

**Advanced Concrete Technology**  
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**Lecture – 10**  
**Cement Chemistry - Part 5**

We were discussing in the last class about how the cement paste structure evolves and how we calculate the wall of the pores that actually form in the system. There are different types of porosity present in the cement based. We discussed that the pores that are present within the structure of the CSH are called gel pores. And these are extremely fine and if you start removing molecules from these pores that result in massive shrinkage.

Whereas the water which is outside the gel is in the capillaries and you have distinction between fine capillaries and coarse capillaries. So, while you can remove a lot of mass of water from the coarse capillaries it does not result in much shrinkage whereas removal of water from fine capillaries causes a lot of shrinkage correct. We were looking in this example as to what happens when you hydrate cement how does the core structure actually work.

We saw an example where we had a high water cement ratio 0.5 and we were trying to work out based on certain assumptions takes the extent of gel porosity and capillary porosity in the system. Okay and we found that to hydrate completely all the theoretically 0.23 is the bound water content which is required you actually overall 0.42 water binding ratio or water cement ratio to ensure that all the pores in the gel, that is the gel pores are completely saturated with water and all the cement is hydrated. So, any water cement ratio below 0.42 may result in a system where you do not get full hydration you will have unhydrated cement present. So, we will take a look at once such system.

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## Cement Chemistry - Part 5 Example 2

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

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

Let water cement ratio be 0.3 and to start with 100 grams of cemen. We assume that a certain amount of cement hydrates let us say there is p grams of cement that is actually hydrating. So again re-applying the principle of understanding; how to calculate the solid hydrated cement based volume. Assuming that p grams of cement hydrates.

So, volume in a solid hydrated cement paste.

$$V_{\text{solid hcp}} = (p/3.15) + 0.23p - 0.254 * 0.23p = 0.489p$$

. So, if 50 grams of cement is hydrating then the bound water is.23 times 50. The volume reduction that happens upon hydration is 25.4% of the bound water, i.e, 0.254 times 0.23p so this works out to 0.489p.

The other assumption that we made which is based obviously on good experimental observation is that the characteristic porosity of CSH is 28%. This 0.28 should be equal to volume of gel pores divided by volume of solid hcp that is 0.489p plus volume of gel pores.

$$\text{i.e, Porosity} = 0.28 = V_{\text{gel pores}} / (V_{\text{gel pores}} + 0.489p)$$

So, that is your first equation and it has got 2 unknowns. So you need to have another equation which is going to say that this 30 milliliters total water is distributed between the bound water and the gel pores.

If the cement has to hydrate the gel porosity has to completely fill with water. So, this 30 milli

litters has to go between the hydrated cement paste; that is in terms of the bound water; that is 0.23p plus if you want to fill up the volume of the gel pores that is actually available in the system. So, with these 2 equations if you solve it you have 2 equations and 2 unknowns. So, you can solve it to get the value of p as 71.5 grams and volume of gel pores at 13.5 milliliters. In other words, the amount of cement that hydrates in the system is about 72% remaining 28% is simply sitting as un-hydrated cement. Now to calculate the capillary porosity, first we need to find out the volume of solid hcp that means volume of solid hcp 0.489 times p plus the volume of the gel pores.

$$V_{hcp} = 0.489 * 71.5 + 13.5 = 48.5 \text{ ml}$$

Volume of un hydrated cement is also there; please remember that un hydrated cement simply sits in the microstructure as a filler. So it is still occupying volume and reducing the pores. So, the volume of un hydrated cement is 100 minus 71.5; because 71.5 is the amount that is hydrated, divided by 3.15 that gives you 9.1 milliliters.

$$V_{unhydrated\ cement} = (100 - 71.5) / 3.15 = 9.1 \text{ ml}$$

And,

$$V_{cap-pores} = ((100 / 3.15) + 30) - (48.5 + 9.1) = 4.2 \text{ ml}$$

. So, that gives you 4.2 milliliters.

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Cement Chemistry - Part 5 **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,  $V_{com} = 100 / 3.15 = 31.8 \text{ ml}$
- Mwater = 50 g, therefore  $V_w = 50 \text{ ml}$ .
- $V_{bound-w} = 23 \text{ ml}$
- Hence,  $V_{solid-hcp} = 31.8 \text{ ml} + 23 \text{ ml} - 0.254 * 23 \text{ ml} = 48.9 \text{ ml}$
- Porosity = 28% = 0.28 =  $V_{gel-pores} / (48.9 \text{ ml} + V_{gel-pores}) \rightarrow V_{gel-pores} = 19.0 \text{ ml}$
- 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,  $V_{cap-pores} = 81.8 - 67.9 = 13.9 \text{ ml}$
- 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.

*Handwritten notes:* Or y = 31.8, 23, 81.8; 48.9 solid hcp, 19.0 gel units, T = 67.9; Reak: W, Prod: 1. cap. pores, gel pores, solid hcp

Comparing this to the previous example, where we had 13.9 milliliters and water cement ratio of

0.5, theoretically you can end up at about 13.9 milliliters of voids space. Whereas when you are reducing the water cement ratio to 0.3 you have almost a 1/3 reduction in capillary porosity,. The total porosity if you look at capillary and gel pore; here it is 19 plus 13.9 that is 32.9 total porosity.

In Example 2, it is  $13.5 + 4.2$  that is 17.7. So total porosity is now reduced by almost 1/2 of what it was earlier. What do you think is typical strength of a concrete with water cement ratio of 0.5? About 30MPa? What about 0.3 water cement ratio assuming that you are taking care of all the proper workability and everything? you may get 65MPa to 70MPa

So with 0.5 you will get around 30MPa strength; with 0.3 you may go 65 to 70 mega pascal. Correspondingly the porosity we saw in example 1 was 13.5 milliliter and here it is 4.2. So, strength of concrete is directly linked to the porosity in the paste. Apart from that there is going to be porosity in the concrete which is external to the paste.

