

Admixtures and Special Concretes

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Lecture - 18

Chemical Admixtures: Air entrainers - Part 1

Okay, so in the last part we talked about retarding admixtures for long haul and regular applications. Hydration control additives like I gave an example of Delvo from Master builders where they are able to control the setting for a period of 6 to 8 hours and then accelerate the concrete setting and hardening so that by one day you get fairly normal strength. Then we also talked about surface retarders which are important to get the kind of surface finishes and kind of aesthetic appearances that sometimes you desire.


Applications of Air entrainers:

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Applications of air entrainers

- Protect against damage due to freezing and thawing cycles
- Side effects:
 1. Improve workability
 2. Reduce segregation and bleeding
 3. Reduce strength due to increased porosity



Today we will continue the discussion on chemical admixtures with air entrainers. So after super plasticizers perhaps the most used chemical admixtures are air entrainers. Super plasticizers and set regulators, accelerators, retarders after that you have air entrainers are perhaps the most used chemical admixtures. So the primary idea of using air entrainment is to protect against damage due to freezing and thawing cycles. That is the primary thing to be done. Damage due to freezing and thawing cycles.

Now what happens upon freezing? Why are we worried about that? Water expands right? Whatever free water is present in the concrete will expand because water has this anomalous behavior that it actually does not contract but it expands upon freezing and this expansion leads to stresses in the concrete. Now when this happens and subsequently the ice becomes water again that is thawing, this water is essentially trying to move into the microstructure of the concrete. Whatever free water is there is trying to move through the pores up and down. So this movement of water in the very fine pores that is leading to the strain in the concrete. It leads to the creation of strain and the resultant stresses lead to damage in the concrete. Now because you are putting air bubbles inside or air entraining agents inside, they also act like ball bearings and improve the workability of the concrete. You will essentially end up having concrete which has a better workability when you use an air entraining agent and in some instances indeed especially when you do plastering for instance. Many people use air entrainers for the purpose of making the concrete a lot more consistent and easy to apply rather than actually using it for freezing and thawing damage because plastering is done everywhere.

Using air entrainers and plaster is a very nice way to actually make it smooth to apply, better consistency to apply. Air entrainers also reduce segregation and bleeding because of the way that they are also surfactants, they will also not allow water to freely rise and because of that they will help in reducing segregation and bleeding and obviously because you are putting air in your concrete you are reducing the solid volume of the concrete so strength is going to reduce. Generally for every 1% air you reduce the strength by 5 to 8%.

So when you do a mix design and decide that for your M40 concrete you need to use a water cement ratio of 0.4, if you want to make the same concrete air entrained you will have to obviously choose a water cement ratio that is lower than 0.4 maybe 0.36. So when you do air entrainment you can expect that there will be a loss of strength because of the air voids.

Freezing and thawing damage:

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Freezing and thawing damage



- Physical problem!
- Could cause 3 types of failure:
 1. Paste failure
 2. Aggregate failure – D cracking
 3. Aggregate failure - Popout

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Now before we talk about air entrainment let us talk a little bit about freezing and thawing, try and understand what the cause of this damage is. It is a physical problem unlike a chemical reaction. This is a physical problem, water transformation to ice and back to water. It can cause 3 types of failure i.e. failure of paste, failure of aggregate in the form of what we call as D-cracking and failure of aggregate in the form of what we call as pop-out. Let us look at what these 3 types of failure are.

Paste Failure:

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Paste failure



- This is related to the failure of the paste.
- Parallel cracks form in the paste and proceed inward from the places where concrete first becomes highly saturated with water.
- Sometimes, scaling of the top surface can occur. Scaling is exacerbated when deicing salts are used.

