Advanced Concrete Technology
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Lecture - 08
Cement Chemistry – Part 3

Good morning everyone. In the last class, we were talking about evolution of hydration products and I was talking about different mechanisms by which hydration actually occurs. So you have the cement particles, which are present in various different sizes. The smallest ones come immediately into solution and rapidly lead to the formation of initial hydration products, but the larger particles, which are of the size 10-40 microns or above have a slightly different mechanism. The surface of these particles starts the dissolution very early.

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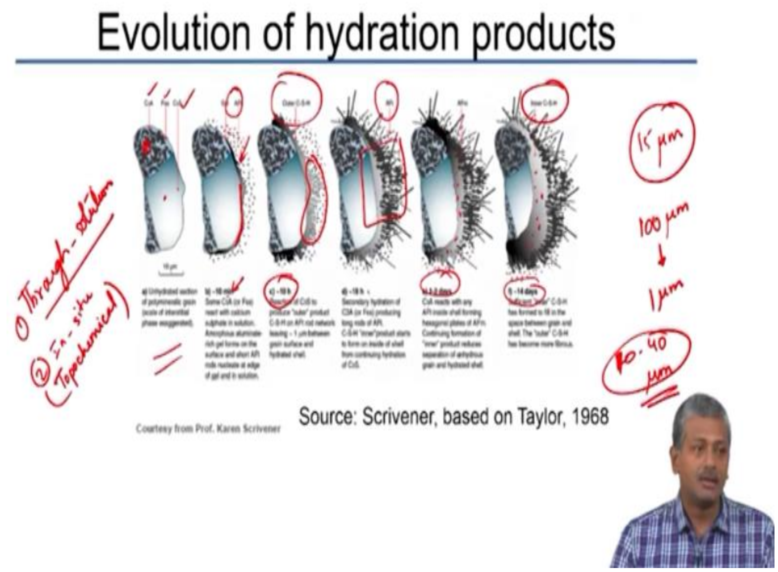

Evolution of hydration products

Source: Scrivener, based on Taylor, 1968

Courtesy from Prof. Karen Scrivener

But once you form the initial hydrate layer on the outside, which is composed of outer CSH and ettringite, the water then has to go through these layers to start hydrating the remaining unhydrated cement that is inside and once that happens, you have what is called an in situ or topochemical reaction that leads to the formation of inner CSH. So this automatically tells you that there is going to be some difference in the structure of the outer CSH and inner CSH.

In other words, outer CSH is forming rather quickly. The inner CSH forms after a considerable period of time. So if you look at the structure by about one day, you will see that mostly have only outer CSH, you will not be able to see the inner CSH on the calcium silicate grains. I will show you later that you can start picking out this inner CSH layer quite clearly after about 7 days of hydration.

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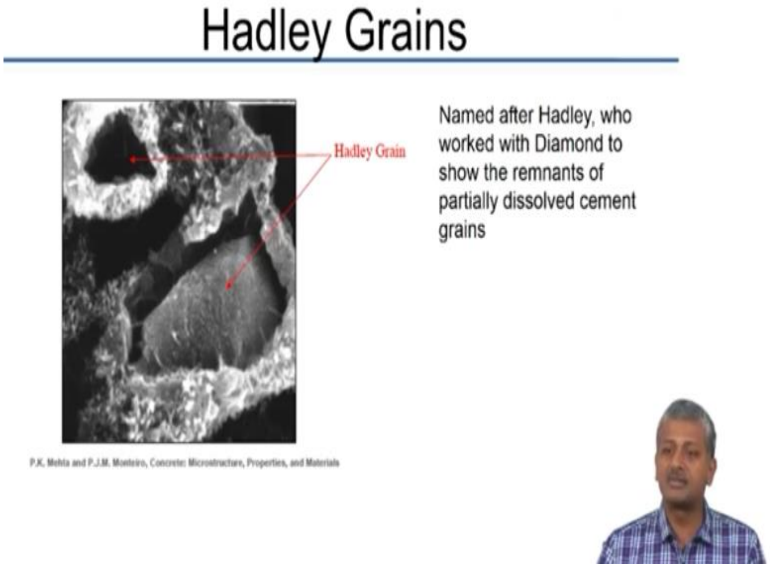

Hadley Grains

Named after Hadley, who worked with Diamond to show the remnants of partially dissolved cement grains

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

Now what happens is, in the initial stages, you may see that some of these particles, which are dissolving to the outside. I told you that there is dissolution from the surface of the particles to the outside that leads to the formation of the outer product. Some particles may be small enough that they completely end up dissolving and producing the hydrates on the outside leaving behind an empty shell. Some particles are small enough to leave behind an empty shell.