The porosity that we are talking about are the voids because of the inefficient mixing and packing, volume shrinkage of concrete that is being caused by the shrinkage of the paste and interfacial transition zone.

So, higher porosity in the ITZ, and porosity in the paste are going to be dictating the strength of the concrete. So, here we are trying to relate the capillary porosity of the cement paste to strengthen the concrete. So, you may not get a perfect relationship. If you look in many textbooks it would have explored the relationship between strength and water cement ratio. And one common aspect that you will find explored in textbooks is the relationship between strength and gel to space ratio. What do you mean by gel to space ratio? Gel is basically referring to the total solid system divided by the total volume of the system. So, what do you think will be the shape of this relationship? It should be an increasing relationship or decreasing? Generally the strength increases as a function of the gel to space ratio in a polynomial fashion. Gel does not mean CSH alone; gel means all hydrated products including any fillers that exist in the system and this relationship also was first shown by Powers.

And what people have found today in modern research is after all the advanced analyses of the concrete micro structure and understanding how structure properties are related, they have come to the same conclusion Powers relationship is still valid. So, what would happen to the 4.2 milliliters of the porosity? It was mentioned earlier that in the early ages you may have water from the external curing which can actually come inside.

There is water that comes into the 4.2 milliliters of porosity; you may get a chance to interact with unhydrated cement. So, that may lead to a greater hydration taking place in the system. Now we will discuss later that one of the common problems with high cement concrete or low water cement ratio concrete is its tendency to drive from within, that is called autogenous shrinkage.

Autogenous means happening on its own and it happen on its own because of hydration of the unhydrated cement. It is leading to shrinkage due to two factors, one is the chemical shrinkage about which we already saw; 25.4 percent of the bound water

This autogenous shrinkage is happening because once part of the cement is hydrated the pore network has become very small. The pores are small and to hydrate any of the unhydrated cement that is still left the water has to travel through the extremely small pore network and that is going to lead to a lot of shrinkage. So, this autogenous shrinkage is a problem in high strength concretes.

Drying shrinkage is a problem in high water cement ratio systems. Because in low water cement ratio systems there is no water to dry out of the concrete. When the pores are extremely small you cannot drive the water out unless you reach very extreme levels of drying or you heat the concrete so much that water actually has to come out like 100°C. So, even if you do completely sealed curing that means you prevent any drying to the external environment they will be drying from within in low water cement ratio systems.

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## ment Chemistry Part 5 Paste composition

Phase data for a Type I OPC paste made with a w/c of 0.45.

<sup>1</sup> Formula 1.7C-S-4H, <sup>2</sup> Formula 1.7C-S-1.6H.

Phase	Density (g/cm <sup>3</sup> )	Volume %	
		At Mixing	Mature Paste
C <sub>3</sub> S	3.15	23.40	1.17
C <sub>2</sub> S	3.28	7.35	0.78
C <sub>3</sub> A	3.03	4.42	0.00
C <sub>4</sub> AF	3.73	2.67	1.38
Gypsum (C <sub>2</sub> H)	2.32	3.47	0.00
C-S-H (solid) <sup>1</sup>	2.65	0	29.03
C-S-H (with gel pores) <sup>2</sup>	1.90	0	49.99
Portlandite (CH)	2.24	0	13.96
Ettringite (AFt)	1.78	0	6.87
Monosulfaluminate (AFm)	2.02	0	15.12
Water	1.00	58.49	31.69
Gel porosity	--	0	20.96
Capillary porosity	--	58.49	10.73

[http://iti.northwestern.edu/cement/monograph/Monograph5\\_6.html](http://iti.northwestern.edu/cement/monograph/Monograph5_6.html)

Some data is given here for typical paste composition based on certain water cement ratio at a certain age for the phases right after mixing and in a mature paste. Looking at the phases as a volume fraction of the paste you know that water will be the greater volume cement will be the lesser volume.

So, within that you have volume fraction of paste is 23.4% of C<sub>3</sub>S and in a mature paste most of that C<sub>3</sub>S is actually reacted. So, we are talking more mature paste of the order of 6 months to 1 year, i.e, technically you allowed hydration to complete over long period of time and ensured that curing happens throughout this duration okay. C<sub>2</sub>S much smaller content and some of it may still remain unreacted.

That is physically it is difficult for water to reach each and every particle of cement right and due to the fact that the formation of the hydrated layer as water has to diffuse through the hydrated layer and then react with unhydrated cement. So, that may or may not happen. Although we saw that 0.42 was technically required for 100% hydration here you see that at 0.45 also we do not get full hydration because you still have the unhydrated phase is still remaining

C<sub>3</sub>A went down from 4.42 to 0 as it is very highly reactive phase and it is present in micro crystal in sizes because it reacts with the sulfates to form the sulfoaluminate products. In case of C<sub>4</sub>AF hardly anything is reactive because the iron in C<sub>4</sub>AF is not easily soluble. So, practically it

remains in the system. Gypsum gets consumed by the  $C_3A$ . So, there is no Gypsum left in the system. The other compound like Portlandite, ettringite, Monosulfate obviously were not there during mixing. The formation in a mature phase indicates that the CSH is forming nearly 80% of the cement paste, portlandite is 14% and calcium sulfoaluminates are about 20%.