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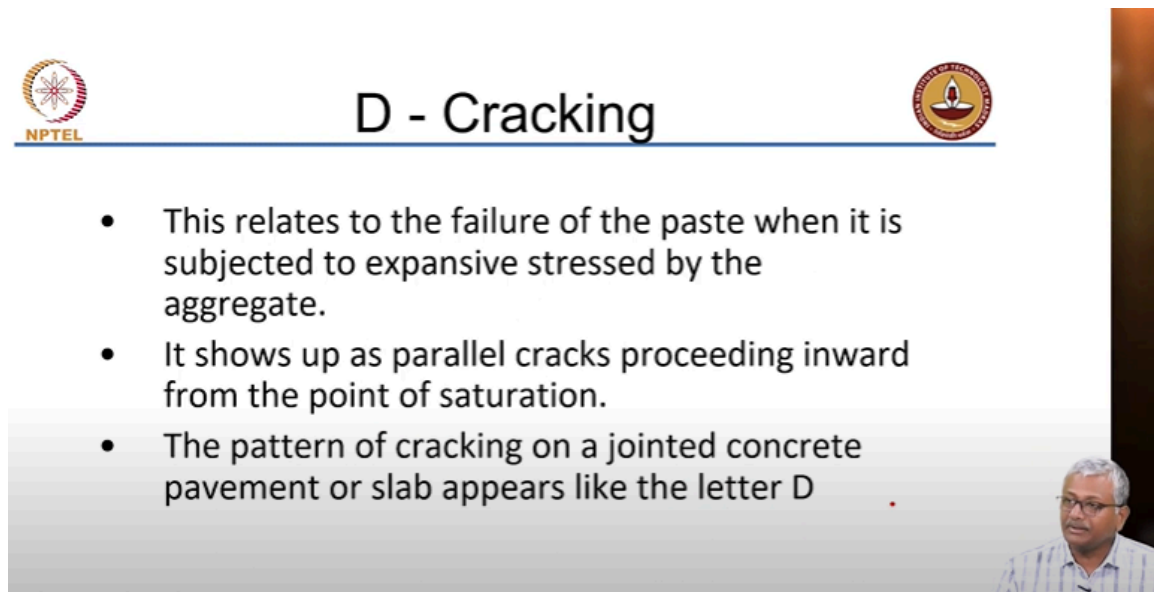


So paste failure essentially happens because of the movement of water within the paste, this water which is freezing and then thawing is causing movements within the constricted pore spaces that are present in the paste. So if you imagine a surface of the concrete which is the highest portion of your concrete, the freezing basically will start from the surface and wherever water availability is obviously there from the external environment that is going to add to your freezing damage. So because of this ice formation on the top surface you may also additionally get apart from freezing and thawing you can also get scaling damage and this scaling damage becomes worse when deicing salts are used. It is interesting because deicing salts are used to reduce the formation of ice but because of the osmosis that happens of these salts into the concrete and the result in crystallization of these salts you can actually cause more and more scaling when the salts are used. So it is a tricky situation because you do not want ice to form so you put salt but then the salts themselves cause scaling. So this is called deicer salt scaling.

The scaling due to freezing and thawing is only happening because water is getting into the pores expanding and then failing the surface of the concrete. That is basically the paste failure that happens because of scaling.

D Cracking:

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The slide features the NPTEL logo on the left and a circular emblem on the right. The title "D - Cracking" is centered at the top. Below the title, there are three bullet points. In the bottom right corner, there is a small inset image of a man with glasses speaking.

