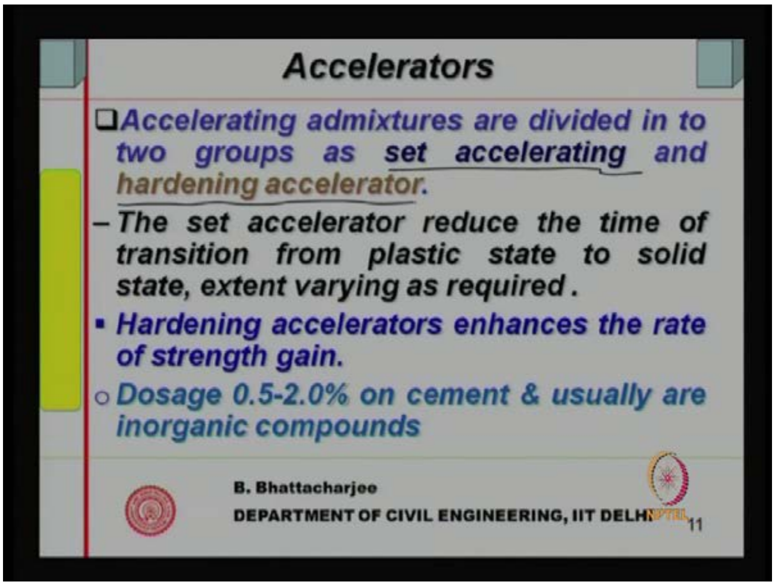

Accelerators

- ❑ Accelerating admixtures are divided in to two groups as set accelerating and hardening accelerator.
  - The set accelerator reduce the time of transition from plastic state to solid state, extent varying as required.
    - ▪ Hardening accelerators enhances the rate of strength gain.
      - ○ Dosage 0.5-2.0% on cement & usually are inorganic compounds

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That was one class. And, just similar to this is the accelerator, which is another class of admixtures. Now, accelerating admixtures are divided into two groups: one is set accelerating; another is hardening accelerator; set accelerating and hardening accelerator. Now, set accelerating means it will enhance the setting time, shorten the setting time. Hardening accelerator will mean that, it will increase the early strength gain. So, set accelerating and hardening accelerator – they are two varieties. The set accelerator reduce the time of transition from plastic to solid state and extent varying as required. Extent would be as required. How much you want? That would as you want. Hardening accelerator enhances the rate of strength gain. That is what I just said early strength you can get from here. Now, generic dosage varies from 0.5 to 2 percent on cement; and, usually are inorganic compounds. They are not organic formations; inorganic compounds.

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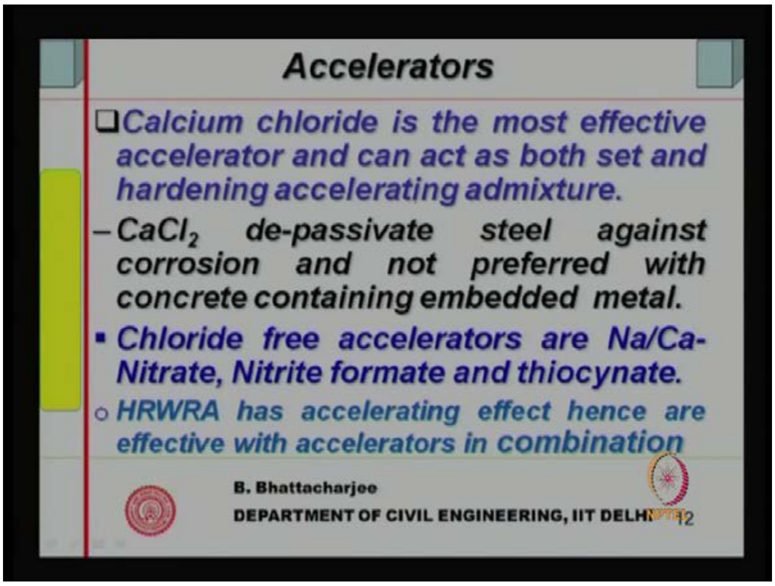

Accelerators

- ❑ Calcium chloride is the most effective accelerator and can act as both set and hardening accelerating admixture.
- – $CaCl_2$ de-passivate steel against corrosion and not preferred with concrete containing embedded metal.
- ▪ Chloride free accelerators are Na/Ca-Nitrate, Nitrite formate and thiocynate.
- ○ HRWRA has accelerating effect hence are effective with accelerators in combination

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Calcium chloride used to be one of them. It is the most effective accelerator and can act as both set and hardening accelerating admixture. So, setting as well as hardening process it can accelerate the calcium chloride. But, unfortunately, calcium chloride is a problem from the durability of reinforced concrete, because it will initiate the rebar corrosion process by what is known as de-passivation of the steel. So, in usually some kind of passive layer forms over steel, which protects the steel. But, if calcium chloride is present, such passive layers get broken down and it is called de-passivation; and, it is not preferred. That is why… So, if you have embedded steel in concrete, calcium chloride is not preferred admixture that will be used. In fact, it is not used anymore.

Chloride free accelerators are… What is preferred? These are nitrites – sodium or calcium nitrate or nitrite formate and thiocynate. So, chloride free accelerators like sodium or calcium nitrite, nitrite formate and thiocynates are useful in this direction. As we have seen earlier, high range water reducing agent has some accelerating effect. Hence, are effective with accelerators in combination. So, use accelerator cum the super plasticizer. High range water reducing agent – this will have an accelerating effect. They themselves have some accelerating effect. And, if you use together with an accelerator, the benefit is even more; it is more effective; it is quite effective.

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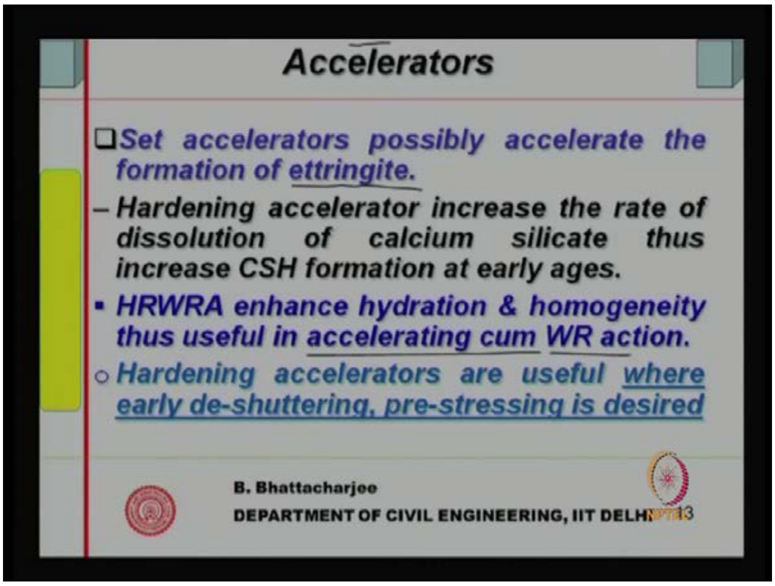

Accelerators

❑ Set accelerators possibly accelerate the formation of ettringite.

