

**Advanced Concrete Technology**  
**Dr. Manu Santhanam**  
**Department of Civil Engineering**  
**Indian Institute of Technology – Madras**

**Lecture - 09**  
**Cement Chemistry Part - 4**

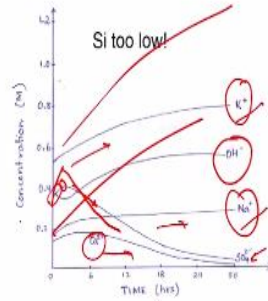
Good afternoon everyone. So in the last class we were talking about the Hydration Kinetics of how the different phases of cement compounds actually start reacting and what factors actually affects the rate at which the reaction happens. We also saw that the reaction of the cement is not happening in water but it happens in the pore solution and the pore solution is composed of the Ionic species that you get when the cementitious compound start dissolving into the water.

The only Ions that remains in the long term in an appreciable concentration are sodium, potassium and hydroxyl ions. So ultimately there is a charge balance that gets maintained. We also briefly discussed how the pore solution can be obtained, we need to do a proper compression of your concrete, hardened concrete and extract the pore solution.

Of course to do the chemical analysis we will have to dilute it many number of times to obtain sufficient sample to do a proper chemical analysis, just for the record generally what is done for Ionic determination is absorption spectroscopy that is how you will actually get the numbers for the amount of sodium and potassium and so on. For the Anions like hydroxide and sulfate ions we will have to do ion chromatography or other methods which can help you determine the correct extend of the ionic species that represent. So it is little bit involved procedure.

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## Composition of pore solution



The evolution of pore solution composition for a typical cement (0.6% equivalent  $\text{Na}_2\text{O}$ , 3%  $\text{SO}_3$ , 0.5 w/c) is shown here.

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

The concentration of  $\text{OH}^-$  is almost a mirror image of that of  $\text{SO}_4^{2-}$ , 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  $\text{SO}_4^{2-}$ .



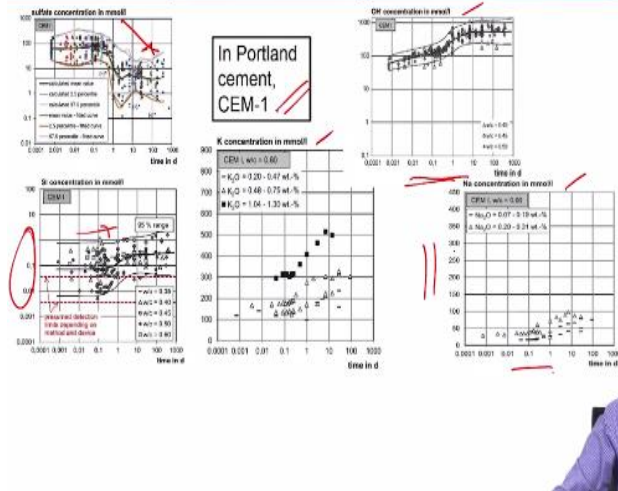
However, there are also guidelines to look at what can be an approximate pore solution composition based on the initial cement composition that means the initial oxide composition of the cement can be used and you can actually do a simulation to determine the approximate pore solution composition. And this is again made possible by some work that is done by NIST, remember I talked about that earlier.

That is the National Institute of Science and Technology based in the U.S., and they done some work where they have actually done simulation based on the original cement composition generating the actual pore solution composition.

So mean most of the people around the world do not use pore solution extraction as part of the research activities, they have to actually fallback on something which is available that can approximate that aspect, that means how to obtain the pore solution without really doing this extraction which is a very cumbersome. So anyway, we looked at this and—

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# Composition of pore solution



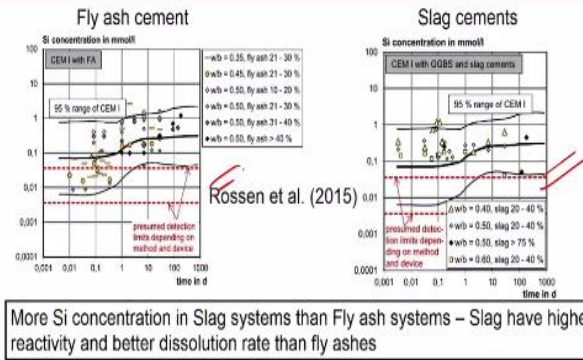
There is also a lot of research which looks at how the pore solution varies when you substitute cement with other sorts of system. For example, here there is a lot of different concretes which have been tested for their pore solution based on, these concretes are entirely made with CEM-1 or Portland cement. This is actually from research paper Rossen et al. So again these numbers are fairly well corresponding with what I presented you earlier in the previous slide so it shows you basically with the passage of time.