The water is given in terms of percentage by volume as the volume of water present system later gets distributed between capillary and gel porosity, as in approximately the same ratio that Powers was talking about. But here it is a little bit different because Powers had mentioned that 1/3 of the water is in gel pores and 2/3 in capillary pores.

Here it is the other way around because what has happened is your gel porosity is higher because of higher degree of hydration in the system. So, this is how your cement paste or mature cement paste after about 1 year of hydration looks like. Essentially what we are saying is your cement paste will have a greater volume of CSH and you cannot total up 'CSH with gelpores' and 'CSH solid' because the solid part of CSH is included in the structure of the CSH. The sum of gel porosity and CSH solid will give the volume of 'CSH with gelpores' which is 49.99.

For this they had used certain formula for the CSH as shown in the slide; for example the type ACSH, the solid CSH, they have assumed a formula of  $1.7C S_4H$ . Whereas for the one with gel they have assumed a formula  $1.7C S 1.6H$  so that you are able to work out the documentary correctly balance the reactions and then propose the extent of the system the extent of the sub element of the system.

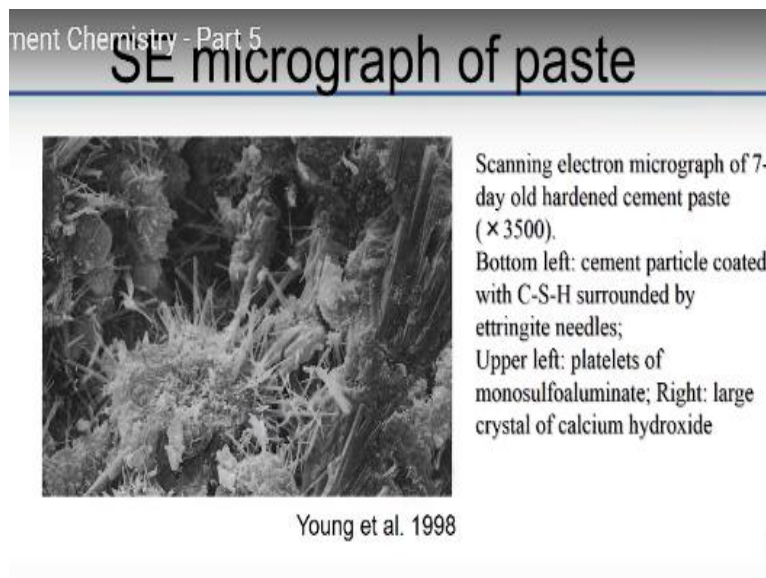
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# Structure of hydration products

Visit:

<http://cementlab.com/cement-art.htm>

Let us now look at some structures of the hydration products (**Refer Slide Time: 17:18**)



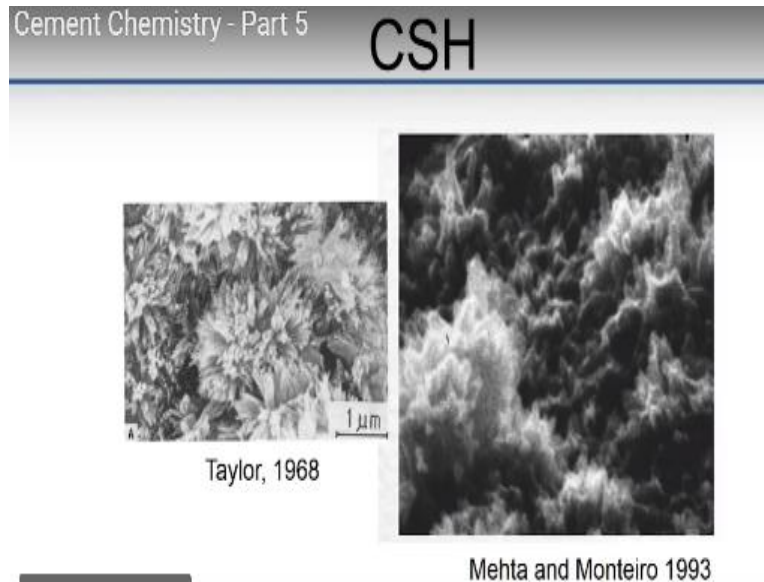
This is a classic picture of cement paste at a fairly early ages 7 days' old of a hardened cement paste using a scanning electron micrograph at a magnification of 3500 x. At the bottom left here you see a cement particle that is surrounded by the fibrous network of CSH as well as you see these ettringite needles.

On the upper left you have these platelets of monosulfate. A platelet is essentially a 3 dimensional object more like a plate, thickness is very small as opposed to the dimension of the plate okay .On the right you see a very large crystal of calcium hydroxid. So, again this seems to show that the crystalline products like ettringite, calcium hydroxide, monosulfate these have low



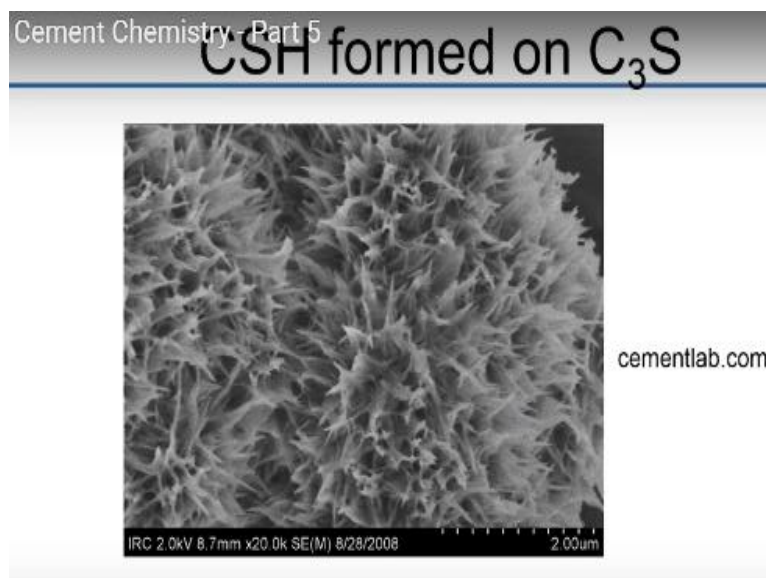
surface area because of their crystalline well-formed shapes whereas CSH does not really have a clear cut shape and it has got a very large surface area.

