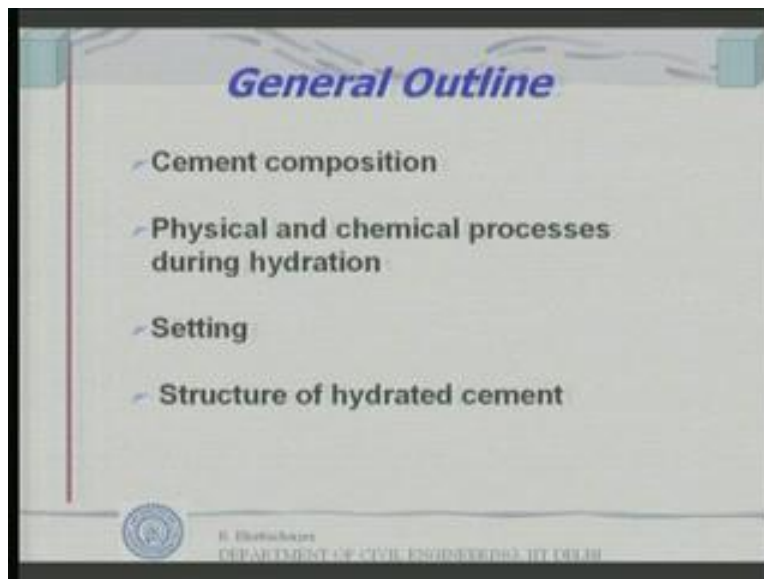


**Building Materials and Construction**  
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**Module - 4**  
**Lecture - 1**  
**Cement: Hydration**

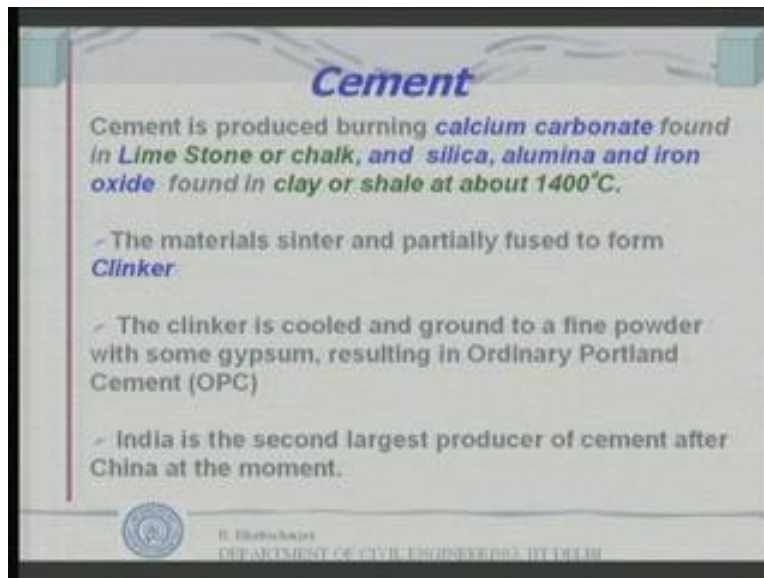
Last class we looked into concrete production process. And now we said that basically the concrete is produced because cement reacts with water and it hydrates. And there by bonds various inert material like aggregate. So, today we will look into hydration process of cement.

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So, general outline of the talk today would be first we will look into general cement composition. Physical and chemical processes involved in process of hydration, and then we looked into what is known as setting and then structure of hydrated cement.

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So, let us look at cement composition now we mentioned earlier it was in the last module sometime. We said that cement is produced by burning calcium carbonate found in lime stone or chalk and silica alumina and iron oxide found in clay or shale at about 1400 degree centigrade.

So, we burn limestone with clay. Now, this material sinters and then partially fused to form what is known as clinker. Clinker is cooled and ground to a fine powder little bit of gypsum is added in the process and this results in what is known as ordinary Portland cement; OPC in short form you call it. Just for the sake of information, India is the second largest producer of cement after china at the moment.

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**Oxide composition**

CO<sub>2</sub> from Lime stone is liberated while burning leaving CaO, SiO<sub>2</sub> etc.

Approximate composition limits of Portland cement

Oxide	Content, percent
CaO	60-67
SiO <sub>2</sub>	17-25
AL <sub>2</sub> O <sub>3</sub>	3-8
Fe <sub>2</sub> O <sub>3</sub>	0.5-6.0
MgO	0.1-4.0
Alkalis	0.2-1.3
SO <sub>3</sub>	1-3

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Then we can look into the oxide composition of the cement. Now, you see we burn limestone. And limestone is calcium carbonate. So, when you burn limestone the calcium carbonate the carbon dioxide from the limestone is liberated and therefore, leaving calcium oxide. The clay and shale or whatever it is that leaves silicon oxide iron oxide aluminium oxide. So, therefore, various oxides are left after burning and they are forming 2 solid solutions. And therefore, cement basically composed you know it is consisting or it is composed of various inorganic oxide.


Approximate composition limits of cement is calcium oxide generally in ordinary Portland cement OPC is 60 to 67 percent, Si o 2 around 17 to 25, Aluminium oxide 3 to 8 and iron oxide 0.5 to 6 percent; magnesium oxide is restricted 0.1 to 4. There will be sodium oxide and potassium oxide alkalis 0.2 to about 1.3, sulphur trioxide 1 to about 3 percent. There are something else called loss of magnesium which actually is a measure of un-burnt material which can burnt and form into oxides. So, those are the additional things. So, this is a typical oxide composition in cement.

Now, 1 point I would like to mention here before w go to the compound composition of cement. You see burning of cement essentially we are actually generating carbon-dioxide. So, therefore, from an environmental concern cement produces carbon-dioxide,

it uses consumes lot of fossil fuel. So, the 2 ways actually it generates carbon dioxide first of all carbon carbonate calcium carbonate limestone generates carbon dioxide.

Since, we burn fossil fuel in heating up to 1400 degree centigrade we further actually generate carbon dioxide. So, from environmental point of view use cement is not really so green material. Therefore cement should be used very judiciously it is a material which gives us artificial stone. But, it should be used very judicious in a judicious manner and consumed as optimally as possible to the least amount. Because you know it has generates so much amount of carbon dioxide.

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<b>Compound Composition</b>	
Oxides forms solid solutions of compounds: $3\text{CaO SiO}_2$ , $2\text{CaO SiO}_2$ , $3\text{CaO Al}_2\text{O}_3$ and $4\text{CaO Al}_2\text{O}_3 \text{Fe}_2\text{O}_3$ etc	
Main compounds & abbreviations	
Oxide/Compounds	Abbreviations
CaO	C
$\text{SiO}_2$	S
$\text{Al}_2\text{O}_3$	A
$\text{Fe}_2\text{O}_3$	F
$3\text{CaO SiO}_2$	$\text{C}_3\text{S}$
$2\text{CaO SiO}_2$	$\text{C}_2\text{S}$
$3\text{CaO Al}_2\text{O}_3$	$\text{C}_3\text{A}$
$4\text{CaO Al}_2\text{O}_3 \text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$
Compound composition can be obtain from Oxide Composition By Bogue's equation	
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Tri calcium 3 calcium oxide Si o 2 tri calcium silicate as we call it this is di calcium silicate tri calcium aluminates and tetra calcium alumino ferrite. So, these are the main compounds of cement right. And in cement in case of cement chemistry we actually have abbreviate because we cannot write this big thing all the time. So, instead of writing calcium oxide we simple write c instead of writing silicon dioxide or Si o 2 we write s. So, instead of writing al 2 o 3 you write a and instead of writing fe 2 o 3 you write f.

So, therefore, this tri calcium silicate becomes c 3 s di calcium silicate becomes c 2 s and tri calcium aluminates becomes c 3 a. And tetra calcium alumino ferrite becomes c 4 af.

So, this is the abbreviations normally used in cement chemistry and that is those are the compounds of the forms are  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$ . They are the main compounds in cements main compounds in cements. They are complexes as you can see this compound composition can be found out you know it can determine from oxide compositions by a formula known as Bogue's formula Bogue's equation.