So in the x-axis there is time, in the y-axis there is concentration, so with the passage of time how much are these ionic species actually changin. And you can clearly see that if you look at sodium, hydroxyl and potassium there is a constant in the increase ionic concentration in the pore solution whereas for sulfate there is a decrease and silicon is more or less constant but if you look in the numbers the silicon concentration is very low.

All the others we are talking about hundreds of millimoles per liter. But silicon is of the order of point one to one millimole per liter because silica is not essentially soluble, it is not easily soluble because of that is does not come into the solution but you can have some limited solubility available from silica also.

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# Pore solution in blended systems



Now what happens when you have blended cements like Fly ash cement and slag cements, what is presented here is silica concentration. Now we expect that because Fly ash and Slag have amorphous silica, there may be a little bit higher silica content in the pore solution, so that is what being shown here in terms of the silica concentration with respect to the pore solution. So you do see that there is a minor increase in the extent of silicon concentration which is available in the system as compare to what you have in the cement system.

But nevertheless, there is not so much silica available because it is not in the soluble form, there is definitely more silica concentration in slag systems than fly ash systems, and that seems to indicate the better reactivity of the slag systems also. We know that Slag's are much faster reactive as opposed to fly ash. Of course what is not showing here is how the ionic concentrations that is sodium, potassium, hydroxyl ion concentration change when you have blended cements, what you will expect to happen in the case of an ionic concentration?

It will decrease or increase? Generally, the allelic concentration that is contributed by cement is far greater than what is contributed by fly ash or slag, so when you replace part of cement by fly ash or slag it is going to be reducing the alkali concentrations. So that is actually a very positive aspect in one way.

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## Hydrated cement paste

- Hydrated cement paste is composed of capillary pores and the hydration product.
- The pores within the structure of the hydration product are termed 'gel' pores. This hydration product includes C-S-H, CH, AF<sub>1</sub>, AF<sub>m</sub>, etc.
- Gel pores are included within the structure of hydrated cement.
- According to Powers, 1/3 of the pore space is comprised of gel pores, and the rest are capillary pores.

Capillary pores > 10 nm  
Gel pores < 10 nm



Because having a lower ionic concentration also means that your system is less conductive. And why is conductivity being important because when you have some phenomena like corrosion, for propagation of corrosion the medium surrounding the steel if it is more conductive then the rate of corrosion can be much higher. So with blended cements, one of the primary reasons why we see a reduction in the rate of corrosion is because our system is more resistive or less conductive as compare to ordinary Portland cement.

So having looked at pore solution now let us look at how these products actually form, what sort of structure is there for the C-S-H, Calcium Hydroxide, ettringite, Monosulfate etcetera. And how do we look at the porosity in the system. In what ways can water be held within the cement paste. So hydrated cement paste is simply composed of the capillary pores and the hydration product.

So part of it is solid and part of it is porous, so porosity contributes a part of your hydrated cement paste. Of course if the pores are small enough that they are within the structure of C-S-H then they are called Gel pores. If the pores are exterior to the structure of the C-S-H they are called capillary pores. Larger pores are called capillary pores and smaller ones are called Gel pores. General distinction is that capillary pores are typically greater than 10 nanometer in size, or always greater than 10 nanometer in size.

Whereas Gel pores are less than 10 nanometer that is generally acceptable as a distinction between Capillary porosity or Gel porosity. Now of course as the pore size become smaller that will become all the more difficult for any liquid to propagate through these pores right because you know very well from your capillary raise equation that the capillary diameter is inversely proportional to the pressure. When you lower the diameter the pressure increases.

So you need greater amounts of energy to push in water through smaller porosity, so obviously that is why smaller pores or systems which have lesser porosity are more durable because you cannot allow water or other chemical to pass through these compounds easily. So gel pores are generally present within the structure of your C-S-H because only C-S-H is the semi-crystalline material, all the other compounds like Calcium Hydroxide, ettringite, Monosulfate they are well developed crystals.

So generally gel pores are present within the structure of your C-S-H where the capillary pores are present outside the structure. According to Powers once again, 1/3rd of the pore space is composed of gel pores and the rest are capillary pores.

So I have told you before Powers was one of the premier scientist who worked in cement chemistry and his work was primarily done at the Portland cement association in the U.S., and the kind of work that they produced actually is still holds very good because the kind of the experiment that was done in those days' top class and because of that a lot of researches still fall back on the results that were proposed first by Powers I think that was in 1940s and 50s, quite a long time ago.