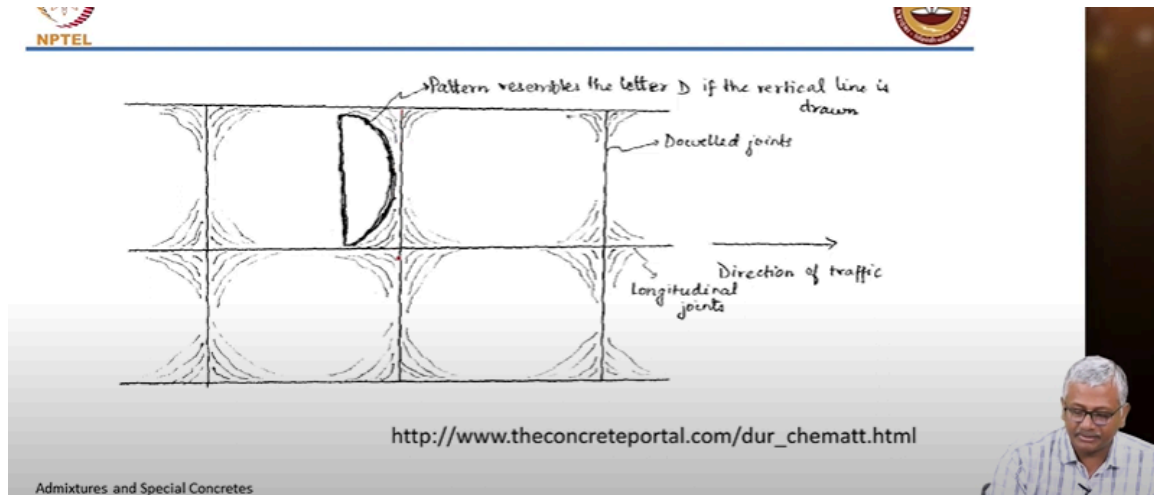
D - Cracking

- This relates to the failure of the paste when it is subjected to expansive stresses by the aggregate.
- It shows up as parallel cracks proceeding inward from the point of saturation.
- The pattern of cracking on a jointed concrete pavement or slab appears like the letter D

So D-cracking is related to failure of the paste when it is subjected to expansive stresses by the aggregate. Now certain aggregates may absorb moisture depending on their porosity levels they may absorb moisture and the moisture may start expanding within the aggregate. When it converts to ice it may start expanding in the aggregate. So the

aggregate where the moisture is turning to ice now starts exerting a pressure on the surrounding paste and leads to cracking in the paste. Now the name D-cracking is arising from the fact that this type of cracking was first seen in concrete pavements where the cracks were in the pattern D. I will just show you just now.



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So these are concrete pavements so you have your joints, you have the transverse joint and the longitudinal joints. Joints are points where water can actually get in relatively easier as compared to other locations. So water basically penetrates the joints and then if there are aggregates that are moderately porous inside they will absorb that moisture and that moisture transforms to ice during freezing cycles and that leads to cracking of the paste. So essentially water concentration is going to be quite high here at that joint and because of that the cracks start appearing almost in a parallel fashion. So these cracks if you join them by a straight line here, do not ask me why, but you join them by a straight line here it becomes a D. I would have said put like this and make it an O but maybe not. The classical literature refers to this as D-cracking. It forms the pattern D if the vertical line is strong.

Popouts:


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Popouts

- Popouts are caused when porous aggregates on the surface of concrete are subjected to expansion on freezing.
- A part or the whole of the aggregate piece cracks and pops out.
- Sometimes, a mortar flake can also pop off as a result of the expansion of an underlying aggregate.



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So the failure was cracking in the paste because of moderately porous aggregates which were absorbing moisture and leading to some expansion. In the case when aggregates have slightly higher porosity, if you have porous aggregates on the surface of concrete what may actually happen is the aggregate itself may expand and get released from the mortar. It is not staying back in the mortar, the expansive stress is so much that it is just popping out. That is called a pop-out. A part or whole of the aggregate piece cracks and pops out. The aggregate can completely come out or only a part of it gets scaled off or removed from the surface. So on the surface of concrete where pop-out is there, this appears like pop marks. It is quite interesting to see, mostly in locations where you have freezing damage.