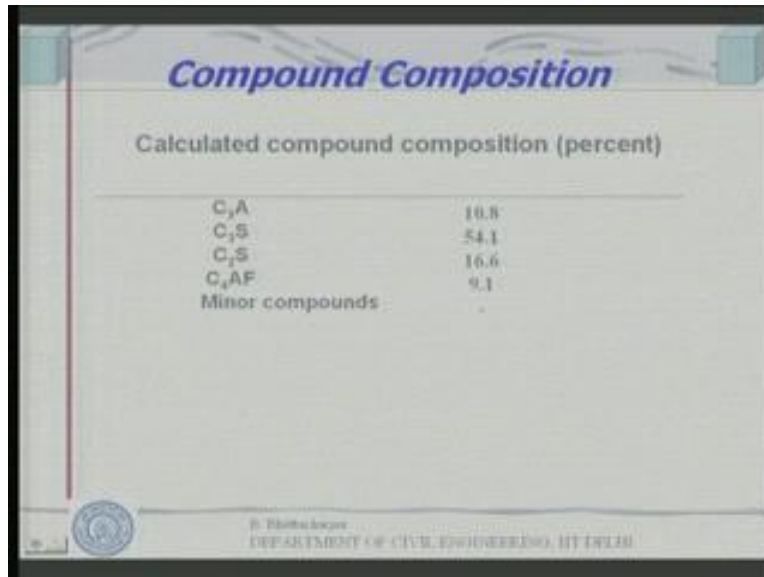
So, that tells you know supposing you know the oxide composition what would be the composition of composition of  $C_3S$ , what how much will be the  $C_3S$ , how much will be the  $C_2S$ , how much will be  $C_3A$  and how much  $C_4AF$  that you can find out. And that is what if I do.

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<i>Compound Composition</i>		
Main compounds in Portland cement		
Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3CaO \cdot SiO_2$	$C_3S$
Dicalcium Silicate	$2CaO \cdot SiO_2$	$C_2S$
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	$C_3A$
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	$C_4AF$

Then I get this is again showing the same tri calcium silicate to remember it because this is a long name tri calcium silicate, di calcium silicate, tri calcium aluminate, tetra calcium alumino ferrite has been repeated. So, this is clearly remembered because that is the terminology one uses again and again in the context of concrete and cement right.

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The slide is titled "Compound Composition" in a blue serif font. Below the title, it says "Calculated compound composition (percent)". A table with two columns lists the compounds and their percentages. The compounds are C<sub>3</sub>A, C<sub>3</sub>S, C<sub>2</sub>S, C<sub>4</sub>AF, and Minor compounds. The percentages are 10.8, 54.1, 16.6, 9.1, and - respectively. At the bottom, there is a small circular logo and the text "B. Huthakota DEPARTMENT OF CIVIL ENGINEERING, IIT TIRUPATI".

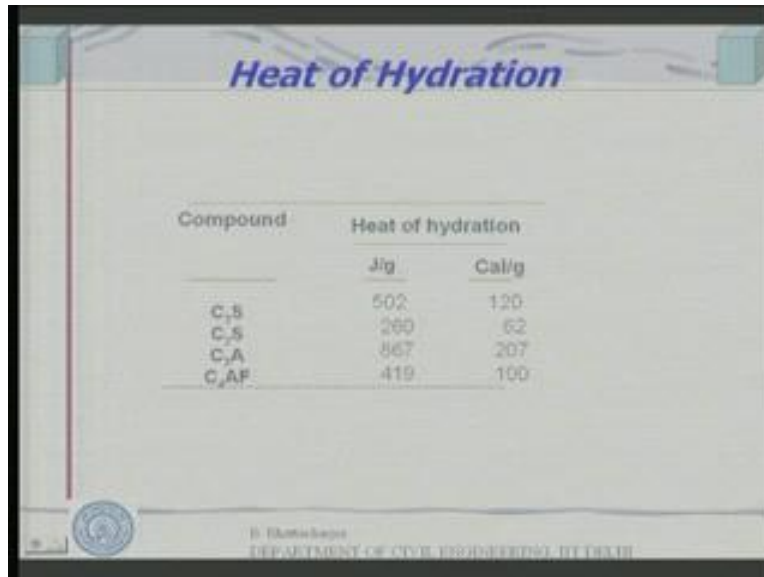
Compound	Percent
C <sub>3</sub> A	10.8
C <sub>3</sub> S	54.1
C <sub>2</sub> S	16.6
C <sub>4</sub> AF	9.1
Minor compounds	-

Now, if I calculate the compound composition based on Bogue's formula that we mentioned we find that  $C_3A$  comes out to be over 10.8 percent  $C_3S$  comes out to be 54.1 and  $C_2S$  comes out to be 16.6 and  $C_4AF$  turns out to be 9.1 percent. Assuming calcium oxide is for that OPC you know 60 to 67 percent which was shown earlier which was actually shown in 1 of those earlier slides. So, you can see that roughly about  $C_3S$  is 54, that is the maximum percentage  $C_2S$  is about seventeen and  $C_4AF$  is nine and  $C_3A$  is eleven percentage.

So, I can calculate without that composition from that side composition, I can calculate the compound composition. Now, this reaction is exothermic it generates heat because you know as I mentioned earlier that you are actually producing cement. Cement is not a man made material we are producing cement at the expense of energy. So, we consumed lot of energy because we burn it up to 1400 degree centigrade and therefore, or about. So, you know.

Therefore, we actually lock up a lot of energy and this energy it can dissipate by reacting with water. Chemical potential is raised and this chemical potential again it can come back to a stable state by somewhat stable state relatively stable state by reacting with water. So, therefore, the reaction is exothermic produces heat.

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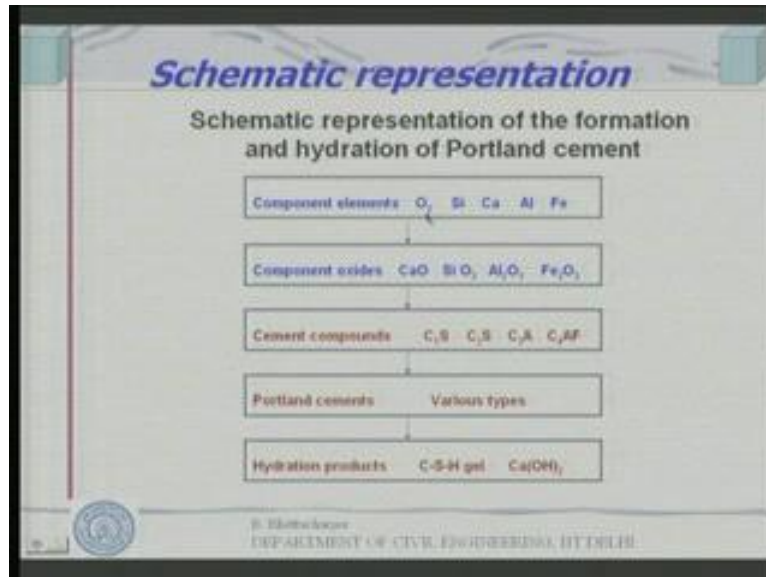
Compound	Heat of hydration	
	J/g	Cal/g
C <sub>3</sub> S	502	120
C <sub>2</sub> S	260	62
C <sub>3</sub> A	867	207
C <sub>4</sub> AF	419	100

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If you see the relative heat produced by different compounds we will see that C<sub>3</sub>S produces about 500 and 120 joules per gram it should be and this is 120 calorie per gram. This should be joules per kg this should be joules per kg C<sub>2</sub>S produces 260 C<sub>3</sub>A produces 867 and C<sub>4</sub>AF produces 419. So, this is the relative heat of hydration and this produces maximum heat of hydration. It generates maximum heat on reaction where as this generates least this is the next and so on so forth.

So, as we can presumably understand that possibly this will react faster than anyone else and this should react at a slower rate because it generates less energy. It will it is not you know explosion is explosion generates lot of energy. So, its instantaneous where as heat of hydration is slow or the reaction heat is relatively less. So, it will be slow it will be a slow process. So, this reacts immediately may be the next thing to react is this and this. And the lastly this reacts. So, this takes a long term for C<sub>2</sub>S reaction to be complete right.

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So, this is the heat of hydration of pure compounds if you do a schematic representation now of the formation of hydration of Portland cement. This is what we shall see you know we shall see that first things is your elements wise if you look at you will have oxides you know oxygen silicon calcium aluminum and aluminium and iron. So, we have this elements components elements oxygen silicon calcium aluminium and fe components oxides this combines into form oxides like calcium oxide silicon oxide aluminium oxide and iron oxides.