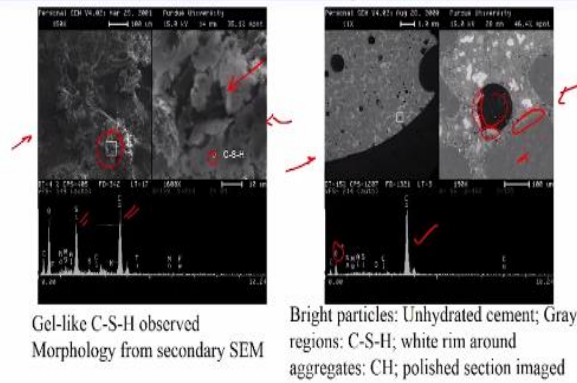
But despite the increase or advances in our scientific achievements the extent of understanding we have seemed to only keep confirming the kind of theories that Powers was able to propose 70-80 years ago, so that shows you extent of further the class of his work. So as per Powers, 1/3rd of the pore space is comprised of gel pores and the remainder is the capillary pores.

Now which porosity do you think will play a large part in your mechanical properties and durability, the capillary porosity because it is easily assessable so if water has to be get absorbed

the water has to permeate through the concrete it will go through the capillary porosity not through gel porosity.

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## Some micrographs



So some examples of cement paste microstructure are presented here through micrographs taken with scanning electron microscopes. On the left you actually have a micrograph which is actually showing you a fracture surface. So here a cement sample was taken and fractured, I think it is a cement mortar sample and not a paste sample it was taken and fractured and directly put onto the scanning electron microscope.

So what you are able to absorb with the fractured surfaces is the topology or the morphology of the hydration products that are actually forming. So here this is a low magnification image on the left and the high magnification image on this area that is marked in the left side of the image. So if you look at the higher mag image, what we are zooming in on, is a cluster of Calcium Silica Hydrate. The problem here is you cannot simply distinguish one set from another it is present like a fibrous mass.

And how do we confirm this Calcium Silicate Hydrate? This point analysis is confirming its calcium Silicate Hydrate because it gives you peaks the calcium and silicon when you are evaluating the x-rays that are coming out from that point. So that is basically the spot analysis that

is typically accompanying scanning electron microscopy, so we look at the x-rays that are coming out from the sample and look at the elements that are composed that are present in that sample.

In the right side is slightly different image that is actually cement mortar which is been polished and you are looking at the polished surface not a fractured surface. So look how different it is. On the left side, we will actually able to see the hydration products in terms of crystals or crystalline morphologies. In the right side, we only see a color differences between different phases. This is more or less similar to your optical microscopy where as I showed you previously that the phases that are brighter will reflect more light.

So in scanning electron microscopy the phases that are denser will simply reflect more electrons, there are more electrons coming out so those phases appear brighter, I showed you previously also in the SEM picture of your inner C-S-H, inner outer C-S-H. So here you can clearly see these are aggregates , the larger pieces are your fine aggregates or silicious aggregate. You have the white unhydrated cement particles because those are the densest.

You have the gray area around the unhydrated particles, in this case you are not able to distinguish very clearly what is what. But if you look very closely around this spherical pore space you will see that there are well-defined deposits of calcium hydroxide which are aligning the pores spaces. That is a very common finding in most cement paste microstructure is that you will start seeing calcium hydroxide in locations where there is free space available for its growth.

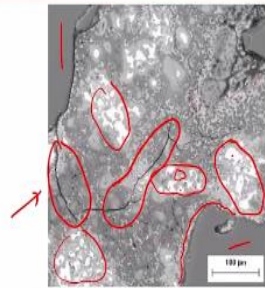
So here its growing in porosities you will often find it growing in the interfacial transition zone between the paste in the aggregate, because we have discussed this earlier, even in the ITZ you have greater porosity around the aggregate. So wherever there is more porosity, you will tend to see more calcium hydroxide deposition. So here you are seeing calcium hydroxide again, how do we confirm it is hydroxide we are looking at the x-ray signal which is coming out of it showing a peak for calcium, and of course oxygen.

So that is how you can look at distribution of a hydration products.

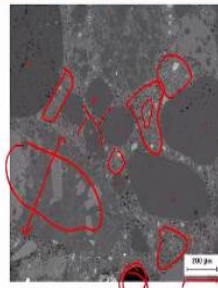
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## Some micrographs



C<sub>3</sub>S mortar showing white unhydrated cement particles and gray C-S-H, along with white rims of



Porosity of paste in concrete is visible in this picture



Moving on, a little bit more descriptive here on the left side we actually have a C<sub>3</sub>S mortar. So instead of OPC mixed with water, you have C<sub>3</sub>S mixed with water to make this mortar, mortar and sand obviously it is a mortar, so you can see the sand particles here, and the paste in between is only composed of hydration products of C<sub>3</sub>S which is C-S-H and Calcium Hydroxide, right. C<sub>3</sub>S + water gives you C-S-H and Calcium Hydroxide.