Mechanism of freezing and thawing:

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Mechanism of F&T

- Water expands by 9 – 10% upon freezing. Thus, the critical saturation of a pore in concrete is about 90%.
- It must be understood that freezing point in small pores is depressed to a large extent. In fact, in some of the small pores in concrete, freezing does not occur until temperatures as low as – 40 °C. Also, the presence of other ions in the pore solution also depresses the freezing point.
- If the concrete remains frozen through its lifetime, then not much of a problem occurs. The deterioration occurs only if there are successive cycles of freezing and thawing.




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So why is freezing and thawing happening? Obvious reasons, obviously water transforms to ice and the expansion level of water upon freezing is 9 to 10%. So if concrete has a saturation level of more than 90% that means in freezing conditions the porosity cannot take up that water. So when water inside a pore starts freezing it expands and pushes out the balance of the water and when it starts pushing this water out it has to start flowing through the very small porosity of the concrete and this flow of water through small pores leads to hydraulic pressure. So that is the primary idea but before that we need to understand that the pores can be very small and when the size of the pores reduces the capillary pressure is so high that freezing cannot happen easily. Further if you remember when cement reacts with water there are alkali ions that are getting dissolved in the water that is why our pore solution is highly alkaline and because the pore solution is alkaline and it is not pure water it depresses the freezing point even further. So in some instances freezing of concrete or water inside concrete may not happen until you reach very low temperatures especially when you go to very small pores in concrete your freezing may not happen until -40°C. So one way to avoid freezing and thawing damage is to simply use high performance concrete or high strength concrete with very low water cement ratio the water inside is not going to freeze at all. Unfortunately most high performance concrete are designed in such a way that their pores are so small that water really does not freeze in these pores and the ionic concentration of pore solution depresses the freezing point even further. It raises the boiling point and depresses the freezing point.

Theories of damage:

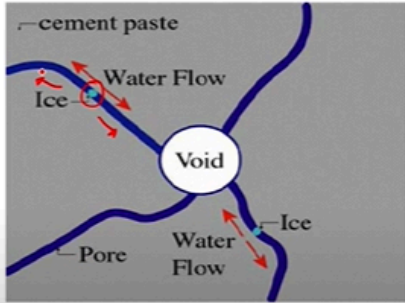
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Theories of damage – paste failure




Hydraulic pressure theory: Water in the large pores near the surface of the concrete is the first to freeze. The freezing of concrete proceeds in a front parallel to the surface. The expansion of water in the large pores on freezing drives out the unfrozen water into the paste. The travel of water through the paste generates a hydraulic pressure. The longer the path of flow of water, the higher the pressure generated. If the flow path is longer than a critical distance (0.2 mm for concrete) then failure occurs.



Source: PJM Monteiro, U. of California, Berkeley

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So in regions where concrete is frozen throughout its lifetime where freezing and thawing do not happen, once the water freezes it becomes ice and then it does not become water again. In such cases there is no problem like what we call permafrost. In such cases there is no change in the volume up and down which leads to cycles of freezing and thawing. The problem happens only when there are cycles. These cycles are the one that cause damage because there is movement of water inside the concrete. So this was described by what is called the hydraulic pressure theory as I said when water in the pores starts transforming to ice it expands and starts pushing the remaining water in the outward direction from the pore. So the water is traveling through the extremely small pores where it is held by capillary pressure and that leads to a strain getting generated in your system.

When you do air entrainment what happens? You provide a nice void space inside. The water that is there comes into the void and now has enough space to expand. So you are providing these air entraining bubbles to allow the water to expand into ice rather than flowing long distances which causes stress. If the flow path is longer than a critical distance generally it is taken to be about 200 μ m in concrete then failure can happen. That means the pressure generated by the flow of water beyond a distance of 0.2 mm is large enough to exceed the tensile capacity of the concrete. For concrete always fails in tension, never in compression. So tensile capacity of concrete is getting exceeded when the moisture or water in the pores flows to a distance more than 200 μ m. So that is the

hydraulic pressure theory. In some instances people also look at osmotic theory but it is not as popular as the hydraulic pressure theory.