You know this is ferric oxides and then compounds this combines to form this compounds c 3 s c 2 s c 3 a and c 4 af. And when you add water to this forms what is known as csh gel and lime calcium hydroxide its slaked lime. We shall this little bit in more detail now these combinations can differ in different types of cements you can have proportions of this 1 would vary. And while varying these proportions you can actually get different types of cements. Again we will discuss this in detail because I can control the proportions of oxides oxide composition of the cement can be controlled relatively it can be controlled from the raw material mixing etcetera.

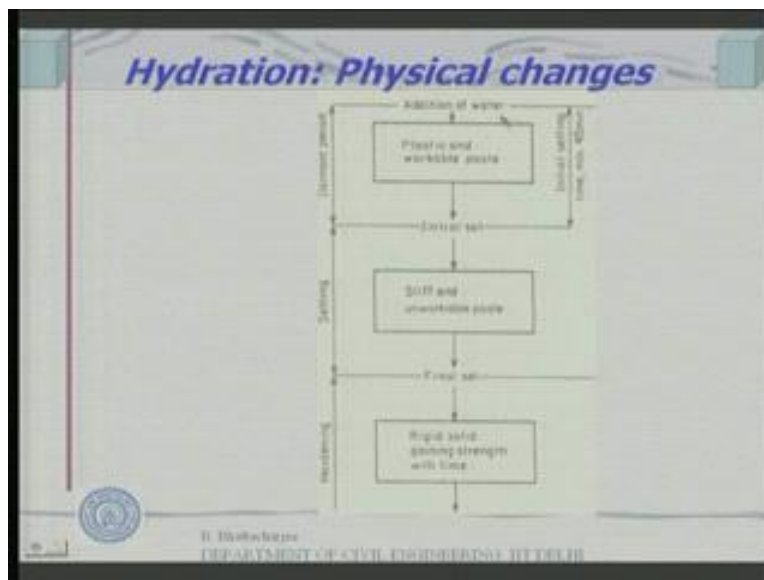
Thereby, the composition of the compound composition of the cement can be controlled. And you know the properties of each of them like I mentioned that c 3 a possible reacts



before anything else reacts, because it has got highest heat of hydration. So, if I want to increase or the reduce the rate of say heat of hydration. Then possibly I have to reduce the  $C_3A$  component or  $C_3A$  compound in the cement.

So, by manipulating they are the this compound composition I can get actually various types of cement and then I can add some additives etcetera. So, Portland cements plus various types of cements I can get and when it adds added with water it gives me hydration products. One of the major compound is called calcium silicate hydrate gel  $C-S-H$  gel and also it produces lime to certain extent we shall we shall see this in detail in next few slides.

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So, let us see this is what happens what happens to cement when I add water physically what happens if you see this physically addition of water when I add water with cement it will be in a plastic state It would be not liquid not solid, it is plastic because you know solid has got definite shape liquid flows on its own and attains the shape of the container itself now a plastic does not really attain the shape of the container by on its own. But you can make it to attain the shape of the container. So, it is plastic if you apply some force it will move or change its shape to attain the shape of the shape of the container. So, when you add to the powder like material as cement water to it.

It forms similar plastic mix and uniform mix would be plastic. So, addition of water makes it plastic and a workable paste as you call it workable paste this paste because of the reaction that is taking place. Because the reaction that is taking place it tends to solidify after all reaction consumes the water. So, it tends to solidify now this solidification process actually we call it sort of setting; we call it setting.

So, it sets to become a solid now initial period we call it the dormant period call it dormant period right. When it becomes from solids to it goes to from plastic state it goes to a solid state. And this should be minimum 45 minutes for ordinary Portland cement specified by most of the code. So, we call it initial setting initial setting means from plastic state it goes to a solid state not fully solid, but reasonably in a solid form. After which you can deform it further without compromising on its properties like strength etcetera. So, if you try to gain give it a new shape after this time well there will be some loss of its property.

So, that is what we call as initial setting. So, you add water the mix is plastic and it is workable you can actually apply force and get it in to a right kind of shape and then its initially sets. This time minimum should be 45 minutes and we call this dormant period. Now, you see how do you measure this now there is the basic ideas of physics and chemistry that was not available during those days when it was started.

So, some specific apparatus was designed and that is called vicats apparatus that has got a mould where actually you prepare a standard paste. The standard paste is prepared with standard amount of water which we call standard consistency. So, this paste you prepare with some specific or standard amount of water which is related to standard consistency and standard consistency is again determined by same apparatus. Whereby you prepare a paste and allow and needle at once ten millimeter dia needle to penetrate through it.

When the penetration has reached the specific level you say that it is a standard consistency similarly we use and find needle one millimeter needle to find out initial set when it pierces such that its depth of piercing you know from the bottom of the mould is five to seven meter or it is set to have a very initial set we define it in a specific manner. Well, since we are not we are looking into a number of materials we can not go into the

details of this test, but initially setting time and final setting time and standard consistency is determined by vicats apparatus.

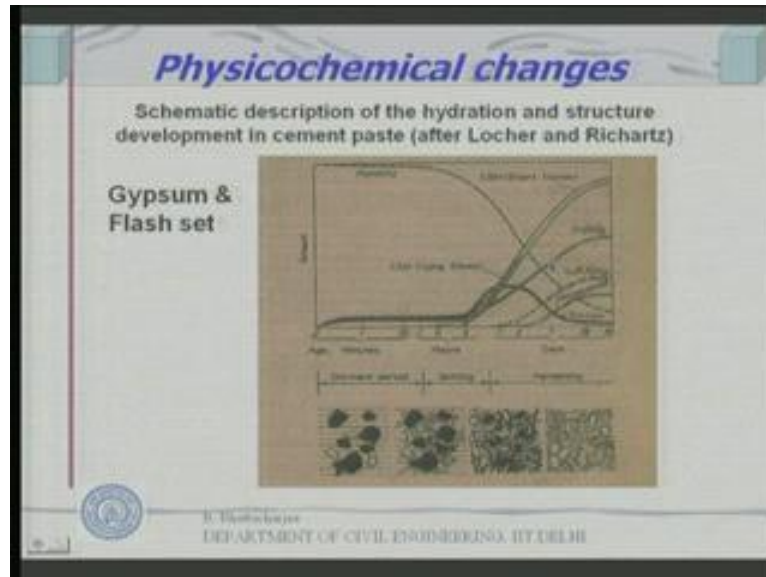
At the moment, I like to mention something called false set and flash set now false set happens when you have added too much of gypsum in to the system. So, that is called false set. You know. So, we can remix it again if the gypsum quickly reacts with water forming a solid. So, as if it is solidified that is called false set. So, we can remix it and that is not and you can get the right kind of setting.

So, that is dormant period initial set, but after that it actually solidifies further and it takes about 10 hours of you know 10 hours of time. The maximum specified is about 10 hours of time by which it should have become fully solid. But, it still does not gain strength it is not hard enough if you try to pull it or push it would have actually break. So, that is after that you know after setting it is hardening; hardening means gaining strength.

Setting means, going from a plastic state to a solid state in initial setting dor it is in dormant state dormant period, and then it is becomes stiffen and becomes a non workable paste you cannot work on it after the initial set. It sets further becomes full solid such that if you open up with the side mould. It will not collapse it has got its now definite shape and if you if you open up if you just expose it side faces of the concrete or cement paste it would no longer collapse.

So, it has become stiffen. So, that is called final set and beyond that of course, it becomes a rigid solid it goes on getting gaining strength and that process we call it as hardening right. So, this also final set also corresponds to the time at which peak temperature is attained peak temperature is attained. You know, because heat of hydration is produced and simultaneously and peak temperature is attained during that period of time. So that is what is initial and final setting time.

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Now, let us see chemically what happens we have seen that physically it solidifies and let us see physicochemical changes in slightly more detail. Now, if you look at this diagram then we can see physicochemical changes that is happening right. So, we can x axis is shows the amount this I mean y axis shows the amount x axis shows the time this is our age after just mixing the water. So, initially these are at thirty minutes then this is an hour.

