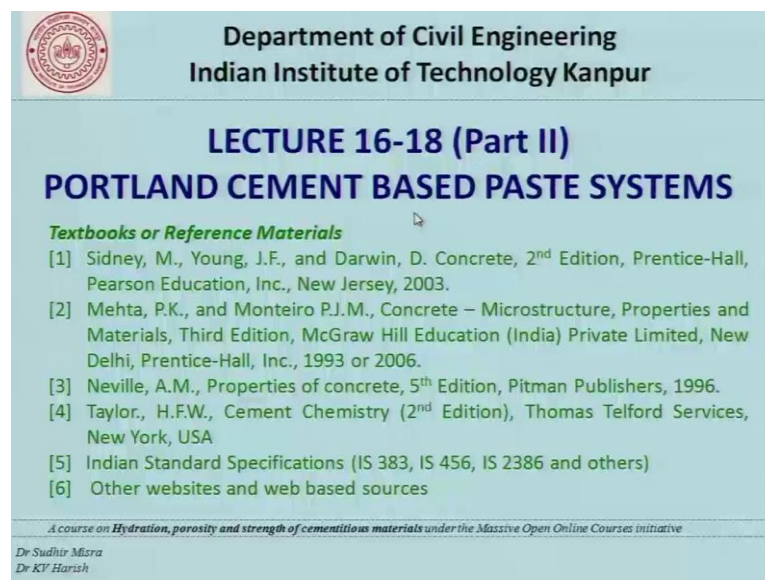



Hydration, Porosity and Strength of Cementitious Materials
Prof. Sudhir Mishra and Prof. K. V. Harish
Department of Civil Engineering
Indian Institute of Technology, Kanpur

Lecture - 16-18 (Part-2)
Portland Cement Based Paste Systems

Hi. Good morning to one and all. I am K. V. Harish, Assistant Professor Department of Civil Engineering, IIT Kanpur. You are watching MOOC lecture course on Hydration, Strength and Porosity of Cementitious Material.

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LECTURE 16-18 (Part II)
PORTLAND CEMENT BASED PASTE SYSTEMS

Textbooks or Reference Materials

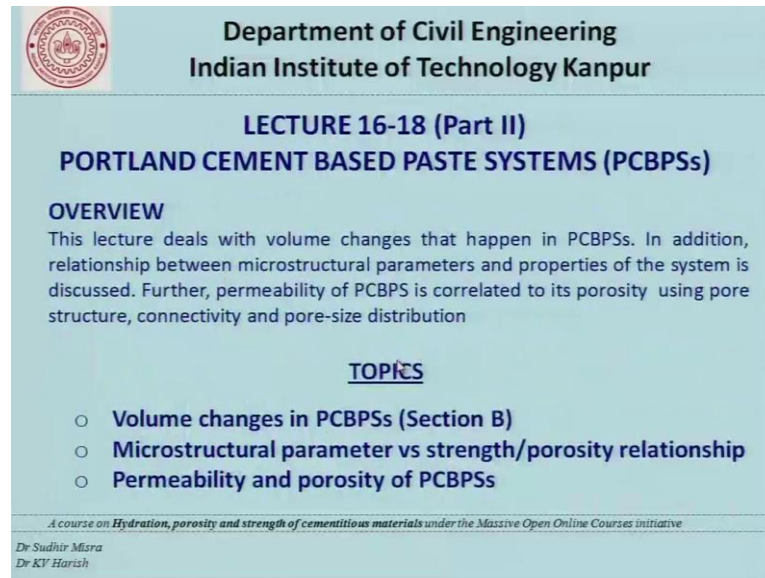
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- [2] Mehta, P.K., and Monteiro P.J.M., Concrete – Microstructure, Properties and Materials, Third Edition, McGraw Hill Education (India) Private Limited, New Delhi, Prentice-Hall, Inc., 1993 or 2006.
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- [4] Taylor, H.F.W., Cement Chemistry (2nd Edition), Thomas Telford Services, New York, USA
- [5] Indian Standard Specifications (IS 383, IS 456, IS 2386 and others)
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A course on *Hydration, porosity and strength of cementitious materials* under the Massive Open Online Courses initiative

Dr Sudhir Mishra
Dr KV Harish

Today, we will see lecture 16 to 18 part 2. Remember that there is no lecture 17 because lecture 16 to 18 has been club together into 2 parts. In the last lecture we have seen part one and we will see part 2. In this lecture textbooks and reference materials are shown.