So again you can see the phases which are looking quite different. You see here the unhydrated cement grains, some remnants of the unhydrated C<sub>3</sub>S grains only the remnants are there because part of it is hydrated, it is showing very clearly the inner C-S-H. Away from it slightly darker, you see the darker gray phases, that is your outer C-S-H and also there are brighter whiter phases here, which is not as bright as unhydrated phases what is that, not as bright as unhydrated phase but brighter than the C-S-H, that is calcium hydroxide.

So these brighter particles are calcium hydroxide, you can also see around the aggregate there seems to be a layer forming of calcium hydroxide. And there are several grains of C<sub>3</sub>S which are partially hydrated. So what I am trying to show here is a system where there is no aluminate present so you will only get C-S-H and calcium hydroxide. Again what sort of images is this? Is it a fractured image or a polished image?

We cannot see any crystalline morphology only what you are saying is a difference in the gray levels so it is a polished surface image. When you see only a difference in gray levels it is a polished surface image, when you see like in the previous slide you actually see the morphology, look at this left side image, you can actually see the gaps and crevices and the flaky and fiber crystals so that is actually a fractured image.

You see that there is cracks here, that cracking maybe shrinkage cracking we do not know, the cracking maybe because of specimen preparation for the SEM. So while polishing you have to really abrade it against very fine diamond paste and before abrasion you also need to ensure that this specimen is properly dried. So when you dry it in a very high temperature you are bound to also create cracking in your system.

So very often when you use the scanning electron microscopy to look at growth of cracks, you can get lot of errors because much of this cracking could be attributed to the specimen preparation rather than any phenomena happening inside. So that is basically some example of  $C_3S$ . On the right side you actually see a microstructure of concrete. There are larger particles probably belonging to coarse aggregate but may even be fine aggregate. You see this much is 200 micron so we are looking at probably about 600 micron in this side maybe about 1.2 or 1.4 millimeter on the other side.

It could be a particle from the fine aggregate also. These are definitely fine aggregate particles why do I say that because they are nicely rounded, mostly river sand is used as fine aggregate, you can find highly rounded particles and they have almost a constant phase that is because most of them are quartz, silica, silica will give you that darkish color under the polished section imaging. You can now see the paste inside, this is the paste in between the aggregates.

How much do you think is there in this image, what area, what extent of area is being occupied by paste in this image? I would say close to about 30%. So now what we will talking about previously is that because of packing affects you have the slightly different density of the paste close to the aggregate as opposed to away from the aggregate. Now looking at this microstructure how do you define what is close and what is away?

you see from the microstructure for example which is of course I do not have the magnification here I only have the length bar or length indicator. But what you think, do you think there is any interfacial transition zone present here? In this picture can you see it? There is some space there. But do you see any difference in the gray levels of the paste close to the aggregate and away from the aggregate?

Yes. You do. May be I do not looked at this picture well enough. So you can see the extent of paste that is between those four small aggregates is extremely less and all of it seems to be more porous as compared to the zones here. My contention was and so as the contention of several people who are against the concept of is this ITZ is that the spaces between the aggregates is in any case not large enough for us to distinguish different properties of paste near the aggregate and away from the aggregate.

So typically what people say is the ITZ thickness is around 50 microns, but here you see that 50 microns could be, from one aggregate 50 microns this way and from the other aggregate 50 microns this way. But you see here between aggregates you have hardly 100-micron space in most cases. So there are ways in which you can actually show that ITZ is maybe an artifact of the way that you are preparing a specimen way that you mixing your concrete and so and so forth.

But there are arguments which are supportive of ITZ also. I will show you later when it comes to strength and durability studies, that our understanding of ITZ as the layer of paste around the aggregate which is much weaker than the rest of the paste seems to be quite strong because it supports a lot of the other experimental observation that we actually notice and that we will look at when we actually get to the discussion of strength and durability.

But for now you need to understand that the concept of ITZ even though we proclaimed that is the weakest link in concrete that leads to the difficulties in concrete properties and so on and so forth, there is a group of people around the world, a group of researcher's, well-known researchers who seems to negate that idea that ITZ is even present. So you need to ensure that you understand both sides of the story.

But later I will show you positive evidences of why ITZ can have very distinct effects on the performance of concrete. But what you do see in this picture is the porosity that is available in the paste. I am not talking about this void here that void is probably because of the effects of mixing. If you have mixed and compact well enough maybe that void will go. But I am talking about the porosity inside the paste.

The extremely fine pores that are distributed within the paste, that is your capillary porosity. This one here, this spherical appearing void is just a void it is not a capillary, so we will look at how we distinguish voids and pores a little bit later.