Then this is in days now the first product to form because I said the c 3 a is the most reactive of all of the material and c 3 a will react quickly to water unless it is controlled. And it will react and give you an impression of what is called flash set; that means, c 3 a reacts and stops elevates the reaction of all other material that is called flash set right. So, in order to control this setting process we add some amount of gypsum gypsum is calcium sulphate. And this calcium sulphate has high affinity for c 3 a that is tri calcium aluminate.

Tri calcium, aluminate and gypsum reacts forming calcium sulphur aluminates the name of this compound is called ettringite the name of the compound is called ettringite right. So, that is the first thing. That is the first thing that forms during the dormant period right. And you can see the dormant period here the cement structures particles are here as it

floated in water and during the dormant period some reaction takes place. And sort of fiber like growth takes place this is phase where the setting is taking place and you know this fiber they grow. And solids the water filled spaces here the water filled these are water filled spaces outside the solid.

Then they tend to become field in which fiber like materials and they this water you know water would reacts. So, the volume occupied by water. Now, get pulled in by solids and gradually more and more solids are formed. And in a very long run you will have structure like this which will have large amount of solids with some pores which were originally occupied by water and some other special pores we will come to this in detail.

So, this is our physical changes that take place. So, this is the period dormant period this is the situation setting which is taking place and that is final setting and the hardening this is the this is the scenario. And then final you know to it will form after after ninety days or. So, you will have a firm solid structure. Now, this phase you can see that this is the ettringite you know this is mentioned with ettringite. So, initially your ettringite is formed during the dormant period. Now, this ettringite formation essentially is required to control the setting.

A ettringite is formed because of tri calcium aluminate reacting with the gypsum which we add if you do not add gypsum tri calcium aluminate quickly will react with water and it will give you impression of flash set. So, that is why we add gypsum and that controls the initial setting characteristic now this gypsum forms ettringite which expands in volume. And more and more ettringite formation that takes place from inside it can burst out the core that has formed on various materials and other reaction of other material can proceed.

The details of mechanism at the moment we are not interested, but understand that initially the gypsum will react with tri calcium aluminate forming what is known as ettringite. And this ettringite then get converted into finally, converted into mono-sulphate later on. You know ettringite gets converted into mono-sulphate later on which you can see there is some amount of formation is you know some amount of ettringite concentration reduces and instead the mono-sulphate concentration increasing.

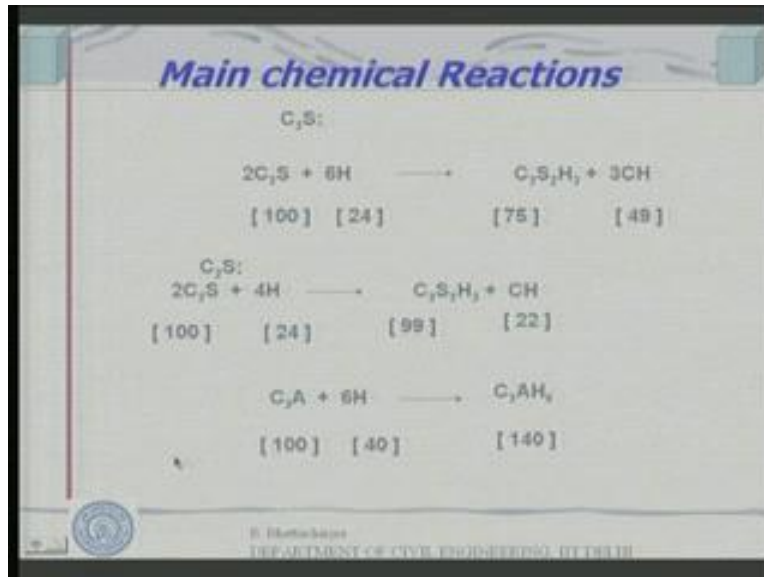
You know this is the mono-sulphate concentration  $c_4$  which is another a minor compound is not. So, very important, but its products hydration products starts forming after about 7 hours or you know like about about 1 or 2 or you know after 7 8 hours and so on and so forth. Now, other main compounds that gives the cementing properties of the cement are the csh gel calcium silicate hydrate calcium silicate hydrate because tri calcium silicate and di calcium silicate. They react with water forming calcium silicate hydrates.

Then lime we will see this chemical reaction in detail little bit later now initially this reaction starts about 6 7 you know not after 2 2 hours, but it really starts after 5 6 hours. And it continues in this manner now this silicates chs initially they are long fiber then they are short fibers because fiber structures are shown here; this short fibers. And these fibers short fibers are the most stable like stable and they remain there. Also another product that is formed is calcium hydroxide. So, the amount goes on increasing these amount increases of the lime and thus calcium silicate hydrate fiber short fibers.

They are go on increasing initially they are long fibers then they are short fibers ettringite initially they increase they get converted into what is called mono-sulphate. Therefore, their concentration reduces mono-sulphate concentration increases. Tri tetra calcium alumino hydrates, which is a minor compound of very little consequence its starts formation from this time. And its concentration also increases main product chs its concentration increases and becomes very high.

And you can see the porosity goes on reducing because the original pore space was original spaces were filled in by the original spaces of water filled space. And they were therefore, solids were less and there was lot of pores interstitial pores between the cement particles. This goes on decreasing because the water filled space are now occupied by solid products of hydration. So, this increases this pores right.

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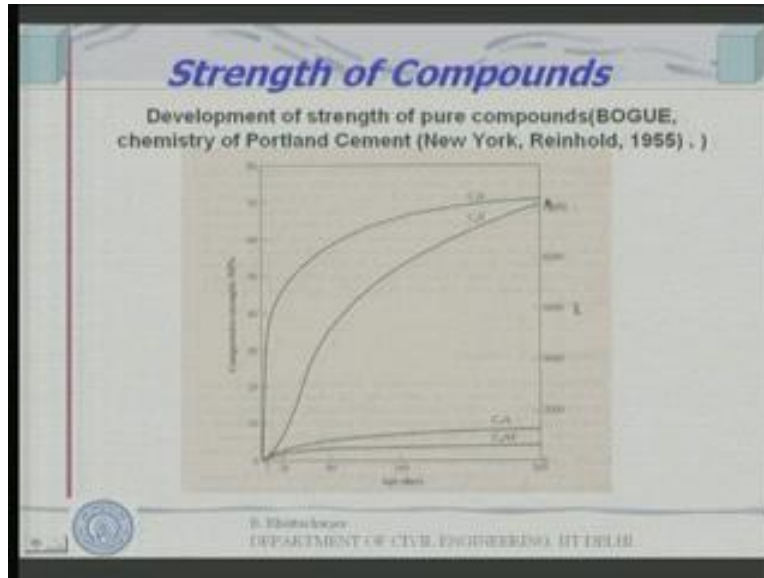
So, we can go to this slide to look into the reaction process actually main chemical reaction. C 3 s it reacts with water in cement chemistry you abbreviate water as h calcium hydroxide therefore, is abbreviated as calcium oxide and h 2 o that is ch. So, ch stands for calcium hydroxide. So, when c 3 h this is one of the major reaction c 3 s reacts with water it forms c this is chs gel it is a gelatinous structure the fiber that we have seen it has got gelatinous structure. And some amount of lime is produced. In fact, 100 grams of c 3 s will react with 24 grams approximately 23 or 24 grams of water forming about seventy 75 grams of chs gel.

Calcium silicate hydrates and forty nine grams of calcium hydroxides it is like a lime you know which is called same compound same composition and same compound as like a lime. So, the lime is found if you see citrus reaction c 2 s reacts with similar amount we have assumes not exactly the same. We shall again discuss, this 100 grams reacts with 24 producing less amount of lime. It produces less amount of lime, but both produces chs gel where as tri calcium aluminate do not produce the same chs gel, but it produces calcium tri calcium aluminate hydrates right.

It has got different stages initially some age age this age six is one product there are other products formed anyway that details you may not look into ... But, there is a main

reaction of cement with products of reaction with of cement with water. So, these are the 2 main cementing properties giving product right.

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Let see which gives the maximum strength. If you look at it, the strength giving compounds are if I this is age in days the comp and this compressive strength given in mega pascal. C<sub>3</sub>S it shows very high early strength right initial ages c<sub>3</sub>S reacts and it has got chs gel which has got the bounding property. Basically, it is like this you see this when cement reacts with water it forms this gelatinous structure. Which has got a mass surface area very large surface area possibly thousand times more than that of the cement itself and the surface forces starts dominating, the this vendor wall kind of forces bonds they are established between the material.