– Hardening accelerator increase the rate of dissolution of calcium silicate thus increase CSH formation at early ages.

▪ HRWRA enhance hydration & homogeneity thus useful in accelerating cum WR action.

○ Hardening accelerators are useful where early de-shuttering, pre-stressing is desired

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Set accelerators possibly accelerate the formation of ettringite, because you see ettringite formation is faster, dormant period will be reduced. So, set accelerators possible accelerate the formation of ettringite, because we know, during the initial face of setting, ettringite is produced during the dormant period. During the dormant period, ettringite is (( )) produced and it accelerates the setting process. Hardening accelerator increase the rate of dissolution of calcium silicate. Hardening accelerator accelerate the rate of dissolution the calcium silicate. And therefore, increases CSH formation at early ages. Hardening accelerator accelerates the CHS dissolution of calcium silicate. And therefore, calcium silicate can react faster.

And thus, early CHS formation can take place. So, that is how early strength you can get. High range water reducing agent enhances hydration and homogeneity. That is what we have seen earlier; thus useful in accelerating cum water reducing action. So, we have seen that, they are good in accelerating cum water reducing action. It would be useful where we want early de-shuttering, pre-stressing is required. So, if you want to do pre-stress, it should have sufficient strength gain, because pre-stressing can be done. If you want to remove the mold early, gain strength then should be sufficient.

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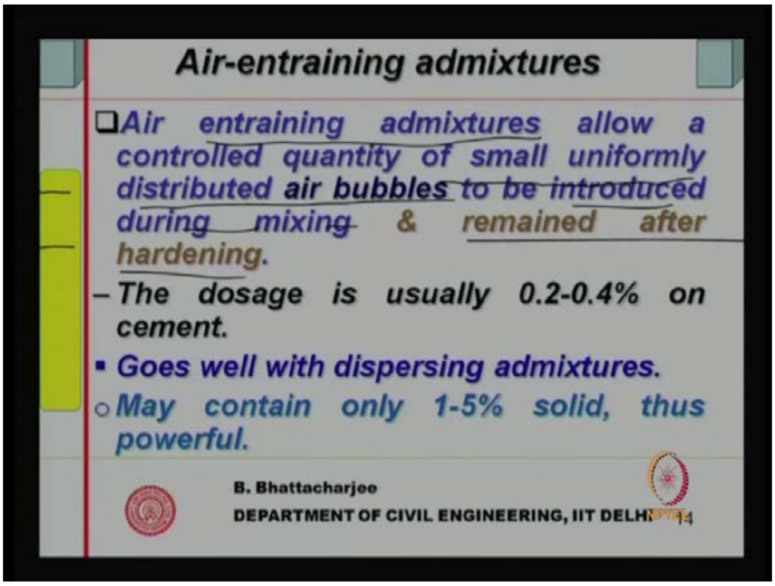

Air-entraining admixtures

- ❑ Air entraining admixtures allow a controlled quantity of small uniformly distributed air bubbles to be introduced during mixing & remained after hardening.
  - The dosage is usually 0.2-0.4% on cement.
    - ▪ Goes well with dispersing admixtures.
      - ○ May contain only 1-5% solid, thus powerful.

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So, this is the second variety. There are two varieties that we have seen other than water reducing agent. One is the retarding – retarders; and, the second one is the accelerators. So, third variety is air-entraining admixtures largely used in for freeze-thaw resistance. We shall be looking at that when we look at durability of concrete; largely used in case of freeze-thaw to improve the freeze-thaw resistance of concrete. So, essentially, how do they act? Essentially these ones – they entrain the air bubbles into the concrete. And, this air bubble in turn cause release of hydraulic pressure generated by frost action. We will explain this process in detail later on.

But at the moment, let us understand what these are. So, these admixtures if you put controlled quantity or small… uniformly it actually puts in mix; it actually forms small uniformly distributed air bubbles. That is introduced into the concrete during mixing and they remain also after hardening. So, that is what it is. So, air-entraining admixtures – they allow for small uniformly distributed air bubbles to be introduced during mixing and remained after hardening. The dosage is usually 0.2 to 0.4 percent on cement. They do not fall with the performance of dispersing admixtures, that is, the water reducing admixtures. Now, may contain only 1 to 5 percent solid; thus, very powerful.

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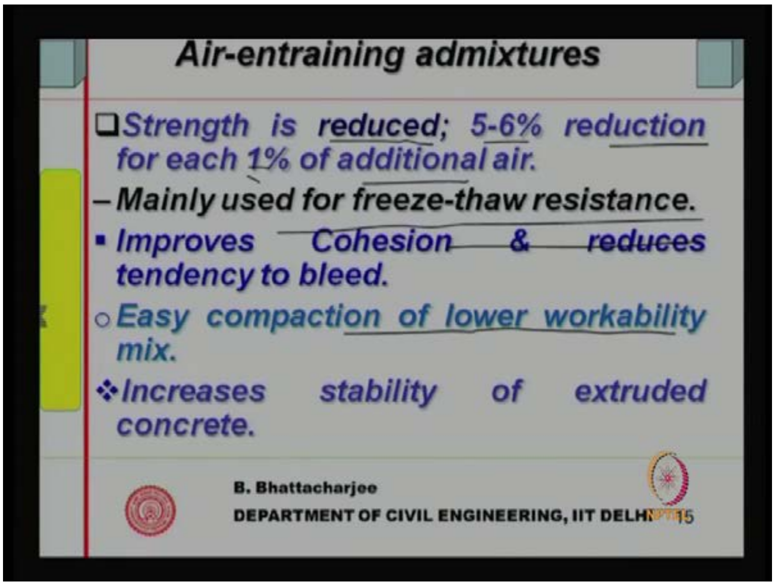

Air-entraining admixtures

- Strength is reduced; 5-6% reduction for each 1% of additional air.
- Mainly used for freeze-thaw resistance.
- Improves Cohesion & reduces tendency to bleed.
- Easy compaction of lower workability mix.
- Increases stability of extruded concrete.

And, let us look at principle – how it works. Obviously, if you are introducing pore, one issue is that, strength would be reduced. So, if you introduce pores, strength would be reduced. Strength would be reduced 5 to 6 percent reduction when you have added each 1 percent of additional air. So, you add one more percent of air; 5 to 6 percent reduction strength will occur. Mainly as I said, used for freeze-thaw resistance – mainly for freeze-thaw resistance. How does it do its mechanism? We will see that. But, improves cohesion and reduces tendency to bleed. That is of course… A little bit of air-entrainment actually improves the workability. That is a side effect. Basically it improves the cohesion within the concrete. And, tendency to bleed is reduced, because it can retain the water more. So, naturally, easy compaction is possible at lower workability. So, essentially it improves the workability of the mix; it increase also the workability of the mix. Increases stability of any kind of extruded concrete or any concrete placed through compressed air – pneumatically placed concrete. So, it improves actually stability of such concrete.