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### Water within cement paste

1. Capillary water: Present in voids larger than 50 Å. Further classified into: (a) free water, the removal of which does not cause any shrinkage strains, and (b) water held by capillary tension in small pores, which causes shrinkage strains on drying.
2. Adsorbed water: Water adsorbed on the surface of hydration products, primarily C-S-H. Water can be physically adsorbed in many layers, but the drying of farther surfaces can occur at about 30% relative humidity. Drying of this water is responsible for a lot of shrinkage.
3. Interlayer water: Water held in between layers of C-S-H. The drying of this water leads to a lot of shrinkage due to the collapse of the C-S-H structure.
4. Bound water: This is chemically bound to the hydration product, and can only be removed on ignition. Also called 'non-evaporable' water.

2 and 3 are together called 'gel' water.

$100\%$   
 Evaporable 20%  
 Non-evap 100%  
 $1000^\circ\text{C}$   
 $600$   
 $1400$   
 $90\%$   
 CS-H  $\rightarrow$  Sheet like

Now, very important part of our understanding of the cement paste is, are understanding of in what different ways is water held within the cement paste, because this movement of water within cement is responsible for a lot of issues that are actually noticed with respect to concrete performance. So obviously, there is porosity inside the paste, so water is held within the pores.

So the water which is held within the capillary pores is the capillary water. Water which is held within the Gel pores is called Gel water and it is composed of 2 types: one is called Adsorbed water the other is called Interlayer water and finally of course there is this water which is within

the structure of the C-S-H or within the structure of calcium hydroxide or within the structure ettringite or Monosulfate that is the Bound water.

Remember, we write C-S-H as Calcium Silicate hydrate, that Bound water corresponds to the hydrate portion of the C-S-H. But apart from this there is free water available in the system and that free water depends on the size of the porosity, will be called as Gel water or Capillary water, okay. So Capillary water is present in voids generally larger than 50 Angstroms so here it says 5 nanometer but the general definition is 10 nanometer.

Today people seem to agree that 10 nanometer is the size that defines capillary porosity. Now if you look at this capillary water you can further distinguish this capillary water into water that is present in larger porosity and smaller porosity. So when you dry out water from larger pores will there be lots of strain associated with that. Again same issue pressure is inversely proportion to diameter and diameter of the pores is large, the capillary pressure upon drying will be less.

On the other hand, when you start drying out water from very small pores, capillary pressures will be very high, associated shrinkage strain will be very high. So again you can classify the capillary water into free water, the removal of which does not cause any shrinkage or you can call it as water held by capillary tension in small pores which results in very large shrinkage strain upon drying. So already now you understand that if you have excess water present in the system some of it may be present in these very large pores.

So you may cause sufficient drying to happen without any shrinkage in the system. So sufficient drying implying the concrete may start losing mass because of drying and that what is actually coming out of the larger pores so you do not create any shrinkage strains in the system. So only when you start drawing this water from smaller pores you result in very high shrinkage levels in the system.

Now of course when you are coming to gel pores you are already coming to very small porosity because of which if you start drying out gel pores you can imagine that, that is going to create massive shrinkage in the system. So gel porosity is again classified into or water is classified into

the Adsorbed water and Interlayer water, so this seems to suggest that part of the water which is present in the C-S-H is adsorbed on the C-S-H particles.

What do you mean by Adsorption? Sticking to the surface. Absorption means going inside, adsorption means sticking to the surface and then Interlayer water means it is something indicating between layers of C-S-H. So already we are sort of assuming a certain type of a structure for C-S-H and what you assume the structure as if it is going to be adsorbed on a surface and between layers.

So what is the best model that we can come up with for C-S-H a sandwich sort of structure maybe Sheet like structure so this sort of tells us that C-S-H, so C-S-H has a Sheet like structure because of which water gets adsorbed on the layers and it is also present between the sheets. Now this is, this makes it more easily imagine what happen when you remove this water. When you start removing the water from the surface of the sheets you may cause wrinkling of the sheets.

When you start removing the water from between the layers you will lead to collapse of the layers, so that will lead to very high levels of strains in your system. So these Adsorbed and Interlayer water are together known as Gel water and the removal of this Gel water will be associated with massive shrinkage in your system. Of course the bound water is something that is within the structure of the product, simply heating your cement paste will not release this bound water.

All the first three types of water if you simply take a cement paste and heat it to 105 degree Celsius you will remove all that water, but the water that still remains after 105 heating is bound water because that is something which you cannot remove by heating, you have to remove it by ignition, you have to burn it up to about 1000 degree Celsius typically 600 but mostly we do Loss On ignition test all the way up to 1000 degree Celsius.

So it is usually enough to heat up to 600, but we generally want to ignite it to about 1000 degree Celsius. The mass difference between what is ignited at 1000 and what remains after drying at 105 that is called non-evaporable water. So you have 2 types of water: evaporable water and non-

evaporable water. So evaporable water is what can dry out when you heat it to about 105 degree Celsius,

Why 105? Because boiling point is 100. So at 105 you are sure that all that water will go out. But the pressure in the, the size of the pores are less so the pressure there will be different than a normal pressure at 100 degree what we talked. Okay, so you are saying that the boiling of water within the porosity may not exactly happen at 100, yes that is correct.