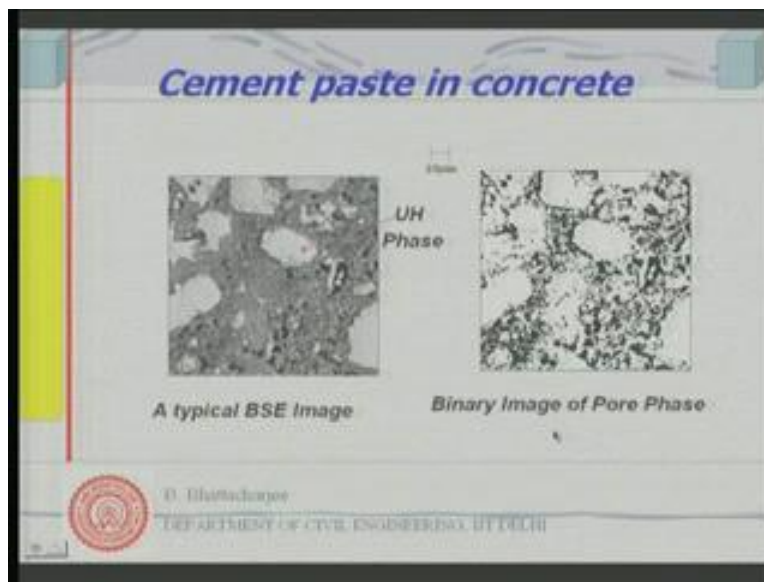
They are and the chs gel chs gels are the ones which has got very, very large surface area can burn inert material such as stones or cement stones or let us say sand and that is how it gives the cementing property. Lime on the other hand is a non cement precipitate it is sparingly soluble it does not go into solution. So, easily goes you know partially into solution sparingly soluble. It remains as non sealing precipitate in the pore structure of the cement paste in the unoccupied space of the cement paste.



So, chs gel is the main strength giving compound in cement and you know c 3 s produces high chs in the beginning therefore, it gives you the early strength. So, it is the c 3 s which gives me early strength. But, later on you can see as the increases this strength probably increases this is nearly becoming flat. Whereas, if you look at c 2 s on the other hand c 2 s initially the strength growth is not so much.

But, it tends to be the long term strength c 3 on the other hand probably contributes very little to the strength of the cement paste. And c 4 af contributes still lesser, but it is at concern because it gives you lot of heat of hydration. And we will also see that this reacts with sulphate. So, in a harden state c 3 it reacts with sulphate and forms a ettringite which occupies more volume can be a durability problem. We will discuss this somewhat later on more detailed.

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So, this is the strength you know we can see the c 2 s and the c 3 s main strength you can perform. Now, if I look at the back scattered electron image of cement paste in concrete this is how it would look. You see back scattered electron. So, therefore, from the places where electron does not scatter back they will look black in a back scattered electron image you know electron microscope image. Actually, the black ones are the pores the

white ones are un-hydrated phase the reflection in a gray reflection in a gray image depends upon how much scattering.

So, un hydrated phase gives there are equations of physics etcetera etcetera which tells us the un-hydrated phase gives us white color. Gray color of these kinds is the hydrated phase and the black ones are the pores. So, cement paste consist of some un-hydrated always unless it is fully hydrated which takes very long time. And it would also depend upon how much water you have added with respect to the cement.

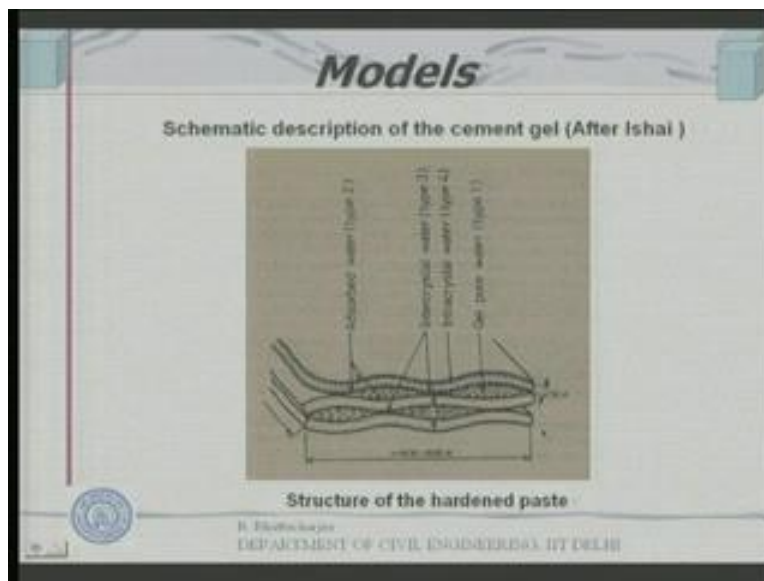
In other words with respect to water cement ratio. So, with respect to water cement ratio if you add less water of course, everything will not hydrate. So, we shall see that again in details. But, there will be some un-hydrated materials some hydrated products which all look gray because they will have different compounds in them, but all look gray color and pores are the blacks. So, it has got some un hydrated product hydrated product which will gain have different chem com chemical composition might have calcium silicate hydrate gel lime. As well as, tri calcium aluminate hydrate tetra calcium ferrite hydrates and so on.

So, those are the composition, but all those you know solids of product of hydration. They look there un-hydrated cement rare metals are the hydrated products solid product of hydration plus some pores large pores capillary pores as you call. If I do binary imaging binary what is called you know I have separate out threshold as it is called. So, what I do, all pores I keep black rest all I make white. So, these are the kind of pores structure you can see.

You know in a binary image. So, the all blacks have been left just like black or all other colors gray and white have been made white. So, un-hydrated phase and the hydrated phase also look white here and this is the pore. So, 2 dimensional pictures of the pores typical 2 dimensional pictures of the pores in case of cement paste in concrete would look like this. So, they are all of irregular shapes and sizes and interconnected and things like that. It will depend upon of course; ratio of water to cement and the degree of hydration etcetera, etcetera, and ten micron is acquired. So, that is what is the paste you know cement paste.

Now, people have tried to model this by various types of analytical experiments. People found the structure of the chs they are like fiber like gelatinous structure and that has been established as early as 1950s by various people who studied through scanning electron microscope in those days. Also people have studied through nitrogen absorption techniques the thickness of interstitial layers or you know thickness between gap between the interstitial layers and so on.

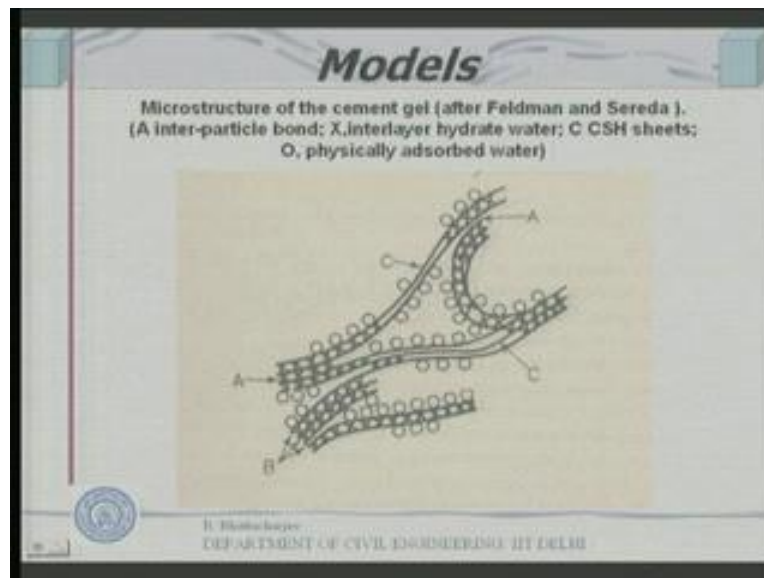
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They found it has got gelatinous structures and one of the models suppose say psi is something like this you knows he feels there are layers structures. And between the layer there are some space where you will have what we call as gel water, because this has got a gelatinous structure. So, therefore, between the layer structures you will have gelatinous gel water.

So, gel pores exist between the layers then there are inter crystal water there are different types right. And also absorb at the layer surface there is absorbed water and absorbed water. And water this water do not have the densities equals to one they are different. In fact, they are different density. So, you have gel water or absorbed water or inter crystal water that is what is I gave a model.