So you only have the hydrate layer surrounding the particle, but the particle itself is not there where it was earlier. This sort of a system is called a Hadley grain. This is named after Hadley who worked with Professor Diamond at Purdue University to show the remnants of partially dissolved cement grains. So these are cement grains that are partially hydrated on the outside and in this case you see actually a remnant of a cement grain, which has a gap between the grain and the hydration product, which is outside.

You see the gap there, that means that this grain is in the process of dissolution and producing the hydrates on the outer periphery. So this gap is getting created. In this case, the gap is completely filled up the entire space where the grain used to be earlier. So this must be true for smaller sized grains, which are dissolving outwards and forming the hydrate products around and leaving behind an empty shell in the place where the grain used to be earlier.

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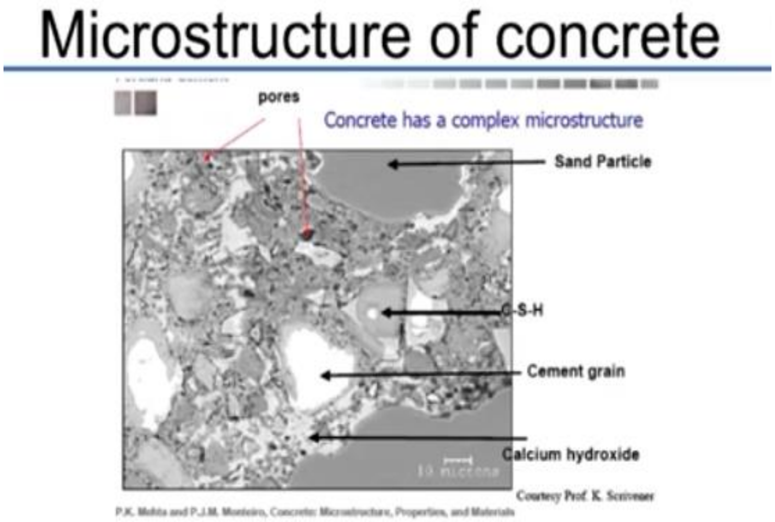

Microstructure of concrete

Concrete has a complex microstructure

Courtesy Prof. K. Scrivener

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

Now when you move towards the larger crystals, you form what is called inner and outer CSH. So one example is shown in this complex microstructure of concrete here. You can see that in concrete, you obviously have different phases, you have the sand particles, you have the cement grains, which are very white in colour here. I will tell you why that happens. You have particles which are almost completely hydrated.

You see this white cement grain and around it, you see a gray layer, what is being marked as CSH, calcium silicate hydrate and then you have these whitish deposits here. You see the whitish deposit around the aggregate and some in the paste, which has a slightly different shade of gray as compared to what is there around cement particles and probably different shade of gray as compared to what is there in that region.

So this sort of a microstructure is obtained from a backscattered electron image. That is called a backscatter electron image. So this backscattered electron microscopy is one part of your scanning electron microscopy, which you commonly call as SEM. Now here what happens is, you have a beam of electrons, which is incident on your object that you want to study and in backscatter your object is very finely polished.

So you have a very fine polish on your object, so the electrons that are impinging on your object will now get reflected, or backscattered. They will get scattered from the surface of the atoms, which are there in your sample and some of these atoms may get completely rebounded and these are the electrons that are actually captured in the backscatter detector to form a backscatter electron image. So now what sort of phases would appear bright?

Please remember in electron microscopy, we are trying to discern the features based on the electrons that are actually coming out of the sample. These electrons could be sample generated electrons or these could be the backscattered electrons that means the ones, which are impinging on the sample and simply rebounding. In what cases, would the rebound be higher? For phases that are denser, obviously. Rebound will be more for phases that are dense.

So more rebound means more electrons, that means it will be a brighter image. Of course in a cement paste or in concrete, the densest phase will be the unhydrated cement grains. That is why when you look in the backscatter image, you will see that the unhydrated cement grains look white in colour. Now of course, from the shape of the grain, you will be able to find out whether it is C_2S or C_3S. What do you think this particle is, the cement grain that is there?