There may be a slightly higher temperature that you require because of the high pressure with which this water is held, absolutely. The same will apply when we talk about freezing because the pores are extremely small, water does not freeze at 0 degree Celsius inside the pore so you will have to actually depress the freezing point further to really cause that water to freeze.

So this boiling point also may actually be must higher than 100, but we generally assume that by 100 we are removing the water which is evaporable. The later part which is non-evaporable will go from 100 to 1000 degree Celsius and look at the mass loss and attribute that to the hydration products. Now not all hydration products last all the way in 1000 degree Celsius. C-S-H for example, the bound water in C-S-H starts going beyond 100 itself.

And by about 300 degree Celsius this bound water and C-S-H is mostly gone and then you start seeing some mass changes because of structural changes in the C-S-H. Calcium hydroxide remain stable all the way up to about 450 degree Celsius, only at 450 the calcium hydroxide starts losing its water and transforms to calcium oxide, right at 450 degree Celsius that water goes out and it becomes calcium oxide.

Now primarily reason why concrete is able to resist temperature is because all the compounds in concrete or all compounds in cement paste do not deteriorate until you reach temperatures of more than 500 degree Celsius. Other compounds like ettringite or Monosulfate they may start disintegrating much earlier, like even 100 to 150 degree Celsius most of ettringite will deteriorate or disintegrate, monosulfate on the other hand there are some compounds within monosulfate that can last for much longer.

But generally you see that by about 500 to 600 degree Celsius all the water which are held, bound water which is held within the structure of the hydration products, that will go away at about 600 degree Celsius. Now generally why we go upto 1000 is that invariably cement also contains some limestone, calcium carbonate. Where is that coming from? During the manufacture of Portland cement we are also adding limestone as a performance improver.

And very often what may also happen is that this calcium carbonate phase may still form from cement which is hydrated because of the action of the Carbon dioxide from the atmosphere. So this calcium carbonate we saw earlier gets completely decomposed only at about 900 degree Celsius. Remember, we talked about this kiln reaction in which the limestone decomposes to release calcium oxide that happens between 700 and 900 degree Celsius.

So depending on the purity and the form of the calcite that is actually forming, this Carbon dioxide from calcite gets di-carbonated at about 900 degrees Celsius. So that is why we actually go all the way up to 1000 to determine the extent of mass change that actually happens when cement paste is heated over a large temperature range.

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## Calculation of hcp structure

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- Theoretically, 0.23 g of bound water is required to completely hydrate 1 g of cement. The remaining water fills up the pores within the structure of the hydrated cement paste (hcp), called the gel pores, as well as the pores external to the hcp, called the capillary pores.
- Upon hydration, a volume decrease in the amount of 25.4% of the bound water occurs in the solid hydration product.
- The characteristic porosity of the hydrated gel is 28%.

$$\frac{V_p}{V_p + V_{\text{hydration}}} \times 100 = 28$$



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So now what we will do is, we will try to work out based on an initial composition of the cement paste what is the composition of your hydrated cement paste. In terms of what is the extent of



porosity that is forming in the system, so for this we will have to do some assumptions, and these assumptions are based on properly formulated experiments which have helped us determine these quantities quite accurately.

First of all, theoretically, 0.23 grams of bound water is required to completely hydrate 1 gram of cement. So if you take 1 gram of cement and say that 100% hydration is happening then that 1 gram of cement needs exactly 0.23 grams of water. In other words, 0.23 is the water cement ratio that is required to completely hydrate 1 gram of cement or required to hydrate cement. Now whatever extra water that we add in the system fills up the first the gel pores and then it will fill up the capillary pores.

When cement hydrates, when cement reacts with water, the resultant product that forms has a lower volume as opposed to that of reactants. And this decrease, volume decrease is equal to 25.4% of the bound water content. So let us assume a cement which is 100% hydrating. If I have 1 gram of cement that hydrates 100% that means how many grams of bound water I have? 0.23.

0.23grams of bound water is same as 0.23 milliliters of bound water because density of water is 1 gram per milliliter that means your volume decreases how much, 25.4% of 0.23 milliliters, that is about 0.06 milliliters for every gram of cement that is hydrating. Generally, what is assumed is, about 6 to 8% volume change or volume decrease when 1 gram of cement actually hydrates, 6 to 8% volume change.