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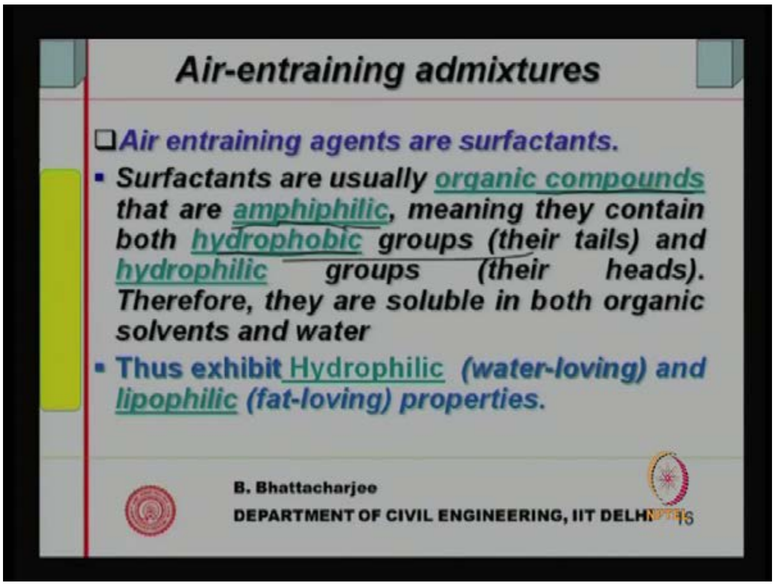

Air-entraining admixtures

❑ *Air entraining agents are surfactants.*

- *Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, they are soluble in both organic solvents and water*
- Thus exhibit Hydrophilic *(water-loving) and lipophilic (fat-loving) properties.*

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Basically, they are surfactants. That is the mechanism. Surfactants are surface acting agents and they are organic compounds. As we can see, they are organic compounds. They are two types; they are both amphiphilic and hydrophilic. What is amphiphilic? Amphiphilic – which means that, they have got hydrophobic and hydrophilic; both – hydrophobic tails and hydrophilic heads. What is hydrophobic? Which will push the water away; rejects the water. Hydrophilic goes well with the water. Since they are hydrophilic, therefore they are soluble in water and they are also soluble in organic solvents. So, they are amphiphilic, that is, hydrophobic and hydrophilic; amphiphilic resulting in hydrophobic and hydrophilic both. One is group tails are hydrophobic and the head is hydrophilic. So, something attracts (( )) kind of chain. On one side, they have got molecules which can attract water; another side molecules which can reject water. Thus, they exhibit hydrophilic – water-loving and fat loving properties; lipophilic – fat-loving properties. So, hydrophobic group – some of them show lipophilic or fat-loving properties.

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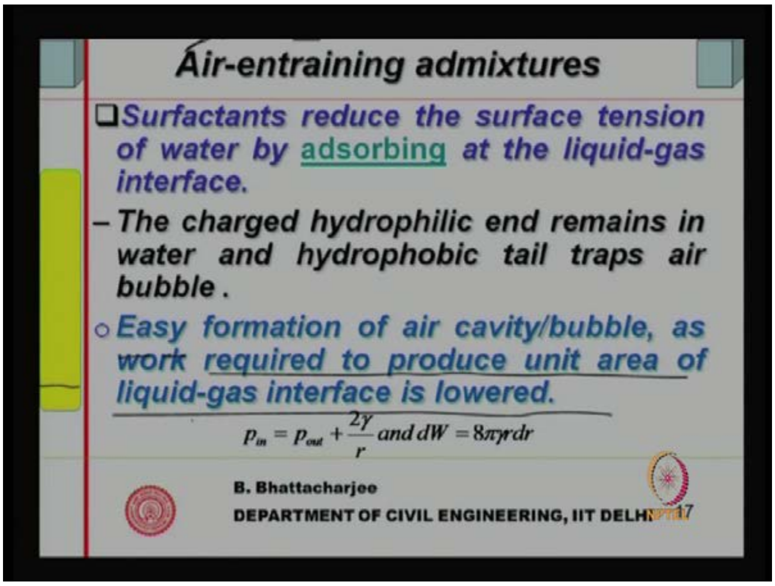

Air-entraining admixtures

- ☐ Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface.
  - The charged hydrophilic end remains in water and hydrophobic tail traps air bubble.
    - ○ Easy formation of air cavity/bubble, as work required to produce unit area of liquid-gas interface is lowered.

$$p_{in} = p_{out} + \frac{2\gamma}{r} \text{ and } dW = 8\pi\gamma r dr$$

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So, these are the two things. Essentially, they reduce the surface tension of water by adsorbing at the liquid-gas interface. So, they get actually adsorbed at the liquid-gas interface, that is, water-air interface; and, change the surface tension properties of the water. In fact, the charged hydrophilic end remains in water and hydrophobic tail traps air bubble. So, therefore, they are at the boundary of water and air. At the air, water interface; they would be there in the water side, the charged part. This remains in contact with water. The hydrophobic tail traps air bubbles. So, at the interface, actually in this process, they reduce the surface tension of water and bubble formation becomes easy.

So, easy formation of air cavity or bubble, as work required to produce unit area of liquid-gas interface is lowered. So, easy formation of bubbles, because easy formation of bubbles as work unit area – work required to produce unit area of liquid-gas interface is lowered. How much is this work? In a bubble, inside pressure must be balanced by the outside pressure. That must be balanced. And, it is actually, p in is given as p in is equal to p out – outside pressure – would be p outside pressure plus twice gamma by r, because inside the bubble there is the interface, the surface tension, the water is there; the water is there at the interface.

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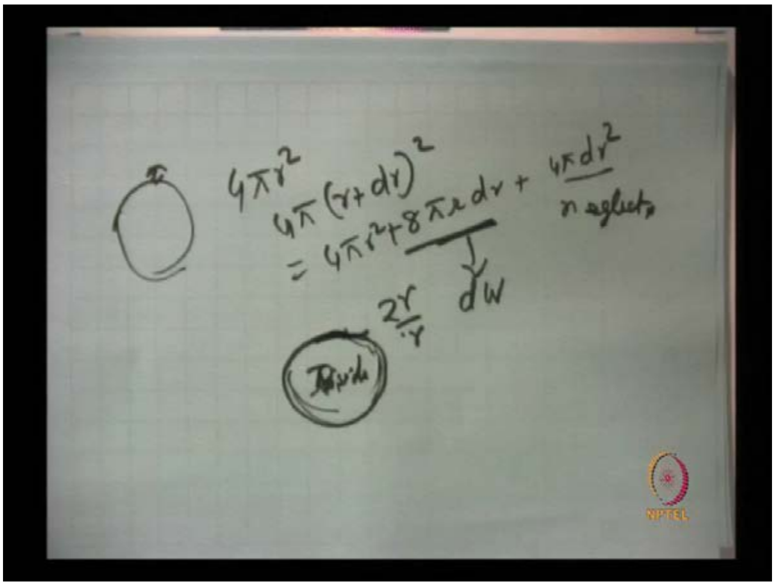

So, water is there at interface; this is the air bubble. Water is there at interface. So, at this, you can show that, the pressure here is twice gamma by r. So, p outside is p out plus 2 gamma plus r is equal to p inside; otherwise, the bubble will collapse. So, bubble should have sufficient pressure inside; p inside must be sufficient such that it can balance the outside pressure and the pressure due to surface tension forces. The work done would be to increase the surface area by d r. It was 4 pi r square. Now, the area will become 4 pi r plus dr square; and, which will be 4 pi r square plus 8 pi r dr plus terms involving 4 pi dr square, which can be neglected. This can be neglected. And therefore, increase in pressure. So, delta W would be given by… d W will be given by this. So, d W is given by this. So, pressure… So, if the surface tension is reduced, less work is required to maintain the surface. In fact, this will also get reduced. Therefore, outside pressure… Inside pressure is equals to p out… So, this itself will get reduced. The possibility of bubble formation increases. So, easy formation of air cavity or bubbles as work required to produce unit area of liquid-gas interface is lowered when surface tension is low.