Is it C_2S or C_3S? Please remember what is the particle shape of C_2S and C_3S? C2S is rounded crystals, which sometimes has striations on top. Of course, here you will not be able to see the striations clearly, but you can see that this is definitely not rounded. It is more irregular in shape and this is essentially a C_3S particle. You have a C_3S particle that is hydrating on the periphery. So you have the hydration on the periphery.

The CSH that is forming from the C_3S is a hydrated material. It is called water of hydration. CSH has got hydrated water molecules inside. That means automatically it’s density will be lower as compared to the original C_3S particle. So CSH appears with a lower density as compared to the original cement grains, because of which it appears to be darker than the original cement grains. Calcium hydroxide is a well defined crystal and because of which it appears slightly brighter than the CSH, but it is still not as bright as your cement grains.

Your silica particles have this nice gray colour, uniform gray colour, which you see here. Those are silica particles, which are present in the sand and that causes a slightly different shade of gray to be produced in a backscattered electron image. Now in these images, you are also able to make out the dark spots, you see the dark spots there in the microstructure. Those dark spots are nothing but the pores.

Now if these dark spots are very large, we won't call them pores, we will call them voids. Voids will be much larger in size as compared to pores. The other distinction between void and pore is void is a distinct 3-dimenstional object whereas pore may be a cylindrical sort of a system, which is not entirely captured in a 2-dimensional image. So this pore may be actually going deeper into the system. So it may be an interconnected network that you are not able to see in a 2 dimensional image.

We will again look at what pores and voids are later. Now one more thing you can see here interestingly is that the amount of calcium hydroxide that is there around the aggregate is substantially large. So around the aggregate, there is a large amount of calcium hydroxide to be formed and that is the common observation in many concretes is that calcium hydroxide tends to nucleate and grow in regions where there is space available.

Now why do think space is available near the aggregate because the density of the filling of the paste is not going to be as good near the aggregate as it is going to be away from the aggregate. Why do I say that again? In any concentration of packing, there is something called wall effect. The packing of a material near the walls of the container is never going to be as good as the packing away from the walls of the container.

Again, when you are, for example conducting your experiment with aggregates in the lab, you pack your aggregates in this cylindrical container. You pack it in layers, you compact the layers and so on to determine the unit weight or bulk density of the aggregate. Now what you will see is if you have a way of actually taking a snapshot of the cross section, you will see that the voids and pores that are left behind in the edges are much more than what is towards inside.

That is generally a tendency for packing to happen like that. It is called wall effect. Around the aggregate, you will obviously have a greater porosity as opposed to away from the aggregate and because space is available, a nice big crystal like calcium hydroxide finds it much easier to grow around the aggregate than in other regions. Why is calcium hydroxide forming once again, because of the precipitation of the solid from the calcium and hydroxyl ions, which are in the solution.

Which are because of the dissolution of the cement grain, you have the calcium ions, they are combing with the hydroxyl from the water, you form calcium hydroxide. So precipitation will happen only if there is substantially large concentration of calcium in solution. So it will try to go to places, where it can actually grow. Any crystal growth will happen generally in areas where there is the least resistance to overcome for growing.

So that is something that you need to look at carefully. So this is microstructure of concrete. Now if you look in the paste, I said there is already lot of calcium hydroxide that is present. There are gray areas, which are your outer CSH and then there is inner CSH. Where is the inner CSH? Look at this cement grain here. Look at the layer around it, this gray layer, which is surrounding it, which has a different shade of gray as compared to what is away from it.

You can make out the different shade of gray. It is not very clear probably on the image, but I will show you more pictures to discern colour of the inner CSH and outer CSH. Before we move to that distinction, what do you think will be the difference in densities of the inner CSH and outer CSH. I mean, which one is going to be denser. You all agree that it is the inner CSH, which will be dense and of course that is also shown in the colour of gray that is, you see here.

You have brighter colour with the inner CSH as opposed to a darker colour with the outer CSH. Why does this happen? Why are the electrons getting better max scattered from the inner CSH as compared to the outer CSH? Density, we have already said that inner CSH is more dense. But CSH is not a completely solid material. I told you that it is gel like substance. So there will be porosity in CSH.

Now can you tell me the answer, which is more porosity? The outer CSH has more porosity than the inner CSH because now it is forming in a through solution mode whereas inner CSH is forming in a topochemical or in situ mode. There is not much space for the pores to occupy the intermediate spaces between the CSH. So you have lesser porosity in the inner CSH and higher porosity in the outer CSH.