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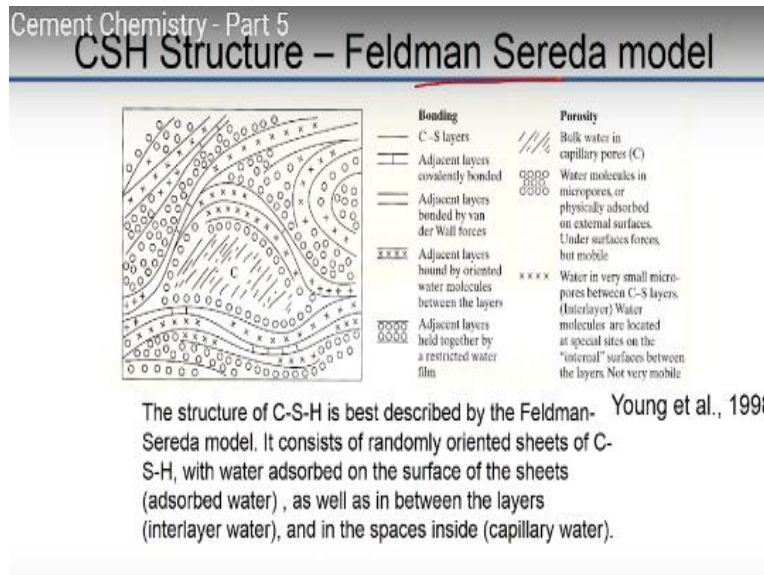
Some more evidence are shown in the slide, of CSH and the fibrous network of CSH particles that is actually existent. You see that the CSH is looking very fibrous and does not have a very distinct crystalline morphology. And this is a very high magnification, for example, this scale is 1 micron so you can imagine were looking at clusters of CSH particles which are only about a few microns in size. So you have to understand the structure at different levels and try to relate this to the overall properties of the concrete which is obviously in macro level.

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The picture shown above is CSH which is forming on  $C_3S$  particles. This is actually the surface of the  $C_3S$  particles and you can see the fibrous nature of the CSH that is formed on the surface.

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All this seems to indicate that CSH has a sheet like structure and there are many scientists who worked on deciphering the structure of CSH associating it with naturally available minerals for instance. But most of them agree that the best representation of the CSH structures brought about by what is called the Feldman Sereda model. According to this CSH is present in layers or sheets.

You can see these sheets indicated in the diagram on the left and some of these layers of CSH may be covalently bonded. Some of the layers may be bonded by weak Van der Waals forces that is more commonly accepted. There are molecules of water which are in between the layers which we call as inter layer water.

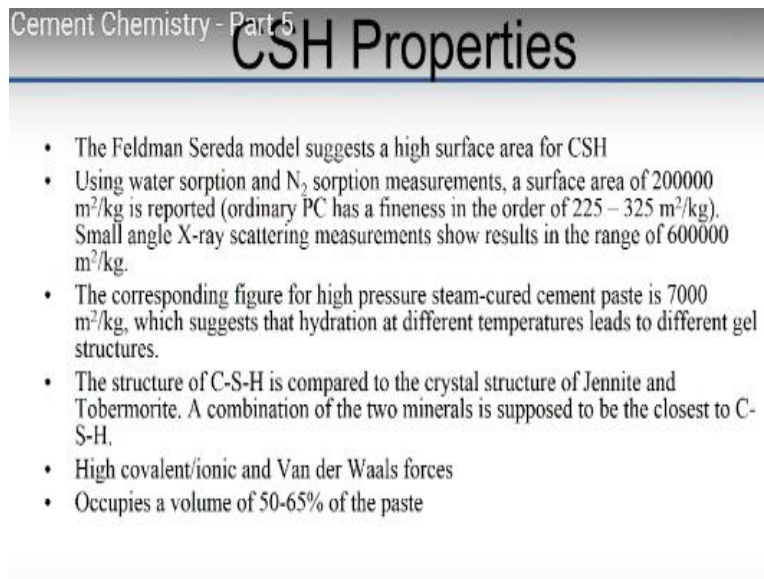
There are molecules of water which form a film on the surface that is adsorbed water. There is bulk water in the capillary porosity marked as C and there are water molecules in micro pores that can also happen and water between the small micropores between the CS layers.

So, all this is represented quite nicely in the structure that you see on the left. Of course to a person who is new to the subject it will must seem like somebody randomly drawing lines and

crosses and dots but the idea is these crosses and dots are representing a structure that we seem to associate with CSH. These sheets are randomly oriented there is no precise orientation of these sheets which causes the cohesive nature of the CSH itself.

The extent of the capillary porosity is depended once again on your initial composition ;what is the ratio for instance like we discussed in the calculation that we made earlier.