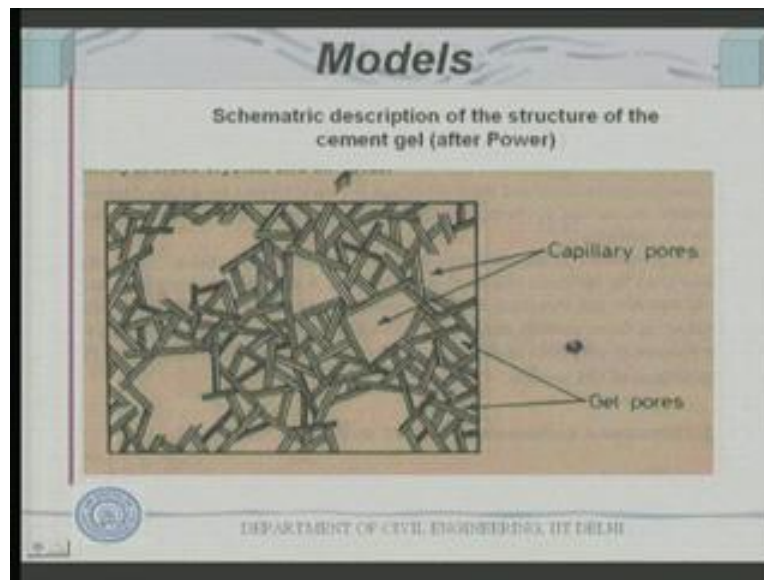
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Similar models were given by other people like this 1 given by Feldman and Sereda and he defines inter particle bond different particles bond between them. Then inter layer hydrated water defined by x and then chs sheets. So, this c stands for chs sheets this o are the physically absorbed water. And in between you have got x this ones are inter layer between the layers you have inter layer hydrated water. So, this is another model. So, what we understand from this well they are layered structured it has got a gelatinous structure the hydrates solid hydrates know solid product of hydration.

They have gelatinous structure chs gel they have gelatinous structures and they are layered structure. And between this layer or at that in a layers themselves there will be some amount of water. Which we can call as some would be of course, chemically combined water plus physically absorbed water and some gel water between the layers right. And there is pores between this layers which we call as gel pores.

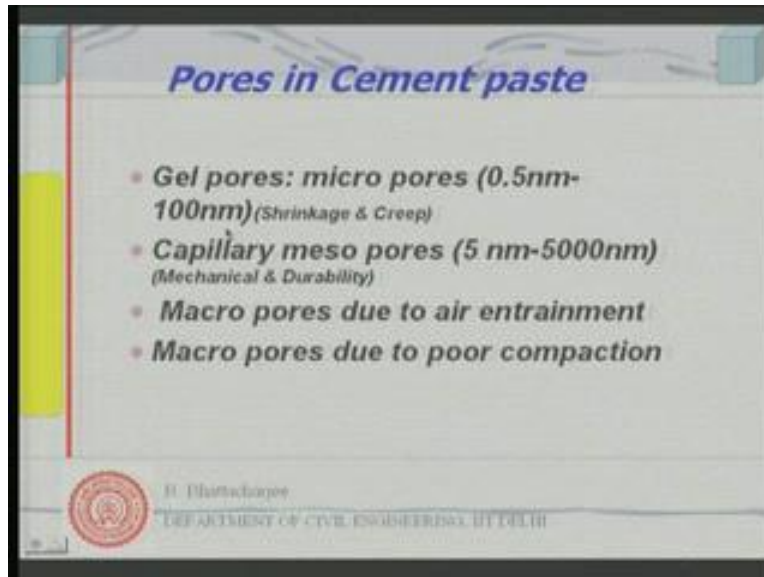
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Well, however, gives this kind of a model. He says that there are gels the layered structure of gel layered structure of gel you know those long long ones. And the spaces between them are a capillary pore which has been left by water filled space which has got evaporated. You know initially you have cement and water and this water filled space, some of it will get occupied by the hydrates; cement hydrates after the hydration reaction hydration product will occupy. Some of it will be required you know occupied by the hydration product. But, some space will remain still vacant and the water will evaporate from depending upon how much water you have added.

If you add more water then more such space will be remain vacant and this space is called capillary pore. Because, their sizes are larger and they are between the you know chs gel structure. So, there is a gel structure in between you have got a capillary pore. These are capillary pores these are capillary pores and within this gel itself there are gel pores within the gel itself there will be gel pores. So, within the gel themselves will be gel pores which are finer in size. So, that is the model given by power.

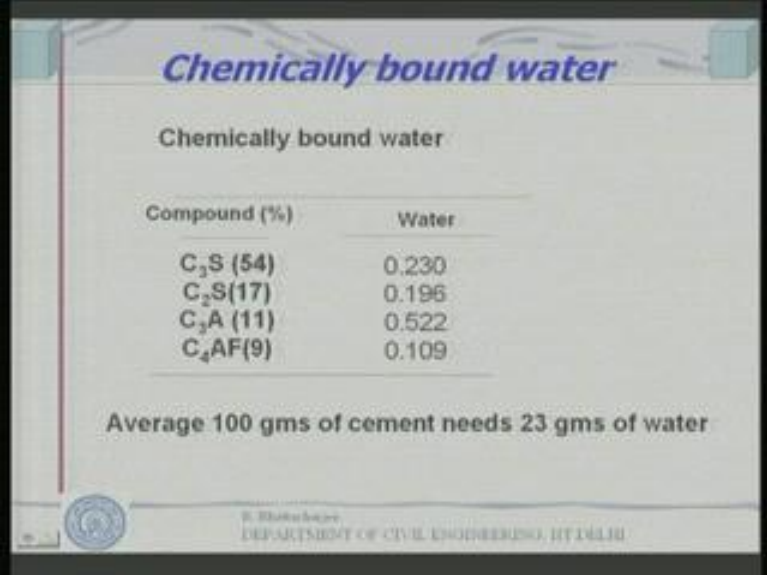
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So, what we see pores in cement are of the 2 types gel pores which are actually micro pores. The sizes will range from 0.5 nanometer to about 100 nanometer 0.5 nanometer to 100 nanometer. Then there are capillary pores which I call as meso pores and their sizes would range from 5 nanometer to 5000 nanometer. Now, we shall see some time later on that these pores are responsible for shrinkage and creep of concrete. Whereas, this pores which are larger in size are responsible for mechanical and durability properties of concrete right.

So, these are the types of pores 2 types of the pores. In addition to this if I add some air entraining agent. Some other mixtures which I mentioned earlier that like add admixtures to the cement. They can lead to something called macro pores due to air entrainment. We would not discuss this at the moment and if you do not do compaction properly then also there can be some large pores macro pores due to pore compaction. But, first 2 are definitely inherent to hydraulic cement binder paste or concrete system right. So, we will see that again.

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**Chemically bound water**

Compound (%)	Water
C <sub>3</sub> S (54)	0.230
C <sub>2</sub> S(17)	0.196
C <sub>3</sub> A (11)	0.522
C <sub>4</sub> AF(9)	0.109

**Average 100 gms of cement needs 23 gms of water**

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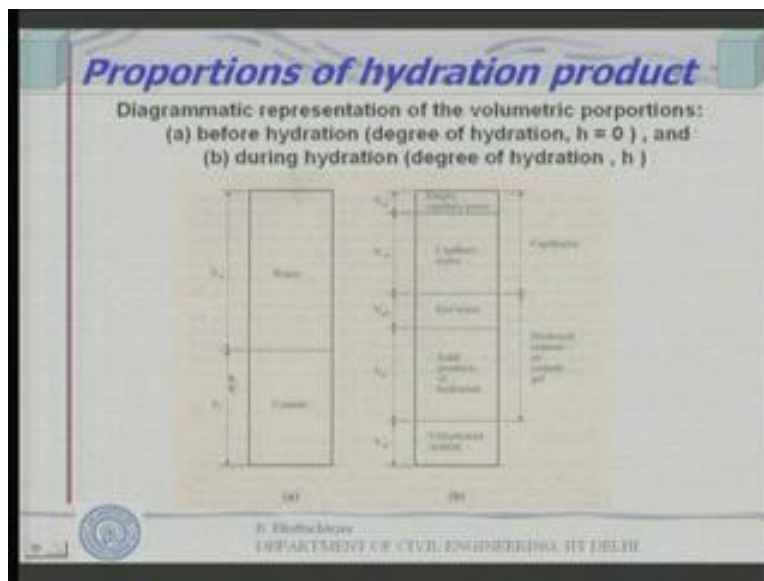
Now, let us look at look to this pore a little bit in more details I can find out how much altered, we know it. How much water will remain chemically bound to various compounds of cement. People have done very long term experiment something like 12, 13 years and they found that one gram of c 3 s consumes actually point 2 3 grams of water. C 2 s 1 gram consumes 0.1996 grams of water although roughly we take for everything s 23 or 24 earlier I 1 of the reactions I showed it 24.