When you talk about durability of the concrete, which phase will govern the durability, the outer CSH. The porosity of the outer CSH will be what will govern the durability of concrete because that is where you will get an interconnected network of pores and your porosity may end up being higher in that region. Let me show you a few more images between inner and outer CSH.

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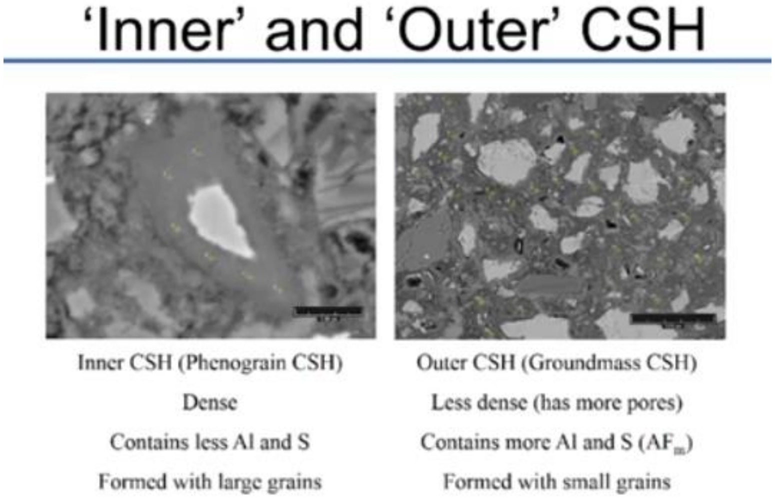

‘Inner’ and ‘Outer’ CSH

Inner CSH (Phenograin CSH)
Dense
Contains less Al and S
Formed with large grains

Outer CSH (Groundmass CSH)
Less dense (has more pores)
Contains more Al and S (AF_m)
Formed with small grains

So you have again Alite grain here, grain of Alite or C_3S, which is hydrating and you have a fairly thick layer of inner CSH that is actually formed around it. It is a fairly thick layer, which is formed around it and this is an image which has been taken under the backscatter mode at about 90 days after the cement has hydrated, after the cement came in contact with water. So 90 days the cement has been hydrating and you see a very thick layer of inner CSH that is actually formed.

Now the right side image is actually showing a much lower magnification image where you see all these yellow points, they are spots that are in the outer CSH. That means they are slightly away from the unhydrated cement grains that are present in the system. Now one thing interesting is you are not finding any rounded crystals at all. There is not much C_2S present in the cement.

That is probably true of most modern cements that when you take a snapshot, it is sometimes difficult to actually see the C_2S particles, because there is so little of them around as opposed to C_3S. The other thing that you need to be worried about when you look at a polished image, is that you are actually taking a section through your concrete. So you do not know whether the image you are looking at is the top of the 3-dimensional crystal or the middle or the bottom.

Or is it like a view that is normal to the crystal or at an inclined plane. You have no way of saying that because you are taking a slice through the concrete and preparing a polished section. So there are various issues with how you interpret these images and often times you can end up interpreting things that are sometimes even not there. You need to be very careful while interpreting SEM images. So just the distinction between inner and outer CSH.

The inner CSH is also called Phenograin CSH and outer CSH is called the Groundmass CSH, just because inner CSH is just around the grain whereas the CSH, which is outer CSH is away from the grain. So that is why it is called the groundmass CSH. Inner CSH is dense. The outer CSH has more pores, so it is less dense. What you will find when you do a proper analysis of the composition of the CSH is that it is not just calcium and silica, it will also contain some alumina and sulfur.

I am sorry, this is not silica here, this is sulfur. This is the regular chemistry notation, not cement chemistry notation. So I should say sulfur here. And the outer CSH will contain more inclusions of sulfur and alumina primarily because I told you earlier, the monosulphate that forms have very fine crystalline sizes and that is generally found intermixed with the CSH. The AF_m phases that are forming in the system are generally at a very fine micro crystalline scale.

And because of that they are intermixed with the CSH. So if you do a spot analysis of the composition of the CSH, you will find that there is a lot more aluminum and sulfur as opposed to inner CSH. Again, as I was talking earlier inner CSH is formed with larger grains whereas outer

CSH is formed with smaller grains of cement. Again, for the most part, we are only talking about C_3S. It is a lot more easier to understand the system with just C_3S rather than with C_2S.

Because most of the times, we will not find sufficient evidence of C_2S having produced this nice a contrast between the different CSH types.