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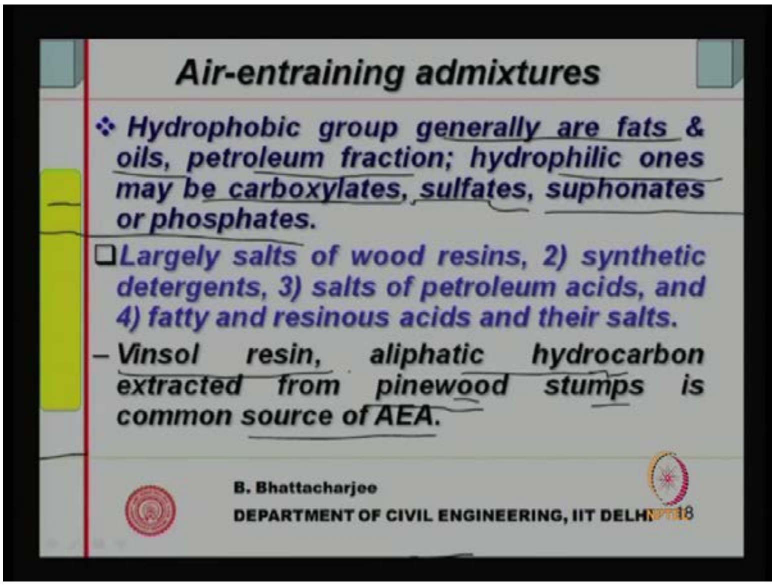

Air-entraining admixtures

- Hydrophobic group generally are fats & oils, petroleum fraction; hydrophilic ones may be carboxylates, sulfates, suphonates or phosphates.
- ☐ Largely salts of wood resins, 2) synthetic detergents, 3) salts of petroleum acids, and 4) fatty and resinous acids and their salts.
  - Vinsol resin, aliphatic hydrocarbon extracted from pinewood stumps is common source of AEA.

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Hydrophobic groups generally are fats, oils, petroleum fractions. Hydrophilic ones are carboxylates; they are carboxylates, sulfates, sulphonates or phosphates. So, these are the ones. Largely salts of wood resins; synthetic detergents; salt of petroleum acids; and, fatty and resinous acids and their salts. So, these are the materials – salts of wood resins, synthetic detergents, salts of petroleum acids, etcetera; fatty and resinous acids and their salts. For example, vinsol resin is obtained from pinewood; vinsol resin is an aliphatic hydrocarbon extracted from pinewood. Pinewood stumps is the common source of air-entraining agent. So, it is from the… Vinsol resin is one which is obtained from pinewood. And, that is the common source of air-entraining agents. So, we said that, salts of wood resins. Therefore, this is one of the examples.

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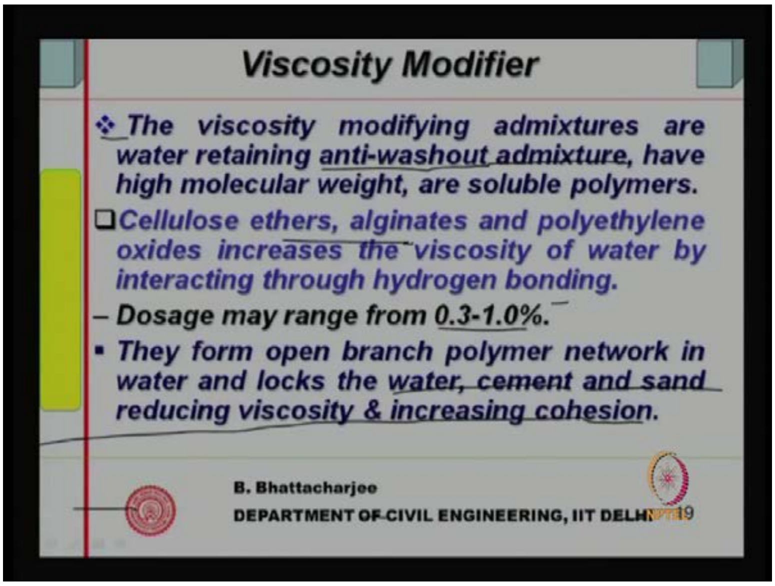

Viscosity Modifier

- ❖ The viscosity modifying admixtures are water retaining anti-washout admixture, have high molecular weight, are soluble polymers.
- ❑ Cellulose ethers, alginates and polyethylene oxides increases the viscosity of water by interacting through hydrogen bonding.
- – Dosage may range from 0.3-1.0%.
- ▪ They form open branch polymer network in water and locks the water, cement and sand reducing viscosity & increasing cohesion.

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So, what we have seen that, is air-entraining agent, which reduces the surface tension. But, then we have another variety called viscosity modifier. The viscosity modifying agents are… Viscosity modifiers are water retaining… They are used in underwater concrete anti-washout admixtures. They are essentially anti-washout admixtures. And, they have high molecular weight. They are soluble polymers. So, cellulose ethers, alginates and polyethylene oxides increase the viscosity of water by interacting through hydrogen bonding. Cellulose ethers – they are basically something like crudely… We can understand something like gum. A gum you put in water, it will increase viscosity.

So, some of those materials increase the viscosity of water; and therefore, then it can hold on water and the cementitious material together more easily. So, they form open branch polymer network in water and essentially lock the water and the cement and sand particles reducing viscosity and increasing the cohesion. So, that is the idea. They lock the water, cement and sand reducing viscosity and increasing cohesion. Dosage may be ranging from 0.3 to 1 percent. So, dosage may range from 0.3 to 1 percent.

So, these are viscosity modifiers used in underground, underwater concreting and nowadays in some of the self compacting concrete. Some of the self compacting concrete uses this material, because when you use poly-carboxylate ether; slightly in larger quantity, it has a tendency to bleed as we said, can cause bleeding. But, if it has got tendency to bleed, one way you can stop is by using a lot of fine particles, which can hold it together; use of very fine materials, which can hold it together. So, very fine like cementitious or inert material, which can hold it together. And, that is viscosity. Or, else you can use viscosity modifier, which will also block the water, cement or cementitious material and sand together. So, bleeding would be reduced.