But, this was observed and c 3 a consumes about 0.9522 amount of water c 4 af on the other hand consumes about 0.109 grams of water. So, 1 gram of c 3 s consumes point 2 3 grams of water one gram of c 2 s consumes 0.196 grams of water and 1 gram of c 3 a consumes 0.52 grams of water and one gram of c 4 af consumes 0.109 gram of water. And also I know how much percentages of this compound is present in ordinary Portland cement they are 54 percent for c 3 s c 2 s is about 17 percent c 3 a is about 11 percent c 4 af is about 9 percent.

So, I can find out one gram of cement will consume how many gram of water calculation simple calculation because log mixture nothing else. Based on that, we can show that hundred grams of cement needs about 23 grams of water. This is has been acceptable you know this has been accepted by various experts. And generally it is accepted by concrete

technologies that about hundred grams of cement needs 23 grams of water. There could be some variation here and there the cement percentage about of the c 2 s c 3 s and can vary small even in OPC. There are little work percentage variation it is based on 1 experiment done. So, now on an average you take it for granted that 100 grams of cement needs about 23 grams of water and complete hydration over a very long period of time.

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So, we can look into those pores in more details. Now, we define something called degree of hydration. We define something called degree of hydration what is degree of hydration because we said that this reaction is not instantaneous. And it takes very long time If all product all compounds of cement reacts with water completely and forms hydration. So, that when we say when we say the degree of hydration is 1, if it is less say 100 grams of cement I take. And let us say all hundred grams have reacted with water then I say degree of hydration is 1.

If you are a say on a 50 grams have reacted and fifty has not reacted then degree of hydration is 0.5. So, it is the ratio of the proportion the ratio of the cement that has the mass of the cement that has reacted to the original mass of the cement that, we call as degree of hydration right. So, before hydration degree of hydration is 0 and degree of



hydration of course, degree of hydration is age. And, then if I look into a diagram see initially I had cement and water a schematic diagram right cement and water.

And this has got a volume let us say  $v_w$  and this is the  $v_c$  volume cement then after hydration what will happen? I will have some un-hydrated cement that we have seen from the b we have seen. You just you will have some solid product of hydration and this is associated with some amount of porosity. This is associated with some amount of porosity right gel porosity this is inherent this is associated with some amount of porosity gel porosity. And this pore pores are occupied by water we call as gel water. In addition we will have some amount of originally water filled space which will remain vacant or will be filled by water call this as capillary; capillary water which is not been filled by the solid.

But, we shall also see that there is some amount of space which will remain empty capillary why? Because, if you see that the volume occupied by the water and solid cement earlier. And the volume occupied by the solid product of hydration after reaction will find that there's a solid. There is a slight reduction in the volume as far as this is concerned this occupies slightly less volume than the volume of water and cement. That has been consumed in you know producing this.

So, therefore, there is some amount of empty capillary formation always takes place while cement reacts with water. So, this is schematically cement and water reacts to form some some unrelated cement some solid products of hydration some space that will be occupied by gel water. Some will be occupied by capillary water and there will be some empty capillaries. So, these total constitutes the capillaries this total constitutes the hydrated product of you know hydrated cement or cement gel to rely hydration production of cements or cement gel.

This is inherent to this if this is whenever this is there this will be there because gelatinous structure. Since, it is gelatinous structure it will have the interstitial pores and that will be occupied by water. We can do a little bit of calculation to find out what will be the possible volumes of all those ones product of hydration.

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**Hydration products**

100 gms of  $C_3S$  reacts with 23 gms .  
*Consider 1 gm cement*

- Density of solid hydration product 2.43-2.59 g/cc (average 2.51g/cc)
- 1.23 gms occupy  $1.23/2.51=0.49$  cc  
( $1/3.15+0.23=0.55-0.49$  cc= $0.06$ cc less than original material); hence 06 cc empty capillaries
- Gel porosity 28 %, thus  $.49/.72-0.49=0.19$  cc
- For C gms of cement and degree of hydration h, Gel volume is  $0.49 Ch$ , gel pores=  $0.19Ch$  and it follows

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We said 100 grams of  $C_3S$  react with 23 grams not  $C_3S$  actually 100 grams of cement, 100 grams of cement react with 23 grams of water. Now, let us consider one gram of cement density of solid hydration products have been experimentally found to be 2.43 to 2.59 gram per cc. In grams per cc cgs unit experimentally it has been observed the solid product of hydration that is found has got a density of 2.43 to 2.59 grams per cc. So, you can assume average density is about 2.51 gram per cc. You know, you have cement its density in cgs system would be 3.15 grams per cc density of water 1 gram per cc.

So, you have 3.1 gram and one gram combined together in certain proportion 100 grams of course, reacts with 23 grams resulting in product which has got 2.5 grams per cc density of solid. So, 1.23 grams because to a 23 grams reacts with one gram of cement. So, if I consider one grams of cement 1.23 grams of cement product of hydration product of cement hydration to occupy 0.49 cc. Because 1.23 divided by 2.51 is 0.49 cc 1.31 divided by 3.15. That is the volume occupied by the cement originally plus this is the volume occupied by water.

Because, the density is 1 gram per cc that will result in 55 that is this side this is equals to 0.55 cc and this is 0.49 cc. So, this difference is you know this 49 cc is a volume occupied by the solid product of hydration. The original volume use the original volume

of the cement plus water is 0.5 this volume remains as empty capillaries. This volume remains as empty capillaries 0.06 cc remains as empty capillaries.

But, this 0.49 cc has got an inherent gel pores gel porosity of 28 percent characteristic porosity of gel is 28 percent. This has been again you know determined from experiments analytical chemical experiments that gel has got a characteristic porosity of 28 percent. So, various kind of absorption techniques people have found out that you know various kind of absorption techniques. Or another analytical test people have found out that gel has got a characteristic porosity of twenty eight percent.

So, whenever this 0.49 cc is there it will always have 28 percent porosity involved in that. And by that calculation 0.49 divided by 0.72 minus 0.49 because some 0.72 is a volume occupied by the solid. So, total will occupy point 4 nine divided by 0.72 where as 0.68 minus 0.49 gives you about 0.19 cc. So, volume of gel pores would be 0.19 cc. whereas, simple calculations one can see that 0.19 cc of gel pores would always be there. So, you have 0.49 cc of gel solid in your earlier diagram 0.19 cc of gel pores if you are taken 1 gram of cement.

Now, supposing I take  $c$  grams of cement and take degree of hydration as  $h$  my gel volume would be  $0.49 ch$  solid gel volume gel pores would be  $0.19 ch$ . And it follows therefore, I can find out the total porosity by subtracting the original volume minus the volume of un-hydrated product minus the volume of solid volume of gel volume of gel pores ...

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**Porosity**

$$P_c = \frac{\frac{W}{C} - 0.36h}{0.317 + \frac{W}{C} - 0.19h}$$

$$P_g = \frac{0.19h}{0.317 + \frac{W}{C}}$$

$$P_t = \frac{\frac{W}{C} - 0.17h}{0.317 + \frac{W}{C}}$$

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What is the volume of capillary porosity? What is the volume of capillary pores, divided by the original volume results in capillary porosity. The expression of capillary porosity is something like this.  $W/C$  by  $c$  you can derive this easily. Very easily it is not a difficult task. Because, what we are doing original volume is known then volume of the gel solid gel is known volume of the gel pores is known volume of unhydrated cement is known for a given degree of hydration.