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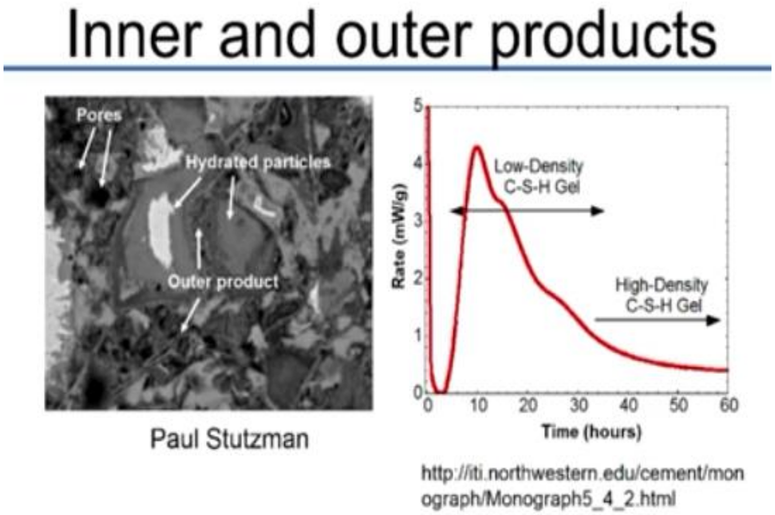

Inner and outer products

Paul Stutzman

http://iti.northwestern.edu/cement/monograph/Monograph5_4_2.html

Another picture of inner and outer products. Again here what is being shown is how is the formation of this inner and outer CSH related to the heat evolution pattern. On the right, you have a heat evolution pattern and what it tells you is that for the first 30-40 hours or so, all you are forming is the low density CSH or the outer CSH and then in the long term you are forming more and more of the inner CSH.

Again the picture, it is a very popular picture, which is shown on the left by a person named Paul Stutzman. He is at the NIST in the US National Institute of Science and Technology and they have done extensive amount of work on understanding the microstructure of concrete by scanning electron microscopy. This is a very nice picture, which shows a very high magnification image of again you have the C_3S particle with the surrounding layer of inner CSH.

In this case, the outer product looks a lot more porous, as compared to the inner product the outer product is almost looking black. It is looking very dark, because it has got a lot more porosity.

Why does it happen you think? Because in the system you may have more water. It may be a high water to cement ratio system. If you want to really make out the distinction between inner and outer CSH very well, you need to move to a high water cement ratio system.

Because then, the porosity in the outer CSH will be very large. Again you can see here the different shade of gray that is produced by the calcium hydroxide. You can see that. There is a different of gray produced by the calcium hydroxide and I will show you some images later, which actually will tell you that. In some cases, the C_3S grain can be completely hydrated to form CSH. I will show you some more images later.

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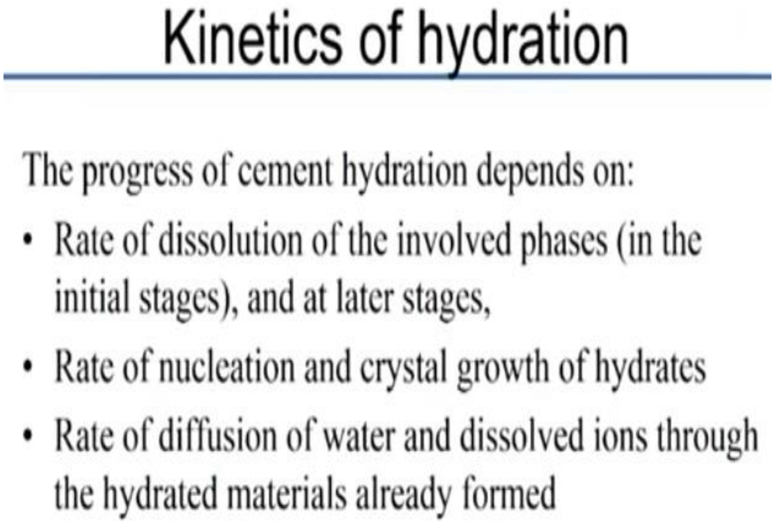

Kinetics of hydration

The progress of cement hydration depends on:

- Rate of dissolution of the involved phases (in the initial stages), and at later stages,
- Rate of nucleation and crystal growth of hydrates
- Rate of diffusion of water and dissolved ions through the hydrated materials already formed

But before that let us try and understand what is driving the speed at which this reaction actually happens. What are the parameters that govern the kinetics or the speed of the cement hydration process? So again, we talked about the fact that first we have dissolution from the surface of the cementitious particles, you have dissolution. The second is hydrate start growing, the crystalline hydrate start growing and then there is diffusion of water through the hydrate layer and again you are forming the inner materials.