Salt scaling:


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Salt scaling

The dissolved deicing salt (typically, NaCl, CaCl₂, MgCl₂) concentrates in the pores of the paste that are partly frozen, and results in a true osmotic pressure that acts along with the other internal pressures.

This exacerbates the problem of freezing and scaling in the surface layers of concrete, which are highly susceptible due to their inferior properties compared to the bulk of concrete.



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Salt scaling, as I said you put salt on the surfaces of concrete to prevent damage or to prevent the formation of ice but these salts can start concentrating over time and then you have an osmotic pressure that acts along with other internal crystallization pressures and that leads to scaling of the surface. This is a realistic problem in many of the pavements that are there in western countries where they put ice to put salts on the surface of the pavement to prevent any skidding of the vehicles. So there is a lot more additional literature on salt scaling also that talks about the performance of concrete with different binder systems which is a fairly interesting subject to look at but we do not really worry too much about this because we do not have this problem in most of our places. Even in the places where a lot of freezing is there, I have travelled in Ladakh where the typical thing is to put sand on the surface of the pavement. They do not really put salts there. At least I have not seen any salt application on pavements like this.

Protection against paste failure:

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Protection against paste failure



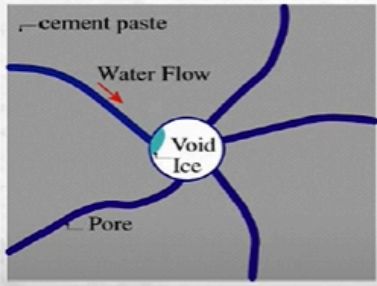
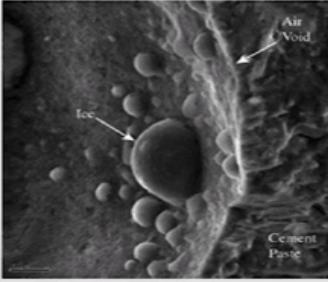
- Use of air entraining agents: Creation of well-distributed air void system (Critical distance: 0.2 mm)
- Low w/c concrete – very small pore size makes freezing difficult

So air-entraining agents basically create a well distributed air void system. Now what is critical with air-entrainment is not just the total amount of air that you need to put in. You also need to ensure that these air voids are distributed uniformly in the concrete so that the critical distance can be less than 200 μ m. How do you do that? How can you ensure that? Salt mixing is obviously needed to ensure that the air-entraining agent is acting but how do you produce this distance between air-entraining, the bubbles? So water should not be able to travel more than 0.2mm. How do you ensure that? There is no way you can ensure that. You can only hope that it happens but you need to check. So this checking has to be done by actually taking the hardened concrete, polishing the surface and studying under the microscope. This is an ASTM test again. So this test method basically tells you how you do an air void analysis inside your concrete that helps you estimate the total air as well as the critical distance between the air voids. This is a very painstaking test. You need to sit in the microscope for at least 3 to 4 hours to really go through even one sample and the sample has to be well polished and then what happens is you have a stage which is moving in the X and Y direction. So you traverse in the X direction first and then you come down to the X line in Y direction and then traverse again. Each time that you traverse when you are viewing under the microscope, the crosshair of the microscope comes and rests on some object in your concrete either on a coarse aggregate or on a fine aggregate or an air void. So there is a counter. So you need to count the number of times this intersects an aggregate, intersects an air void. It is a very difficult exercise. In laboratories there are people who are working on this day in and day out. Imagine what a boring job it must be but that is how it is. But of course when you want to qualify the admixture performance this has to be done once or twice. When you get confidence that a certain dosage of admixture is able to produce a certain air content and also able to produce distances between the air voids which are within this critical distance, in such a case you do not have to do it again and again unless there is a problem with some performance. Freezing and thawing damage has been noticed in spite

of the concrete being air entrained. In such a case you may want to bring a sample from that concrete back to your lab and assess it that becomes more of a forensic analysis. As I said, low water cement ratio concrete, very small pore sizes make freezing and thawing difficult. When you have pore sizes that are extremely small and the presence of ionic concentrations of sodium, potassium and alkali present in the air view system you are going to depress the freezing point even more. So freezing does not happen in this case.