And where is this volume change going, what it is creating in the system? It is creating the porosity in the system. Now what is also needed for calculation is the characteristic porosity of the hydrated C-S-H Gel. In other words, that is nothing but

$$\frac{\text{Volume of Pores}}{\text{Volume of Pores} + \text{Volume of Solid CSH}} * 100 = 28\%$$

Now how is that determined? Obviously there is some experimental evidence that seems to show that if you have pure C-S-H and you study the porosity by an appropriate methodology mostly what is done is they we have methodologies that are based on adsorption and based on that they

have worked out that the characteristic porosity of C-S-H is 28%, so volume of pores to the total volume, the ratio of that is 28%. Total volume is porosity + solid C-H-S.

Now given this background information let us now try to calculate what would happen in the cementitious system at a high water cement ratio. Let us say 0.5.

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### Example 1

w/c = 0.50; Assume 100% hydration and no drying; Calculate the volume of capillary pores.

- Let mass of cement = 100 g. Hence,  $V_{\text{cem}} = 100/3.15 = 31.8 \text{ ml}$
- Mwater = 50 g, therefore  $V_w = 50 \text{ ml}$ .
- $V_{\text{bound-w}} = 23 \text{ ml}$
- Hence,  $V_{\text{solid-hcp}} = 31.8 \text{ ml} + 23 \text{ ml} - 0.254 \times 23 \text{ ml} = 48.9 \text{ ml}$
- Porosity = 28% = 0.28 =  $V_{\text{gel-pores}} / (48.9 \text{ ml} + V_{\text{gel-pores}}) \rightarrow V_{\text{gel-pores}} = 19.0 \text{ ml}$
- Hence total hcp volume = 48.9 + 19.0 = 67.9 ml
- Total reactant volume = 31.8 + 50 = 81.8 ml.
- Therefore, volume of capillary pores,  $V_{\text{cap-pores}} = 81.8 - 67.9 = 13.9 \text{ ml}$
- Of these, (50-23-19) = 8 ml will be filled with water, and the remaining (5.9 ml) will be empty.

From the above scenario, 23 ml + 19 ml = 42 ml of water is required for complete conversion of 100 g of cement to the hydration product. In other words, a w/c of 0.42 is required. What would happen if the w/c is less than 0.42? Consider the next example.

So let say, our water cement ratio is 0.5, we assume 100% hydration and no drying of this water out of the cement paste. So we are conducting this experiment in an insulated environment there is no drying. So what we want to calculate is what is the volume of capillary porosity in the system. So let us first look at the volume of the reactants. So cement is 100 grams let us say we start with 100 grams of cements.

So volume of cement is 100 divided by density that is 3.15 grams per cubic centimeter or gram per millimeter that is 31.8 milliliter. The cement has a volume of 31.8. Mass of water is 50 grams because we have water cement ratio 0.5 so that the volume of water is the 50 milliliters. All clear so far? Okay now we say that 100% hydration has happened, that means every part of cement is reacted so 100gms of cement is reacted, so we have 23 grams of bound water or 23 milliliters of bound water volume is present.

What we do next? We calculate what the volume decreases because of this reaction and volume decrease should compensate or should be taken into the calculation of the solid hydrated cement paste. So

$$\begin{aligned} \text{Volume of Solid hcp} &= \text{Volume of Cement} + \text{Volume of Bound Water} \\ &\quad - \text{Volume decreased due to Hydration} \end{aligned}$$

So volume of solid hydrated cement paste is equal to the volume of cement because all of it is reacting we have to take the entire volume of cement + volume of the bound water in the cement that is 23 milliliters - volume decrease that is happening upon hydration that is equal to 0.254, 25.4% of the bound water content 23 milliliters. So this works out to 48.9 milliliter.

$$\text{Volume of Solid hcp} = 31.8 \text{ ml} + 23 \text{ ml} - 0.254 * 23 \text{ ml} = 48.9 \text{ ml}$$

So what now? Our next aspect to look at what the total volume of the hydrated cement paste is?

So we know that the 28% is the characteristic porosity that is equal to volume of gel pores by solid hcp plus gel pores, why gel pores only why not capillary pores? We are only considering C-S-H. We are only considering the volume of solid hydrated cement paste in the C-S-H. So when we write this formula we can find out that volume of gel pores is 19 milliliters.

$$0.28 = \frac{\text{Volume of Gel pores}}{48.9 \text{ ml} + \text{Volume of Gel pores}}$$

$$\text{Volume of Gel pores} = 19.0 \text{ ml}$$

Now one important aspect that you need to understand here is that 19 milliliters is now the additional volume of water that is absolutely required in the system for obtaining a 100% hydrated cement paste.

Only if this 19ml of extra water is present will my hydrated cement paste get be composed of a properly hydrated C-S-H and all the pores filled inside with water. So what is that tell you about systems which have 0.42 water cement ratio or higher, if my water cement ratio in the system is 0.42 or higher, I can get theoretically a system that hydrates completely. If I have anything less than 0.42 some part of the cement only will hydrate.