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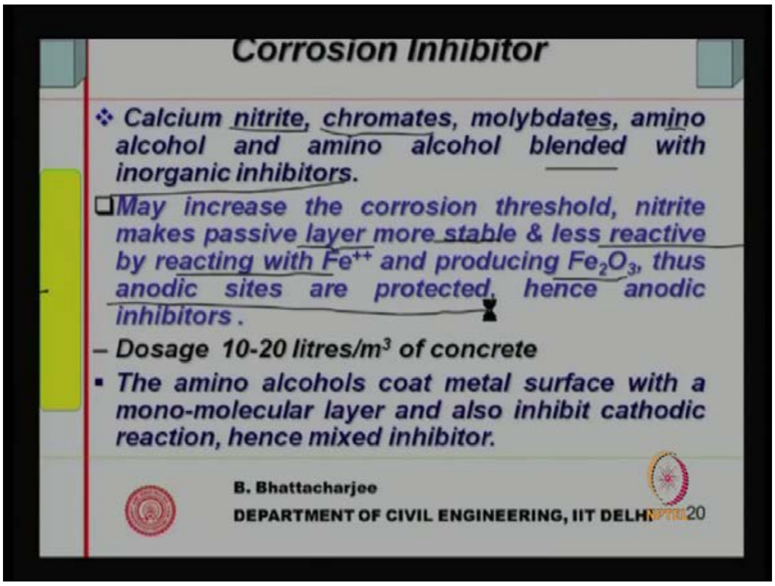

Corrosion Inhibitor

- Calcium nitrite, chromates, molybdates, amino alcohol and amino alcohol blended with inorganic inhibitors.

☐ May increase the corrosion threshold, nitrite makes passive layer more stable & less reactive by reacting with Fe^{++} and producing Fe_2O_3, thus anodic sites are protected, hence anodic inhibitors .

– Dosage 10-20 litres/m^3 of concrete

- The amino alcohols coat metal surface with a mono-molecular layer and also inhibit cathodic reaction, hence mixed inhibitor.

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That was viscosity modifier. Then, we have got corrosion inhibitor. They can stop the corrosion process, because rebar corrosion is one of the major problem – one of the major durability problem in concrete. And, corrosion inhibitor stops this. How do they do it? They actually can block anodic or cathodic reactions. Examples of these are nitrite – calcium nitrite, chromates, molybdates, amino alcohol; and, blended it inorganic inhibitors. Calcium nitrite, chromates, molybdates, amino alcohol and amino alcohol blended with inorganic inhibitors – they are the ones; they are the examples of corrosion inhibitors. They can act in two different ways. May increase the corrosion threshold; so, the point at which corrosion – active corrosion starts; they may just increase that. They might delay the starting of corrosion. Nitrites helps in making what is called a passive layer more stable.

Now, a passive layer is the oxide coating over ion or rebar, which protects the steel, because steel you cannot… Iron is not a stable thing; it will get oxidized. But, if it does not get oxidized to at a very fast rate or to a product, which is dangerous; then, it is tolerable. So, dense product at the surface oxide film at the surface of the steel bar is sometime desirable. So, generally, they increase corrosion threshold by making that passive layer stable. So, the oxide layer that is formed over the rebar becomes stable. Nitrite acts that way. And, they are less reactive. So, they protect the steel. So, less reactive by reacting with Fe and producing Fe 2 O 3. So, they might first react with Fe and then allow production of Fe 2 O 3. Thus, anodic sites are protected. So, these are anodic inhibitors. Anodic inhibitors actually protect the steel by ensuring that, oxides are stable at the surface of the steel, so that ion does not get dissolved; the protective layer protects this. These are called anodic inhibitors. Nitrites essentially does this job. They react maybe with the Fe; but, then finally, Fe 2 O 3 or such oxides would be forming at the surface of the rebar, because it will breakdown. Reacting with Fe and then producing Fe 2 O 3 at the second stage; and thus, protecting the steel.

Oppose to this, there are some others, which are cathodic inhibitors. Now, dosage of 10 to 20 liter per meter cube of concrete as we can see. Amino alcohols for example, coat metal surface with a mono-molecular layer and also inhibit cathodic reaction. Hence, mixed inhibitor. So, the mixed inhibitor both protects anodic sides and cathodic sides. Rebar corrosion is an electro-chemical process. And, in the electro-chemical process, there are some anode in the rebar, some cathode in the rebar. So, the anode – if the coating is there on top of the anode, Fe cannot dissolve; at anode, Fe dissolves; at cathode, cathodic reaction takes place. We will discuss this sometime later on when we talk of rebar corrosion. Now, amino alcohols coat the metals and therefore inhibits the anodic reaction. But, also inhibits the cathodic reaction; and hence, mixed inhibitor.

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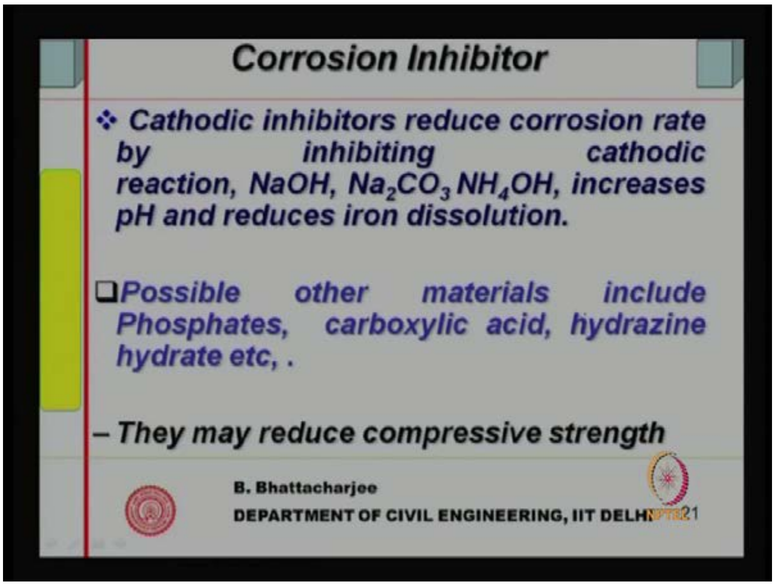

Corrosion Inhibitor

- ❖ Cathodic inhibitors reduce corrosion rate by inhibiting cathodic reaction, NaOH, Na_2CO_3 NH_4OH, increases pH and reduces iron dissolution.

- ❑Possible other materials include Phosphates, carboxylic acid, hydrazine hydrate etc, .

– They may reduce compressive strength

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Now, what is the cathodic reaction? Cathodic reactions are essentially the reaction between oxygen and hydroxide absorbing electron to form hydroxyl ion. So, if you can stop that reaction, that is cathodic reaction we stop. Then, anodic reaction will automatically stop. Somewhere in the circuit, you have to break it. So, cathodic inhibitor reduce corrosion rate by inhibiting cathodic reaction. Stop the cathodic reaction of oxygen and water, which takes electron to form hydroxyl ion. So, sodium hydroxide, sodium carbonate, ammonium hydroxide increases pH and reduces iron dissolution. So, they increase the pH and reduce… because already there are certain amount of hydroxyl ion in the system. No further hydroxyl ion can form. It reduces the formation of more hydroxyl ion.