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Source: PJM Monteiro, U. of California, Berkeley




So again this is again a picture from University of California Berkeley where very nicely they are showing the formation of ice in the walls of a void, air void. What is the difference between a void and a pore? Voids are usually discrete. Pores are more or less continuous channels through which your water is flowing.

Admixture Chemistry:

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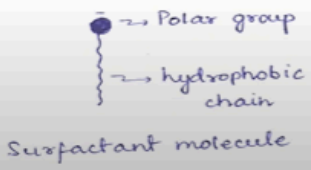
Admixture chemistry

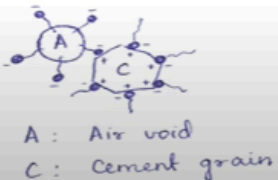


Air-entraining agents are also surface-active chemicals.


Unlike the water-reducing surfactants, the hydrocarbon chain does not have any polar groups, and is entirely hydrophobic.

The hydrophilic polar groups ($-\text{COO}^-$, $-\text{SO}_3^-$, $-\text{NO}_3^-$) are similar to water reducers.





A : Air void
C : Cement grain



So in terms of the admixture chemistry there is some similarity but a lot of difference between the chemicals that are used as air entraining agents and as water reducing chemicals. So here in water reducers if you remember there was a main chain and there were side chains and there was charge on the main chain that led to either electrostatic repulsion or when the side chains were bulky it led to steric repulsion, steric hindrance. In the case of air entrainment the molecule is much simpler. All you have is a hydrophobic chain and a polar group at the end. So polar groups will have affinity towards water and it will reduce the surface tension of the water.

When you reduce surface tension of water what happens? It helps in generating more bubbles just like your detergents, your mixture detergent to the water and agitate, you produce bubbles. That is happening because surface tension is reducing. So these are similar to detergents, they are surface active chemicals. They do not have a main hydrocarbon chain which is hydrophilic. Here you have a polar group attached to a hydrophobic chain. Polar groups that are used here, carboxylate, sulphate, nitrate are similar to what you have in your water reducers. So a general scenario is these hydrophobic chains are stabilizing the air bubble whereas the polar group is oriented outwards lowering the surface tension of the water and making the air bubble stable. And because of this kind of a fact that the negative polar group also gets attracted to the positively charged cement particle surfaces, there is some electrostatic repulsion also that leads to perhaps some water reduction to some extent. Improvement in workability happens.

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(a) Formula of a typical air-entraining surfactant derived from pine oil or tall oil processing; (b) mechanism of air entrainment when an anionic surfactant with a nonpolar hydro-carbon chain is added to the cement paste.

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

Again another picture from the book by Mehta and Montiro, essentially the same. So this is one of the types of compounds, ibetic acid. Most of the entrainers are actually

derivatives from plants. There are plant derivatives, Vinsol resin, pine rosin and so on which are quite popular as water reducing air entraining agents. Even the chemicals that are used for foaming of concrete, what is the difference between air entrained and foamed concrete? Air entrained concrete and foamed concrete, what is the difference? Air entrained means we are protecting against freezing and thawing. Foamed concrete you are producing a special type of concrete which is intended not for main structural applications but for infill walls and for insulation. So there we are looking at water sorry air entrainment to the tune of nearly 40% of your concrete. Porosity of foam concrete is 40 to 50%. So it is almost like a shaving gel, shaving foam. You take a shaving foam and mix it with cement paste that is foam concrete. Whereas air entrainment you are getting an air entrainment of around 5 to 8% early, not more than that. That is to help reduce the damage in freezing and thawing. Foam concrete is not for freezing and thawing.