Looking at this, what do you think will be the parameters that will affect the speed at which this happens. Can you tell me something, which can speed up the rate of dissolution of the cement, higher specific surface, yeah if you make the cement more finer, then obviously the rate of dissolution is going to be increased. What are the conditions will lead to an increase? Temperature.

If you increase the temperature of the system, the rate of dissolution will go up, possibly the rate of crystal formation also will go up and possibly the rate of diffusion will also go up. So temperature is a way to increase your hydration significantly. I will show you some examples later. What else, yes the impurities and water because again please remember you have ionic concentration in the pore solution, so if there are ionic species involved they may affect one way or the other the dissolution process that is happening.

The dissolution process can be affected by the ionic strength of the pore solution and that may be contributed somewhat by the water also, which is why for the most part when we do construction, we want water quality to be properly maintained. We need to check the content of alkalies and sulfates and so on in the water and chlorides, of course, in the water. So these are the kinds of things, which are affecting.

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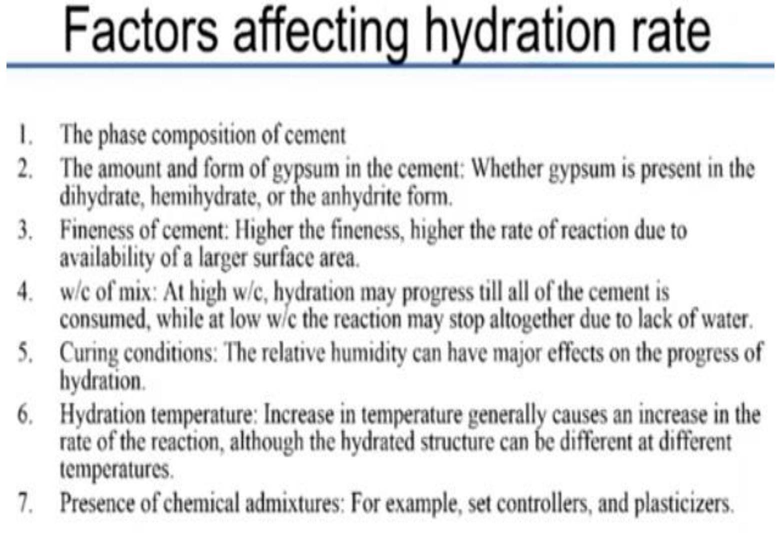

Factors affecting hydration rate

1. The phase composition of cement
2. The amount and form of gypsum in the cement: Whether gypsum is present in the dihydrate, hemihydrate, or the anhydrite form.
3. Fineness of cement: Higher the fineness, higher the rate of reaction due to availability of a larger surface area.
4. w/c of mix: At high w/c, hydration may progress till all of the cement is consumed, while at low w/c the reaction may stop altogether due to lack of water.
5. Curing conditions: The relative humidity can have major effects on the progress of hydration.
6. Hydration temperature: Increase in temperature generally causes an increase in the rate of the reaction, although the hydrated structure can be different at different temperatures.
7. Presence of chemical admixtures: For example, set controllers, and plasticizers.

I am just giving a snapshot of what all is affecting the hydration rate. Obvious one is the phase composition of the cement. The more C_3S, you have the faster reaction will be. The more C_3A, the faster the reaction will be obviously. Interestingly, a lot has been written and a lot is still being researched about the amount and form of gypsum in the cement. Now this is a very critical component in early age behavior of cement pastes because not only is the hydration dependent on this, the interaction with the superplaticiser, which we will discuss in more detail later, is also dependent a lot on the extent of gypsum and the type of gypsum that is present in the system.

What are the different types of gypsum? The dihydrate that is $2H_2O$, hemihydrate that is half H_2O and anhydrite, which does not have any water molecules present in the structure. Now interestingly, gypsum can be also obtained from a natural anhydrite. That means calcium sulfate can be also obtained from natural anhydrite. That is a completely different material as opposed to a synthetic anhydrite. What do I mean by synthetic anhydrite?