And, that is how they protect it cathodically. Phosphates, carboxylic acid, hydrazine, hydrates, etcetera. Hydro (( )) acid is HN 3, is hydrogen and nitrogen. So, I think it is NH 3 is ammonia. This is HN 3. So, that is hydroic acid. Hydrazine hydrate is one of the compounds (( )) But, it has been observed that, some reduce the compressive strength. There are some side effect from corrosion inhibitors. Therefore, they may reduce the compressive strength. So, that is not very popular, but still there are some available… And then, can protect the rebar to certain extent. But, they have their own negative effect. So, that has to be remembered.

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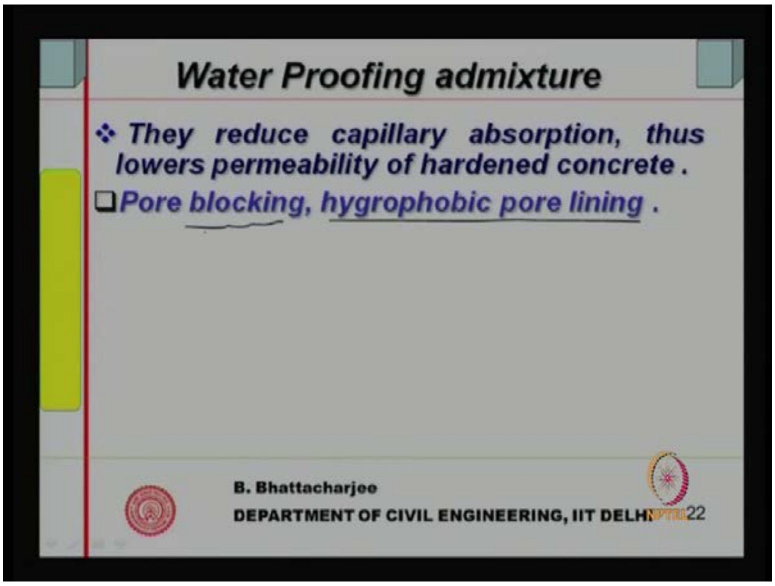

Water Proofing admixture

- They reduce capillary absorption, thus lowers permeability of hardened concrete.
- ☐ Pore blocking, hygrophobic pore lining.

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Water proofing admixtures – they reduce the capillary absorption; thus, lower permeability of hardened concrete. These admixtures when you add to the concrete system during mixing; in the later stage, they act on to the capillary pores in some manner or other and lowers the permeability of hardened concrete. They can be of this kind like pore blocking treatment or hygrophobic pore lining treatment. So, pore blocking treatment, hygrophobic, that is, water repelling pore lining treatment. Now, hydrophobic property is essentially because of the contact angle between this material and water. Water and normal surface of concrete or many other things, glass let us say; it is 0. Contact angle is 0. So, water is a waiting liquid for this kind of material. Surface tension properties – I think we discussed sometime or we may be discussing sometime later on. So, the surface tension properties…

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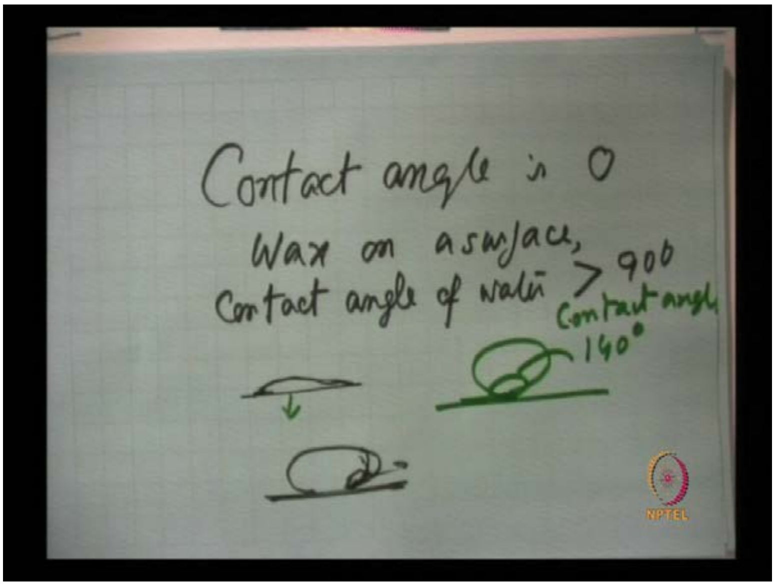

Contact angle is 0

Wax on a surface,

Contact angle of water > 90°

Contact angle 140°

Just let us quickly we can have a look at this. It will be something like this. Water you put; water spreads like this. So, the contact angle – this angle is 0. But, if you look at mercury; mercury on the other hand will form some sort of bubble. This angle is 140 degree with glass. Therefore, mercury is a non-waiting liquid. So, this we call as contact angle. Now, contact angle of water with surface is contact angle of water with most of the surfaces is 0. Contact angle is 0. But, if I can make it; if the surface changes, let us say waxy surface – wax on a surface; contact angle of water – all changes; contact angle of water becomes greater than 90 degree. Therefore, in a waxy surface, you find that, water is possibly not spreading easily; not spreading. So, it is forming some sort of a bubble-like mercury does in glass. Therefore, this hydrophobic pore lining uses this principle.

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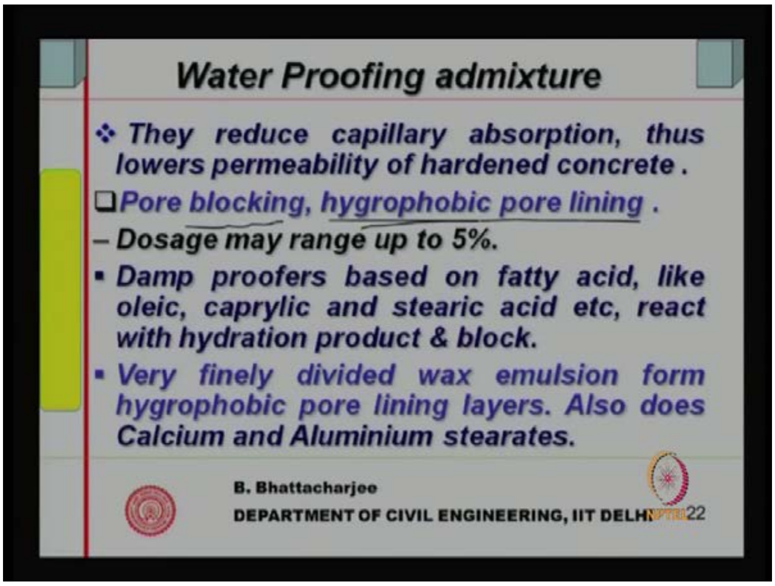

Water Proofing admixture

- They reduce capillary absorption, thus lowers permeability of hardened concrete .

☐Pore blocking, hygrophobic pore lining .

– Dosage may range up to 5%.

- Damp proofers based on fatty acid, like oleic, caprylic and stearic acid etc, react with hydration product & block.
- Very finely divided wax emulsion form hygrophobic pore lining layers. Also does Calcium and Aluminium stearates.