So, we can find out what is the rest of the volume since the original volume minus this volume of volume of gel pores. Volume of gel solid volume of hydrated cement will give me the volume of the pores capillary pores. So, I can find out the capillary porosity. So,  $p_c$  denotes capillary porosity and it is given by  $w$  by  $c$  minus  $0.36h$   $h$  is the degree of hydration. This is the volume occupied you know its related to volume occupied by original cement and water.

$1$  divided by  $0.315$  is  $0.317$  and  $w$  by  $c$  water to cement ratio. Similarly, gel porosity is given by this formula  $0.19h$  divided by this. And total porosity is the sum total of this  $p_c$  plus  $p_g$  will give you  $0.1936$  minus  $0.19$ . So, it gives you  $w$  by  $c$  minus  $0.17h$  divided by  $0.317$  plus  $w$  by  $c$ . So, this is capillary porosity this is expression for gel porosity this is the expression for total porosity right. Now, what is important out of this is that if you

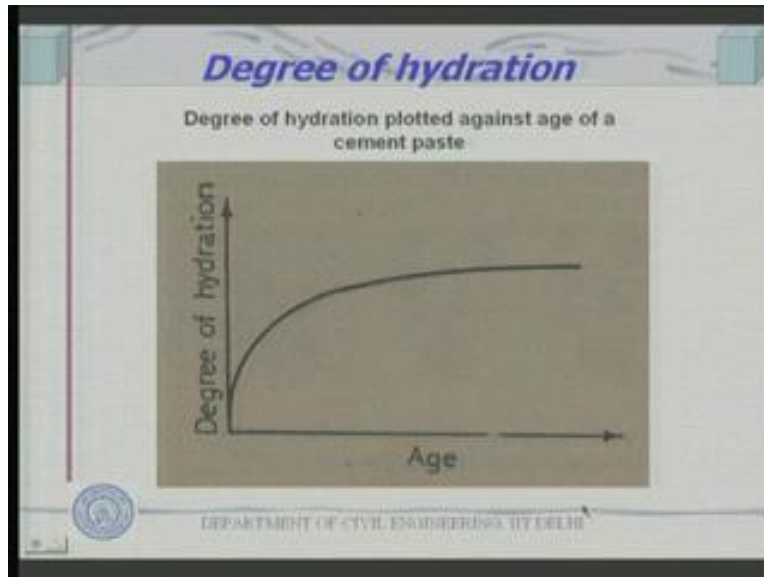
have higher water to cement ratio capillary porosity will be more. Physically you have understood this, because volume occupied by the water in the original water cement system would be high and which will not be filled in by hydration product.

So, more the water with respect to the cement more will be the capillary pores gel pores is a function of hydration degree of hydration simply. So, more the degree of hydration more will be gel pores. Because this is associated with the product solid product of hydration chs gel more the chs gel more will be the gel pores it inherent, it would be there and total porosity again is a function of water cement ratio. So, higher water cement ratio high will be your total porosity this is same everywhere  $0.317 + w \text{ by } c$ . So, higher the water cement ratio more will be the capillary porosity and more will be the total porosity.

Higher the degree of hydration this would be gel porosity would be more, but as I said gel porosity do not really you know contribute to poor performance with reference to strength and durability. It is mainly the capillary porosity which is which governs the strength and also durability properties of cement based system. And right now, we are looking at cement paste you can extend this idea to concrete sometime later.

There is an interesting point here suppose I put  $p_c$  equals to 0 capillary porosity is equals to zero then I'll get value of  $a_{ge} \text{ max } a_{ge} \text{ max}$  you know this cannot be negative the porosity the total pores cannot be negative. So, this has to be if I put this equals to 0 this term has to be 0 and for this term has to be 0 you can find out pores are  $h \text{ max}$ . So, if you have water cement ratio less than 0.36. From this it follows that if you have water cement ratio less than 0.36. You will have you can never have full degree of hydration some unhydrated cement will remain. So, that is what it is right.

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So, degree of hydration right changes with age as you as you have defined degree of hydration changes with age. So, as the age increases degree of hydration increases fraction of cement that is reacting increases right. But, in some cases if water cement ratio is less than 0.36 you cannot get complete degree of hydration. In fact, the  $h_{max}$  will be given by  $w/c$  divide by 0.36  $w/c$ . For example, if there are water cement ratio is 0.3 degree of hydration will be 0.3 divided by 0.36 maximum degree of hydration attained is 0.3 divide by 0.36.

But, this is no problem anyway because un-hydrated cement if it is there in the system it does not cause any harm to the concrete or cement paste; in general, because strength of such system or performance of such system is not necessarily governed by volume hydration product. On the contrary it is governed by the negative aspect that is the pores because the pores are the essential flaws in such system. So, you have if you have pores they bring down the strength.

So, if you have if you reduce down the capillary porosity strength would still increase in respective to whether you have got un hydrated cement in the system or not un hydrated cement will act like inert particle in that case very fine particle. And they will be bonded by the other hydrated particle. So, you will have a very sound particulate system bonded

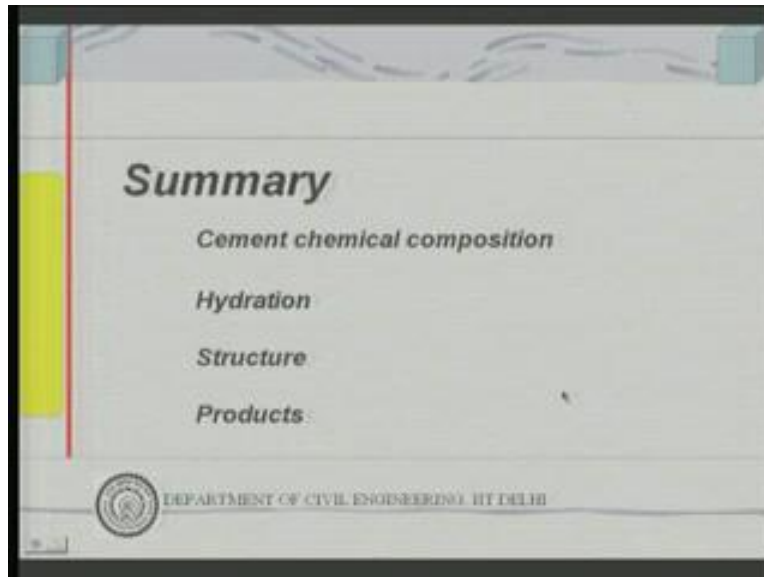
together with very little pores in the system. So, degree of hydration even if you do not achieve one it is not a problem.

Since, capillary porosity dictates the strength and durability property of concrete higher water cement ratio means, high capillary porosity which means lowering of strength and lowering of durability performance of concrete. Because, cement is the contributing you know cement paste or hydrated cement product contributes to the capillary porosity in the concrete as well. In addition to something else and this is true for all other cement based materials hydraulic cement based material.

So, therefore, our motto always remains to reduce down the capillary porosity as much as possible to improve upon the strength and durability purpose right. So, that is that is why complete hydration is not required not necessary. But, if there are pores otherwise that is you have got high porosity high water cement ratio system where the pores are there. Capillary pores are there they are more the degree of hydration it would actually ensure that the overall capillary porosity is reduced. So, degree of hydration is important to that extent in high water cement ratio system.

But in low water cement ratio system it will never achieve full hydration below 0.36 water cement ratio it will never achieve full degree of hydration, but that is not a concern. That is not a major concern because this is always an equation that whether when need. You know if there are hydrate cement particle we literally we literally be determinate to the strength development of the concrete or not. Well, in low water cement ratio system where the capillary porosity are less it is not a problem. So, main concern is capillary porosity in case of cement paste and this can be extendable to concrete also.

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So, if we summarize now. What we have looked? We have looked into chemical composition of cement. Then we looked into hydration, how physically the hydration what are the physical changes that takes place in hydration. And how do we define certain things physical from the physical consideration. As well as somewhat from chemical consideration like setting etcetera remember there is this is this is very difficult to actually have a sharp chemical demarcation as far as setting and such things are concerned.

Therefore, we define them somewhat arbitrarily with respect to vicats then we have looked also into structure physical structure how it changes. And chemically what happens that also we looked into ... Then we looked into products we have identified in the product solid products are always there. But, then there are pores in the system and this pores are responsible for various performance characteristics of cement paste and hence to concrete as well. I think that is we conclude our discussion on cement and cement hydration right. Next, class we look into types of cement and other cement issues.

Thank you for hearing.