If you take gypsum and increase the temperature, you lose the water of crystallization, that becomes a synthetic anhydrite. A natural anhydrite is naturally available calcium sulfate. Now the interesting difference between these two is the solubility of the sulfate is completely different in these two. As you move from gypsum to hemihydrates to synthetic anhydrite, the solubility of the sulfate increases. While if you choose your source as natural anhydrite, there is very low solubility of sulfate.

Now obviously you know very well that the sulfates are responsible for attracting the aluminates into the formation of ettringite. So the faster the sulfates are available, the quicker they will be able to react with C_3A. The slower the sulfates are available, there is more chance that your C_3A will have it's own reaction, especially when there is very low solubility or no sulfate available, you may actually get what kind of condition? Flash set.

You will get a Flash set when C_3A will not have any gypsum to react with, because the gypsum solubility is extremely low. So that is something that can govern to a large extent the rate of your reaction. Of course, fineness is something which you have already said, higher the fineness, higher the rate of reaction. Water-cement ratio of the mix is important to consider. We discussed this earlier. At a higher water-cement ratio, there is going to be more complete hydration.

However, what will happen, at low water cement ratio, because there is not enough water, you may actually have more unhydrated particles in the system. However, that does not really mean that you have produced a structure that is not dense. You may actually have a much denser structure at low water-cement ratio as compared to higher water-cement ratio. Curing conditions, the relative humidity obviously is important, because it defines whether water is available within your system or not.

Your hydration temperature is definitely important. Hydration temperature will have an effect on all the three different stages that we discussed in the previous slide. Then finally presence of chemical admixtures and that is something we will discuss in a separate chapter later. Because again, these three stages of hydration can be affected in different ways by different sorts of chemicals. Primarily the dissolution stage is what is affected.

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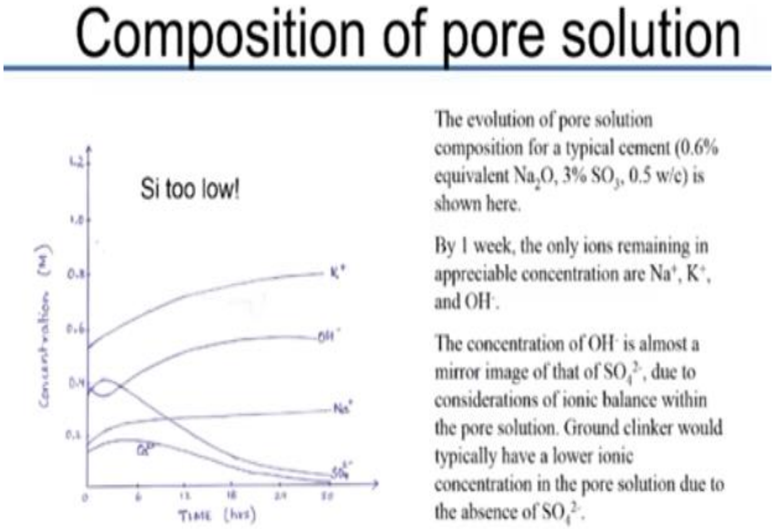

Composition of pore solution

The evolution of pore solution composition for a typical cement (0.6% equivalent Na_2O, 3% SO_3, 0.5 w/c) is shown here.

By 1 week, the only ions remaining in appreciable concentration are Na^+, K^+, and OH^-.

The concentration of OH^- is almost a mirror image of that of SO_4^{2-}, due to considerations of ionic balance within the pore solution. Ground clinker would typically have a lower ionic concentration in the pore solution due to the absence of SO_4^{2-}.

Now again, we have discussed this earlier that cement hydration is not taking place in water. It is taking place in a pore solution and this pore solution is essentially composed of the components from cement that are rapidly dissolving into the water. So we know very well that there are alkali sulfates present on the clinker surfaces and these alkali sulfates will be the first to dissolve. So as a result, the concentration plot versus time here indicates that you have a steady build up of sodium and potassium ions in the pore solution.

Now first of all, to do this study, you need to get the pore solution. How will get your pore solution? Let us say first you have a fresh cement paste, how can you get the pore solution out of this fresh cement paste? How do you get the water out? Maybe you can press it hard and get the water out, the other thing is you can do centrifuging. What will centrifuging do, it will push the heavier particles of cement paste on one side and water on the other side.