Because when I am creating the hydrated product I also have to create the Gel porosity. Why it is important? See what will happen is if that gel pore is not filled up with water, for example why is the gel pores created because you are creating C-S-H. And if you do not have sufficient water to create the associated wet gel porosity that means you do not have enough water to hydrate the cement.

But we already provided 0.23 which is required for hydration? No, 0.23 is the bound water content, so the hydrated cement paste will have bound water + gel porosity, for the cement paste to form as a mass the water should be sufficient to bind with the paste and have a 100% humidity atmosphere provided in the gel porosity and that is being provided by this extra 19 milliliters.

So for now what we understand is to hydrate cement and produce a properly bound structure of C-S-H, I need to have the additional 19 milliliter of porosity also to be filled up with water. So what is happening now, I have 48.9 milliliters of solid hcp, I have 19 milliliters of Gel water, so the total volume becomes equal to 67.9 milliliters, that means volume of hydrated cement paste now is 67.9 milliliters. What is the original volume? Original volume is 31.8 + 50 that is 81.8 milliliter, because I had 31.8 as the volume of cement, 50 as the volume of water.

But now I have only 67.9, so all my reminder,

$$\text{Capillary Porosity} = \text{Total Volume of Reactant} - \text{Total Volume of hcp formed}$$

So let us say you have a system here is got some cement and some water, that is the reactant system. The products are in this side, I have the products here, I have solid hcp and gel pore and capillary pore.

The product we are taking 50 gms of water, 31.8 ml of cement, the total volume become up to 81.8, it will not reduce? That volume has to be the same in your product also. The distribution of your phases in the volume will change. In the past you had 31.8 ml occupied by solid, now of course you know that this solid is going to react with the water and it is going to be spread

throughout the system as a network of hydrate products but the network of hydrated products is only actually occupying this much solid volume.

And additionally its got this volume of the Gel porosity, all the remainder which is left in the space is the capillary porosity. So this volume decrease upon hydration is accounted for in the calculation of the solid hcp volume. The remainder of it will go into the porosity in the solid porosity maybe that is what we are trying to say.

So now 13.9 milliliters of capillary porosity is available, but how much extra water is available? Only 8 milliliters, because 23 went here to the bound water 19 went to gel water, remainder is  $50 - 23 - 19$  that is 8 milliliters, and the remainder of the capillary porosity is empty its air filled so there is partly water filled porosity there is partly air filled porosity. What may also happen if you are doing wet curing of this concrete what will happen?

The remainder 5.9 milliliter may also start getting filled up with the water but that will happen only in the early ages because that is when the porosity will be large enough for curing water to enter but later maybe as early as about 2 to 3 days, your system maybe waters tight enough for outside water, curing water, preventing curing water from entering the concrete.

So what we are saying is with this assumption we are actually able to work out the approximate amount of capillary porosity in system. Now there is an interesting problem. You see here that 0.42 is the absolute minimum required to ensure that 100% hydration takes place. Now we know that by increasing or by reducing the water to cement ratio below 0.42 we are going to be reducing the amount of hydration that is happening in the system.

But we know that reduction in water cement ratio is important to produce a concrete that is stronger and more durable. So what you think should be affected here? Essentially capillary porosity is getting reduced. And one more important part is when you move to a lower water to cement ratio system your products will contain the solid hcp, the gel pore, capillary pore and the one more ingredient, unhydrated cement.

That means it is also a part of your solid structure now which is why your capillary porosity is reducing, and that example is actually worked on next slide.

**(Refer Slide Time: 42:21)**

## Example 2

w/c = 0.30; Cement = 100 g, water = 30 g; Assume that p grams of cement hydrates.

- Hence  $V_{\text{solid-ncp}} = p/3.15 + 0.23p - 0.254 \times 0.23p = 0.489p$
- Porosity =  $0.28 = V_{\text{gel-pores}} / (0.489p + V_{\text{gel-pores}})$  ..... (1)
- Total water =  $30 \text{ ml} = 0.23p + V_{\text{gel-pores}}$  ..... (2)
- Solving 1 and 2,  $p = 71.5 \text{ g}$ , and  $V_{\text{gel-pores}} = 13.5 \text{ ml}$
- Thus,  $V_{\text{ncp}} = 0.489 \times 71.5 + 13.5 = 48.5 \text{ ml}$
- $V_{\text{unhyd-cem}} = (100 - 71.5)/3.15 = 9.1 \text{ ml}$
- Hence,  $V_{\text{cap-pores}} = (100/3.15 + 30) - (48.5 + 9.1) = 4.2 \text{ ml}$

That means there are 4.2 ml of empty capillary pores. If this cement paste gets any external moisture (for example, from curing) more cement will hydrate and fill up this space.



But we are out of time for today we will our resume our discussion tomorrow morning and complete this segment on cement chemistry.