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Cement Chemistry - Part 5

## CSH Properties

- The Feldman Sereda model suggests a high surface area for CSH
- Using water sorption and  $N_2$  sorption measurements, a surface area of 200000  $m^2/kg$  is reported (ordinary PC has a fineness in the order of 225 – 325  $m^2/kg$ ). Small angle X-ray scattering measurements show results in the range of 600000  $m^2/kg$ .
- The corresponding figure for high pressure steam-cured cement paste is 7000  $m^2/kg$ , which suggests that hydration at different temperatures leads to different gel structures.
- The structure of C-S-H is compared to the crystal structure of Jennite and Tobermorite. A combination of the two minerals is supposed to be the closest to C-S-H.
- High covalent/ionic and Van der Waals forces
- Occupies a volume of 50-65% of the paste

From this structure the one aspect that comes out clearly is that CSH should have a very high surface area. And there are different techniques for measuring surface area one of the common techniques is adsorption technique. So, you can do an adsorption on CSH surfaces either by water molecules or by nitrogen is absorption which is quite highly favored.

And that seems to suggest that CSH has a surface area of nearly 200000  $m^2/kg$ . That doesn't mean the sheets are fine sized because they are sheets there is a large surface available on CSH. So, 200000  $m^2/kg$  as the sorption suggested surface area of CSH. You know that using Blaine we associate the total cement to have a surface area of about 225 to 325  $m^2/kg$ ; more typically around 300  $m^2/kg$  Sp CSH is a completely different entity as compared to your average cement particle because of the cement particles being 3 dimensional granular objects whereas CSH being sheet because of which it has an extremely high surface area and depending on the technique you can actually show this surface area of CSH to be even as high as 600000  $m^2/kg$ .

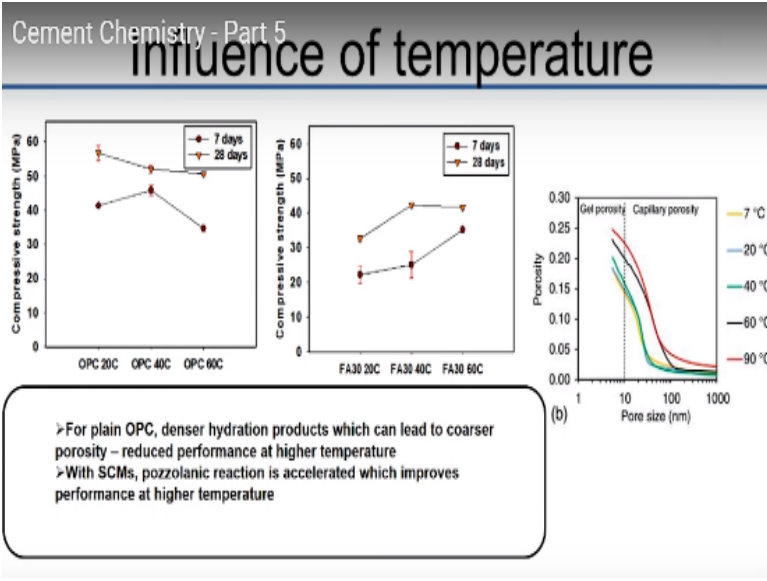
But we are not here to discuss the technique but our idea is try and understand what happens to the cement which is a fine grain particle how does it convert into a sheet like structure which has extremely high surface area. Now interestingly what people have found that if you heat cement during the early stages of hydration if you do steam curing or heat curing which we often do for precast materials to increase the rate of strength development, it turns out that the surface area of the CSH that forms as a result of heat curing is about 7000 m<sup>2</sup>/kg. This suggests that you are leading to a different gel structure formation when you do steam curing and indeed turns out that the steam cured concrete while it gives you a very high rates of strength development in the beginning, In the long term the strength that is attained by steam curing concrete is of a lower order as compared to the strengths attained by normally cured concrete and that is happening primarily because you are creating more coarse porosity in the system. This happens because in the early fresh cement paste system when you increase the temperature you are rapidly causing dissolution from the surface of the particles

In other words you are forming this hydrated barrier structure much faster and you do not give a chance for complete hydration to take place inside. Research has shown that the inner CSH seems to be even denser at high temperatures. So, the problem actually lies in the coarse porosity; that is outer CSH.

And that is of a higher extent in the case of heat curing or steam curing. So, this gel surface area that we are actually measuring is of the CSH that is in the outer CSH. The inner CSH we are not really bothering about in this case because we are not having a problem with heat curing in that case. What people have tried to do is associate the structure of CSH which with some naturally occurring minerals. So, here they have said that it resembles a combination of the structures of 2 different calcium silicates one is called the Jennite and the other is called Tobermorite.

The sheet structure obviously suggest that it is going to be very high he the covalent or Van der Waals forces and the volume occupied in the paste is typically more than 50% of the paste.