You can actually extract this water and then do a compositional analysis. For hardened concrete, what do you do, for concrete that is 1-year-old? Water is held in very small pores, vaccum is never going to be sufficient. So what is typically done is again you press it, you compact the material, but here you are having almost a triaxial sort of a cell in which you are putting extremely high pressures.

Pressures of the order of 400 megapascals are applied to the concrete in an almost triaxial sort of a condition and that level of pressure will probably get you about 1-2 milliliters of the pore solution. It is not an easy job to do. So there are very few labs around the world, which are actually engaged in determination of pore solution. Now we are trying to create this facility here also.

The pore solution is very important to understand because you will see later that the composition of these pore solution has a role to play in other durability related activities also. For example, in corrosion, there is a lot that depends on how your pore solution is and alkali-silica reaction is another thing, because again alaklies for alkali-silica reaction are getting contributed from the cement, so the pore solution having high alkali means, you have higher susceptibility for alkali-silica reaction.

So now, again sodium and potassium are building up slowly in your pore solution. What about your sulfur or sulfate which is getting contributed first of all from the gypsum and also from the alkali sulfate, so the rapidly soluble sulfate is available immediately, but then slowly the more soluble sulfate also comes into solution, but after reaching a certain peak, you see that the sulfate starts going down. Why is it going down?

Because you are starting to form the calcium sulfoaluminate products, ettringite and then later monosulfate. So sulfate basically goes down, in a mature cement paste you may not find much sulfate present in the pore solution. What about calcium? Calcium also initially goes up, because there is rapid dissolution from the cement particles. It builds up the ionic concentration, but then sometimes the concentration may be high enough that you have to start precipitating calcium hydroxide.

When you start precipitating calcium hydroxide, your concentration of calcium goes down. It may not go to zero, it may be there in your system, but it is going to be much much lower as compared to the alkalis. The other species that is present in substantial concentration is your hydroxyl species and that needs to be present because you need to have a balance in your system with a positive ionic species, that is the alkali ions.

So after about one week, the only ions remaining in appreciable concentration are sodium, potassium and hydroxyl ions. The silicon concentration is way too low to be plotted on the same scale as the other ionic species. Again please remember this is for a particular type of cement, which has a certain equivalent alkali concentration, a certain sulfate content and a certain water-cement ratio. If you change any of these conditions, your pore solution may have a slightly different composition.

For example, if you have more sulfate or more sulfate of the anhydrite type, maybe this might go up very high in the beginning and then come down. If you had high alkali cement, which is 1% sodium oxide equivalent content, maybe your potassium concentration and sodium concentration may go higher. There are differences in the pore solutions of different concretes of different cement paste systems.

Especially, if you are replacing cement with fly ash or slag or silica fume, or metakaolin or LC3, you are going to get the system that has a completely different pore solution and very interestingly, that will have a large impact on different kinds of durability properties. Just to give one example, supposing I want to check the electrical conductivity of the cementitious paste system, if I have electrical conductivity to be determined what is it going to depend on.

Ionic concentration, if you have more ions, there will be greater conductivity. If you have less ions, there will be lesser conductivity. When you replace cement by other mineral admixtures, you first of all bring down the extent of cement, so already you bring down the extent of the ionic species that can be contributed by the cement. Your alternative materials like fly ash or slag may or may not have soluble alkalis that are available in the system.

Secondly, these fly ash and slag particles may start trapping the alkalis that are available because of cement. These alkalis can start getting trapped by the unhydrated silica that is present in the fly ash and slag, because of which the ionic concentration of your pore solution will be generally much lower in the case of blended cements. So conductivity is also going to be much lower. Some of you may have heard of this test called rapid chloride permeability test.

Again it appears in several specifications around the world for determining the durability of the concrete. Here what you do is, you have a potential difference of 60 volts applied across concrete and you determine the charge that is passed by the concrete in 6 hours. So major criticism of the test is actually it is mainly measuring the conductivity of the system and systems that are having low conductivity are given an undue advantage.

For example, when you have silica fume in the system, the charge passed is so low that you can really show a major difference between silica fume concrete and plain cement concrete and that is why this test became popular because the silica fume manufacturers were the ones who were really promoting this test and trying to push as much as possible, these tests into the research articles. When we discuss durability, you will see that there are several other tests which are trying to overcome the shortcomings of the rapid chloride penetration test.

However, there is no way that this test can be completely eliminated from the industry, because everybody seems to know it, everybody likes this test, because it is fairly quick and it gives you results that sometimes are comparable. We will stop with that for today.