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Pore blocking is simply blocking the pore. Dosage may range up to 5 percent. So, these damp proofers are based on fatty acid, oleic, caprylic, stearic acid, etcetera; react with hydration product and block; that means they will react. So, pore blocking – blocking product will react with substrate – mainly, the calcium hydroxide and produce CHS-like product, which can block the pore. So, if these materials are added to the concrete, they can come… They should be able to migrate to the capillary pores at the surface and react with the substrate itself later on to form such products, which will block the pore. So, fatty acids like oleic, caprylic and stearic acid, etcetera – they react with hydration product and block. Wax emulsion forms hygrophobic pore lining layers; and then, of course, calcium and aluminum stearates. Therefore, hygrophobic pore lining layers.

Now, this should do what? When they are coated on to the capillary surface; they come on to the capillary surface; the contact angle of water change. Water wants to… When water is trying to enter… When water by capillary suction… the (( )) of water by capillary suction becomes then difficult like mercury. Mercury you cannot force into… Mercury – you just do not go on its own into any pore, any capillary; you have to force it. So, here also, on its own, once the surface changes, it becomes hygrophobic. Liquid water cannot penetrate into it; you have to force it. But, vapor can of course move. So, these are hygrophobic lining.

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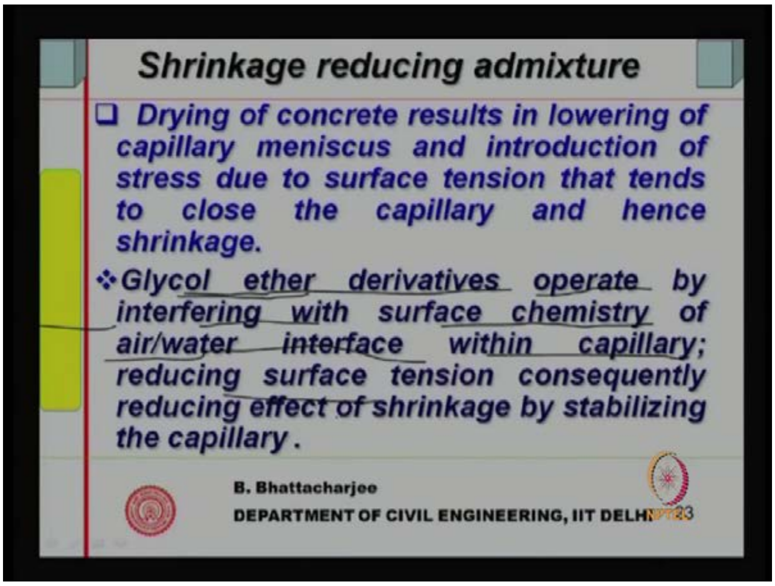

Shrinkage reducing admixture

- ❑ Drying of concrete results in lowering of capillary meniscus and introduction of stress due to surface tension that tends to close the capillary and hence shrinkage.
- ❖ Glycol ether derivatives operate by interfering with surface chemistry of air/water interface within capillary; reducing surface tension consequently reducing effect of shrinkage by stabilizing the capillary.

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There were varieties of other materials in this line of course, which does the job. But, then generically, there are two types: one is hygrophobic pore lining and another is pore blocking treatment. Then, there are shrinkage reducing admixtures. Drying of concrete results in lowering of capillary meniscus; and, since capillary meniscus will lower, the stress is introduced due to surface tension forces. Surface tension forces would tend to actually introduce a kind of stress at the capillary boundaries, because it is lower. When the capillary meniscus is lower, this surface tension forces… because it was at a balanced condition. Now, it has got lowered, because some drying has occurred. And, there will be some surface tension forces that tend to close the capillary and hence shrinkage. So, capillary will try to collapse under this surface tension forces. So, shrinkage do occur and then of course gel pores will also become empty. The water will move out from the gel pores subsequently and there could be shrinkage of concrete. So, drying – there is a shrinkage of paste and hence the concrete occurs.

Now glycol and other derivatives operate by interfering the surface chemistry. So, glycol and other some derivatives… For example, glycol and other derivates… Some of its glycol ether derivatives – they operate by interfering with the surface chemistry of air water interface within capillary. Thus, reduce the surface tension and consequently, reducing effects of shrinkage by stabilizing the capillary. If you look at it, air-entraining agent also reduces the surface tension. But, it has got a head and tail; one of them being hydrophobic and another being hydrophilic. So, hydrophobic side actually traps the air bubble. But, here this will not happen. This simply changes the surface tension at the surface tension of the water at the air-water interface within the capillary. And therefore, surface tension is reduced and shrinkage action is reduced. So, that is what it does; it does not have a tail, which can entrap air. So, no bubble formation could occur; but, only surface tension reduction will occur. So, this was shrinkage reducing admixtures.

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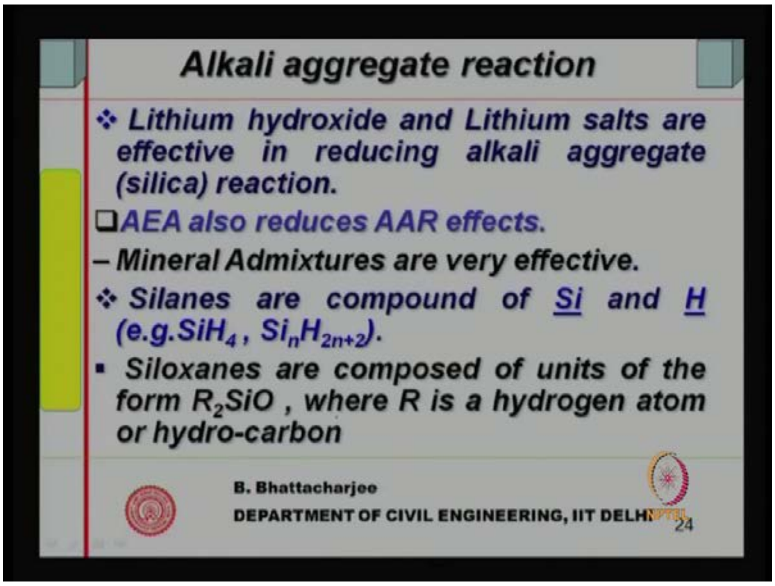

Alkali aggregate reaction

- ❖ Lithium hydroxide and Lithium salts are effective in reducing alkali aggregate (silica) reaction.
- ❑ AEA also reduces AAR effects.
- – Mineral Admixtures are very effective.
- ❖ Silanes are compound of Si and H (e.g. SiH_4 , Si_nH_{2n+2}).
- ▪ Siloxanes are composed of units of the form R_2SiO , where R is a hydrogen atom or hydro-carbon

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Then, we have got alkali aggregate reaction inhibiting admixtures. Now, alkali aggregate reaction – as you know, some of the aggregates, some of the minerals present in aggregate can react with sodium and potassium hydroxides that would be present in cement water system, because sodium oxide and potassium oxides are present in cement. They are there in the cement usually in small quantity. And, this might form sodium hydroxide and potassium hydroxide. Now, these ones will react with some silica mineral forming alkali silica gel. And, this gel can adsorb (( )) and expand in volume – result in cracking of concrete. We will again deal with this somewhat later on when we talk of durability of concrete. But, then there are some inhibitors, which can stop this kind of reaction. Of course, you have other means of controlling them.