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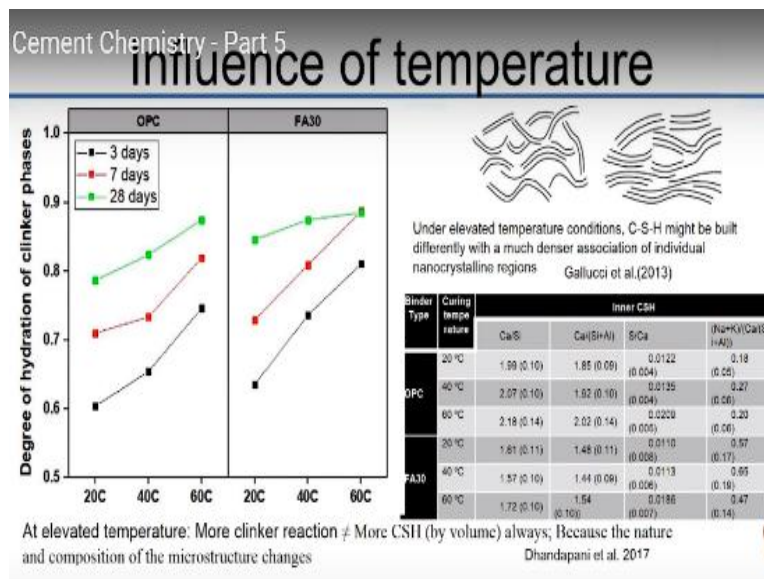
To show the effect of the influence of temperatures, OPC and cement with e 30% fly ash is compared. For OPC att 7 days; with an increase in curing temperature from 20 to 40°C there is a minor increase in the strength. But when you increase it to 60°C there is a decrease in the strength. By 28 days, the strength is decreasing irrespective of the temperature and that means when increase the temperature the strength is dropping. Interestingly the fly ash system; it is not so what is happening. In this case at 7 days you see a fairly rapid rise between 40°C and 60°C. Whereas by 28 days you see that the strength drop that is associated with 60°C in the case of the OPC is not visible in the case of fly ash concrete. So, generally if you look at precast concrete construction nobody wants to use fly ash. Because they feel that rate of strength development reduces when you use fly ash. In fact in pre-stressed concrete the use of fly ash is not even permitted in many regulations. But here you have evidence exactly to the opposite that when you do heat curing with fly ash concrete you actually obtain strengths which are not deteriorating in the long term. So, there is positive advantage of using fly ash in precast and pre-stressed systems.

Shown on the right side is an example of how the porosity varies with different temperature. This is determined with a technique called mercury intrusion porosimetry. So, in this case what we do is we have cement based or mortar samples which are enclosed in a chamber and the pressurized mercury into entering the pores and at higher pressures you will penetrate the smaller and smaller diameters of the pores.

So, all we do is simply penetrate or make the mercury penetrate into the pores under an increasing set of pressures. So, the pore size distribution can as a result be obtained from this experiment. So here as I am increasing my temperature pore sizes are getting larger and larger. So, I am coarsening my porosity because of increase in temperature.

So, the most important aspect about OPC concrete which is exposed to high temperatures is that it will end up having more capillary porosity when you do heat curing in the system. So, any system which you make to react in a fast manner in the beginning will ultimately attain a lower level of packing and microstructural development in the long term. So, for example if I use an accelerating chemical in the concrete, and I get an extremely rapid rise for the first 2-3 days' strength, in the long term I see that my normally cured will go beyond the strength obtained by the accelerated system. Concrete if its slowly hydrated if its normally cured it tends to develop a much greater microstructure that leads to a long term strength and durability.

What I am not shown here is the real effect on durability that is even more drastic as opposed to the effect on strength. In the coarser porosity that is produced by high temperature curing, you actually get poorer durability of the concrete. **(Refer Slide Time: 30:36)**

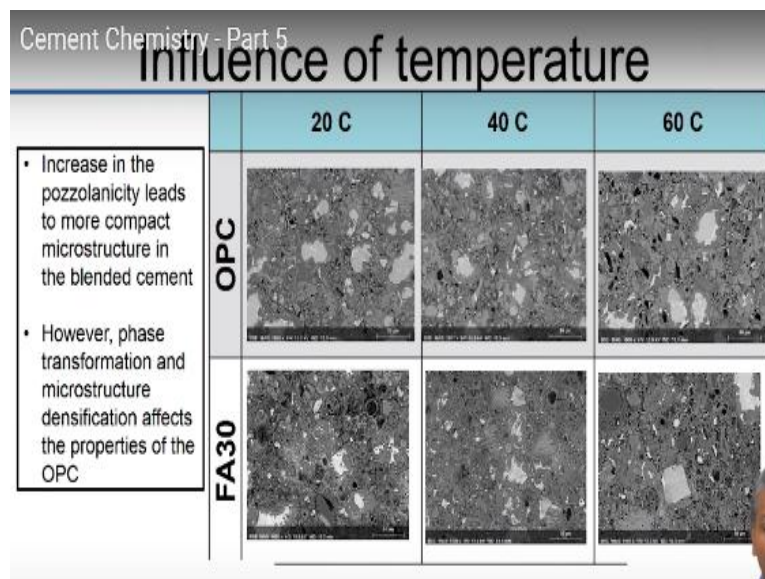


But what happens to the degree of hydration? My degree of hydration is going up as increase the temperature. What you think is happening in this case? The high temperature ensures that the other processes that take place in terms of diffusion across the hydration barrier reaching the un

hydrated particles all that happens much faster than your normal temperature. So, the inner CSH that is produced in the system will tend to have a much better density at higher temperatures. So, what you will see is that the calcium to silicon ratio of inner CSH goes up as the temperature increases.. What we will also see is there is a great amount of sulfur and alumina inclusion in the system and probably even alkaline inclusion in the system. Though the results are not conclusive, what people have shown is there is a greater extent of Sulphur inclusion in the inner CSH at higher temperatures. So, you are packing the inner CSH more densely at higher temperatures which are leading to this increase in the degree of hydration of the clinker phases. Some of these results may also be attributed to the way that the measurement is being done.

So under limited temperature conditions CSH may be built differently which are much denser association of individual nanocrystalline regions. In other words, what we are saying is we are making the CSH itself denser but more outer porosity is created with the influence of temperature.

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Looking at some scanning electron micrograph images of polished sections which seems to show that as the temperature is increased from 20°C to 40°C to 60°C, in the outer grey area you can clearly see there is a clear distinction in the extent of porosity at 20°C 40°C and 60°C

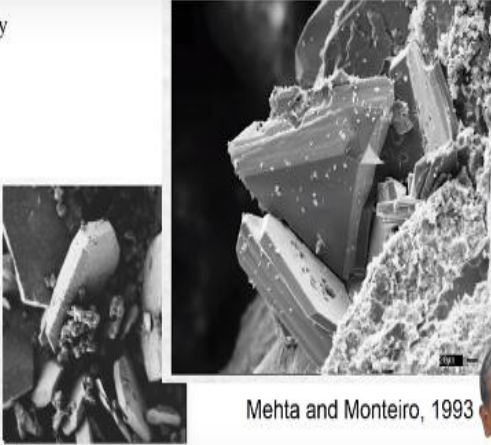
But what is interesting is when you do the same with fly ash the result is not exactly as you see with Portland cement; there is a distinctly better performance when you increase the temperature with fly ash concrete. When you increase the temperature the reaction of pozzolanic reaction also increases. So, fly ash is also increasing its reaction with the calcium hydroxide to produce additional CSH so its leading to more densification of your outer process

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Cement Chemistry - Part 5

## Calcium Hydroxide

- Hexagonal crystals, generally oriented tangentially to pore spaces and aggregates along the longitudinal axis
- Low surface area ( $0.5 \text{ m}^2/\text{g}$ )
- Low Van der Waals forces
- Volume – 20-25%



Mehta and Monteiro, 1993

Calcium hydroxide is known to form hexagonal crystals and generally it is oriented tangentially to spaces available for it to grow. For example, pore spaces in areas around the aggregate. The well-developed crystal structure seems to indicate that the surface area is going to be low at about  $0.5 \text{ m}^2/\text{g}$  or  $500 \text{ m}^2/\text{kg}$ . Van der waal forces are low because very well formed crystals do not have any force of attraction between them; gels or colloids experience much greater forces that bind them. Volume is about 20% of the overall matured cement paste. So, after CSH this is the second largest contributor to the volume of the cement paste.

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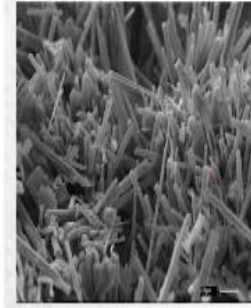
## Calcium sulphoaluminates

- Ettringite: Acicular, columnar, hexagonal crystals (seen as prismatic needles). The presence of tubular channels in between the columns can lead to high water absorption and swelling by ettringite. This is one of the theories explaining the expansion caused by ettringite formation.
- Monosulphate – plain hexagonal
- Volume occupied is 15 – 20%

There is a lot of debate about the structure of Ettringite and we will revisit this when we actually discuss Sulphate attack as to what type of ettringite is actually produced and what type of Ettringite really causes expansion. Ettringite is seen as needles in the microstructure. It is basically columnar structure but it is also hexagonal which are seen primarily as needles in the system because you have very small dimension of the hexagon. The presence of tubular channels between the columns can lead to a very high rate of water absorption and the reason why ettringite expands is primarily because it absorbs water and there is absorption of water in hardened concrete can lead to obviously expansion and cracking the system. In the fresh cement paste we do not worry about expansion because paste is still pliable. It can take the stresses created by expansion. Monosulphate on the other hand is a hexagonal platelet and volume occupied by ettringite and monosulphate is about 15 to 20%.

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# Ettringite and monosulphate

**Ettringite**

Mehta and Monteiro, 1993

**Monosulfoaluminate**

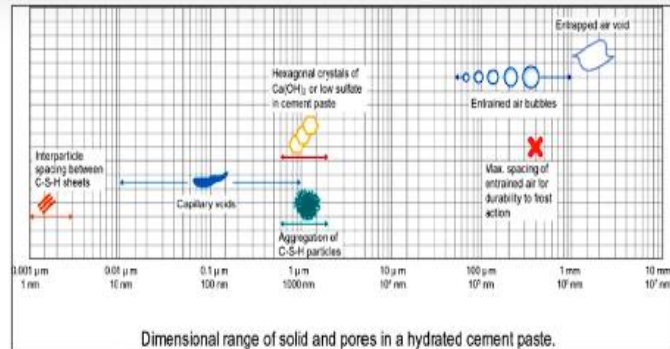
Mindess and Young, 1981

Ettringite needles are shown very clearly in the picture on left side and on the picture on right; you can see here monosulphate and ettringite which are co-existing. Some others look like needles but they are actually the orthogonal view of the platelet.

It is mentioned earlier that ettringite monosulphate are present in micro crystalline sizes very small sizes. You can see here at least Ettringite is present in larger sizes. The pictures are taken at magnification of 2 microns. Even with techniques such as x ray diffraction you may not be pick out sometimes mono sulphate because it occurs in very small crystals. So, what we assume is mono sulphate or other sulfoaluminate phases are present in a mixture with the CSH. That is why we assume almost that this mono sulphate is also an amorphous phase whereas this ettringite shows very clearly as a crystalline phase when you do techniques like extra diffraction because of this long needles that actually forming in the Ettringite.

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# Pores and Air Voids



Mehta and Monteiro, 1993

The other important part of your cement paste microstructure are the pores and voids in the system. At the furthest end is the entrapped air void, which won't generally be there in paste unlike mortar and concrete; because there is inefficient mixing that you do with the aggregates of the paste and that leads to entrapment of air voids inside the system.