But, inhibitors can also be used. For example, lithium hydroxide or lithium salts are effective in reducing alkali aggregate reaction, because sodium, lithium, potassium – they belong to same group in the periodic table. So, lithium replaces sodium. And, lithium silicates gel… It is not gelatinous. This does not cause any expansion. So, air-entraining agent also reduces the alkali aggregate reaction effects somewhat, because the air boils, which are available; the expansion can be taken. And, mineral admixtures are very effective in this. But, mainly like fly ash addition in the beginning; or, granulated ground blast furnaces slags – they are very useful. Compounds like silanes, which are silicon and hydrogen compound like SiH 4 or Si n and H 2 – this sort of formula. These are called silanes. So, silanes compounds. And, siloxane are composed of units from R 2 SiO; where, R is the hydrogen atom or hydro carbon. So, R 2 SiO, H 2 SiO to any other CH 3, etcetera. So, these are siloxanes. So, silanes and siloxanes materials.

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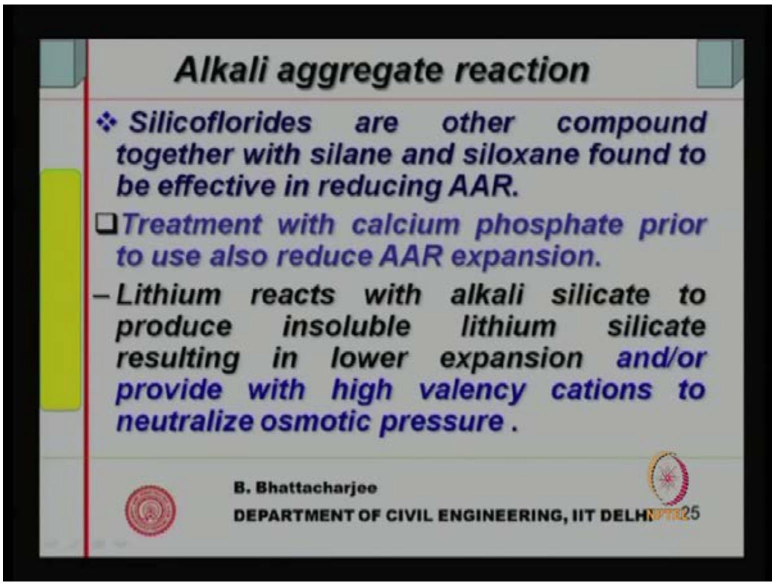

Alkali aggregate reaction

- ❖ Silicoflorides are other compound together with silane and siloxane found to be effective in reducing AAR.
- ❑ Treatment with calcium phosphate prior to use also reduce AAR expansion.
- – Lithium reacts with alkali silicate to produce insoluble lithium silicate resulting in lower expansion and/or provide with high valency cations to neutralize osmotic pressure .

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Then, silicoflorides together with these ones – silicoflorides are the other material. They are found to be effective in reducing alkali aggregate reaction. In fact, silanes and siloxanes are used in water repelling system as well, water proofing system as well. We might look into this sometime in connection with surface coating and durability of concrete. But, silicoflorides together silanes and siloxanes also are found to be effective in alkali for reducing alkali aggregate reaction. Calcium phosphate prior to use, also reduce… If you use calcium phosphate with the aggregate prior to their use, this also reduces the alkali aggregate reaction expansion. As I told you, lithium reacts with alkali silicate to produce in soluble lithium silicate. So, this does not form gel; and therefore, load expansion. And, they also provide with high valency cations to neutralize osmotic pressure, because the pressure, which causes cracking, has something to do… It is osmotic pressure in the system. We will discuss about that sometime. So, lithium – in a second way, it acts is, it provides with high valency cations to neutralize osmotic pressure. So, that is how alkali aggregate reaction can be controlled by use of this kind of innovating admixtures, alkali aggregate reaction inhibiting admixtures.

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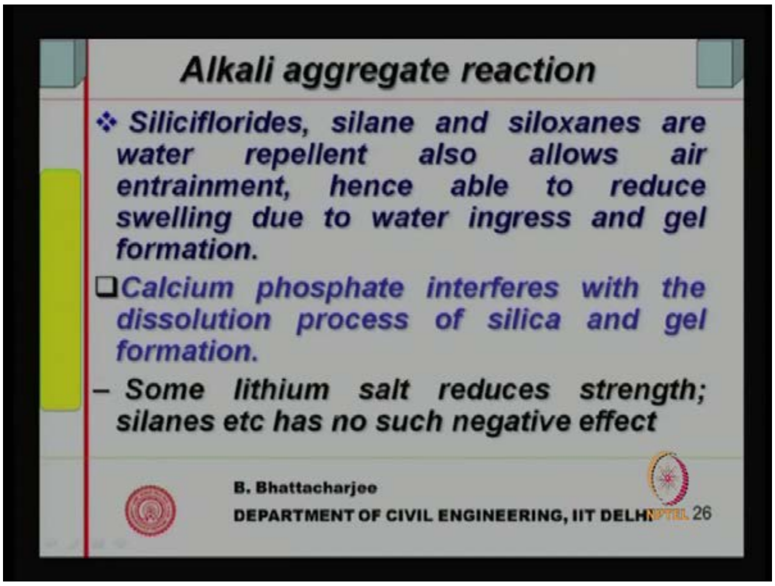

Alkali aggregate reaction

- ❖ Siliciflorides, silane and siloxanes are water repellent also allows air entrainment, hence able to reduce swelling due to water ingress and gel formation.
- ❑ Calcium phosphate interferes with the dissolution process of silica and gel formation.
- – Some lithium salt reduces strength; silanes etc has no such negative effect

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Silicoflorides, silanes, siloxanes – water repellent; as I told you, they are also water repellent. And, it allows air entrainment; hence, able to reduce swelling due to water ingress and gel formation. So, they are used in water repelling; as I told you, water proofing system. Calcium phosphate interferes with the dissolution process of silica and gel formation. These are some other material used for alkali aggregate reaction inhibitors. Some lithium salt reduces the strength; silanes etcetera has no such negative effects. They are reduced as, used as water reducing agent as well as can inhibit the… And, there is another side of it. Since they can reduce the water ingress, water ingress is a must for alkali aggregate reaction. So, that is another effect of silanes, silicoflorides and siloxanes.

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Summary

Water reducing agent
Accelerators, Retarders
AEA, Corrosion inhibitor &
Misc admixtures

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I think that is what finishes our discussion on chemical admixtures. So, in total, what we have seen is, we have seen actually water reducing admixtures, which in more detail than any other admixtures, because they are… In the last two lectures actually we have seen. Because they are the one, 60 percent of the admixtures are these ones. They are the most common ones; then, follows accelerator, retarders. And, we also looked into air-entraining agents, corrosion inhibitors, shrinkage reducing admixtures and alkali aggregate reaction inhibitors, etcetera. So, I think with this, we finish our discussion on chemical admixtures. In the next lecture, we will look into mineral admixtures.

Thank you very much.