Entrapped air voids are greater than 1 millimeter in size. Sometimes we forcibly put air in the concrete to get good resistance against freezing and thawing. Freezing and thawing produces damage to the concrete microstructures because of that we need better resistance and for that we actually provide spherical air bubbles in the concrete and that is called air entrained concrete. These entrained air bubbles are typically a few 10s of microns all the way up to about 1 millimeter in size standards say that the air bubble should not be separated by more than 200 microns. So, the spacing between the air bubbles also should be minimized to ensure that you get a good resistance to freezing in thawing.

In the region of about 10 to 100 microns you do not have anything but you have something what is that? It is the un-hydrated cement. At some size smaller than that you have calcium hydroxide hexagonal crystals which is about less than 1 micron to about several microns. And you see those clusters of CSH; not individual CSH but clusters of CSH; is it that is of the size of because you will not be able to see individual CSH because it is present at a nano level right.

So, mostly you will be able to make out only clusters which are several microns in size. Smaller than that you have capillary voids which occupies a very large range right all the way from 10 nanometers to about 1 micro meter. Below the capillary voids you have the gel voids or gel spaces. In this case inter particles spacing between the CSH; we were looking at only about 5 nanometers in size and maybe some small porosity may also be present in the less than 10 nanometer range, So, this is the extent of void spaces and particle sizes that you see in cement paste

So, you see very clearly that we are ranging all the way from over 20 millimeters in the case of coarse aggregate to 1 nanometer in the case of inter particle spacing between the CSH. So, we are dealing with a material that is having a wide range of particles and void shapes and sizes present in the system because of which the properties can be quite complex how these interact at different levels can lead to very different behaviors in concrete.

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Cement Chemistry - Part 5

## Types of pores

Type of Pore	Description	Size	Water	Technique*	Properties
Capillary Pores	Large	10 $\mu\text{m}$ - 60 $\mu\text{m}$	Evaporable Bulk water	SEM, OM	Permeability, strength
	Medium	50 - 10 nm	Evaporable Moderate menisci	SEM	Permeability, strength, shrinkage (high RH)
Gel Pores	Small	10-2.5 nm	Evaporable Strong menisci	Absorption MIPAS	Shrinkage, creep (to 50% RH)
	Macropores	2.5-5.0 nm	Non-evaporable No menisci intermolecular interactions	Absorption MIPAS	Shrinkage, creep (to 11% RH)
Interlayer Spaces	Structural	< 0.5 nm	Non-evaporable -ion-covalent bond	Absorption Thermal	Shrinkage, creep (to 11% RH)
Other Features	ITZ	20-50 $\mu\text{m}$	Bulk Water	SEM/OM	Permeability, strength
	Microcracks	50 -> 200 $\mu\text{m}$	Bulk Water	SEM/OM	Permeability, strength

\* SEM: scanning electron microscopy, OM: optical microscopy, IS: impedance spectroscopy

[http://iti.northwestern.edu/cement/monograph/Monograph7\\_2.html](http://iti.northwestern.edu/cement/monograph/Monograph7_2.html)

There is one more indication of the types of porosity and also the technique for determining the porosity. That is also important as depending on the limits of one technique you will have to actually choose a different technique and so on. As shown in the table, most of the techniques are either just scanning electron microscopy or optical microscopy but sometimes when we get down to gel porosity and CSH structure we need to start using adsorption or mercury intrusion porosimetry or impedance spectroscopy. But for most of the larger features like ITZ for example

micro cracks the scanning electron microscope, optical microscopy is good enough to get to the features that you want to study.

We have larger capillary pores between 10 microns and 50 nanometers from which if you dry water, it is not going to lead to large shrinkage but from the smaller capillary pores 50 to 10 nanometer when you remove water there is going to be very large amount of shrinkage. Under gel pores you have small pores and micro pores and these are very difficult to actually remove; almost the micro pores are leading to non-evaporable water.

Although earlier we said non-evaporable water that is bound within the crystalline structure; but here some micropores may be holding the water so tightly that you are not going to be removing that water at all. That we are talking about less than 2.5 nanometer size and if you do mercury intrusion porosimetry you may not even be able to determine that porosity because of the extent of pressure that you can go to.

Typically, about 3 nanometers is the limit of what you get by mercury intrusion porosimetry. Interlayers space is even less than 0.5 nanometer; so you can imagine pulling out waters going to be next to impossible. Other features could include ITZ which is 25 to 50 microns in size and micro cracks which obviously depends on the mechanism that has caused those cracks to appear in the first place.

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## Further reading

- <https://www.youtube.com/watch?v=Ast3dpdLBR8>
- <https://www.youtube.com/watch?v=8cz9WFj534U>
- [http://iti.northwestern.edu/cement/monograph/Monograph1\\_4.html](http://iti.northwestern.edu/cement/monograph/Monograph1_4.html)
- <https://www.youtube.com/watch?v=k02fOFB2-iQ>
- <http://www.engr.psu.edu/ce/courses/ce584/concrete/library/construction/curing/hydration.htm>
- <https://www.understanding-cement.com/hydration.html#>
- <https://www.nist.gov/publications/chemical-vs-physical-acceleration-cement-hydration-cacl2-vs-limestone-powder>

There is a lot of further reading you can do with cement chemistry, the subject I only touched upon is the tip of the iceberg; there is a lot more that is beneath the surface of the sea that you cannot see and there is a lot more studies you can do. Cement chemistry is still a subject of a lot of research around the world primarily because people do not realize that if you get down to the fundamentals in cement chemistry, you can actually explain a lot of the fundamental parameters and properties experienced by concrete in its service. So, primarily if you pay attention to the cement chemistry you can associate it with most of the other characteristics of concrete behavior that we later learn about like strength, elastic modulus, we learn about aggregate paste relationships, we learn about durability of concrete. So we will see that all of that is related quite nicely to cement chemistry.