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LECTURE 16-18 (Part II)
PORTLAND CEMENT BASED PASTE SYSTEMS (PCBPSs)

OVERVIEW
This lecture deals with volume changes that happen in PCBPSs. In addition, relationship between microstructural parameters and properties of the system is discussed. Further, permeability of PCBPS is correlated to its porosity using pore structure, connectivity and pore-size distribution

TOPICS

- Volume changes in PCBPSs (Section B)
- Microstructural parameter vs strength/porosity relationship
- Permeability and porosity of PCBPSs

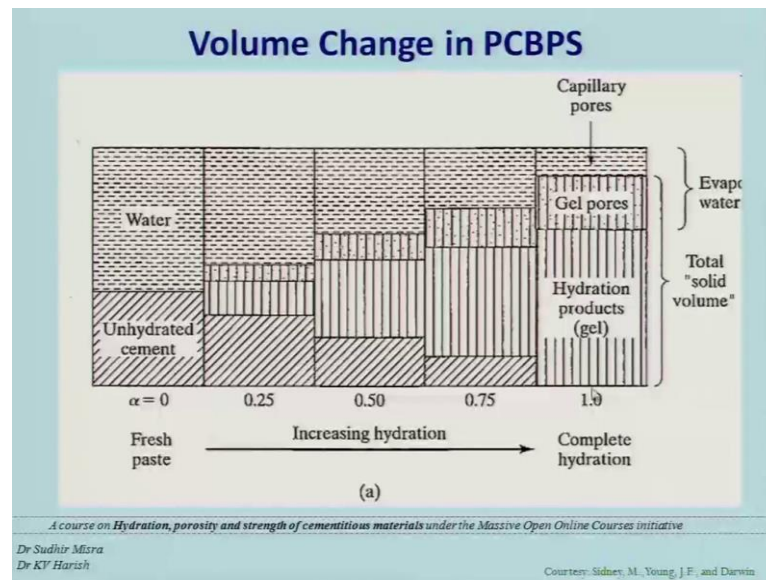
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So, the topics that will be covered in this lecture is volume changes and Portland cement based paste systems. And the section here is B in the last lecture we have seen A and here we will see B and microstructural parameters verses strength porosity relationship, permeability and porosity of Portland cement based paste systems. Pore permeability of porosity of Portland cement based paste systems. And an overview is provided this lecture deals with volume changes that happen in Portland cement based paste systems.

In addition the relationship between micro structural parameter and properties of the system is discussed. Further the permeability of Portland cement based paste system is correlated to it is porosity using special parameters like pore structure connectivity and pore size distribution.

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Now, in the last lecture we have seen volume changes, we have seen the basics of powers model representation and other things. Now in this lecture we will actually go to the changes that happen in the volume of the products. So, one volume representation is shown, where in the X axis you will find alpha varying from 0 to 1. Or in other words 0 percentage to 100 percentage. Remember that 100 is a theoretical value. Usually in well hydrated Portland cement based paste systems typically the alpha value will be somewhere between 0.72 as high as 0.9. So, 1 is a hypothetical case. And alpha equal to 0 is the moment you add water to cement. So, cement will be the unhydrated state and in this figure what you see is water is shown in dotted lines unhydrated cement grains are showed in slash lines and remember this is the 2 d representation.

Now, as a time passes we now that cement is hydrating. And what you see is that the unhydrated cement basically reduces. And remember that alpha equal to 0 is a fresh state of the paste and with increasing values of alpha what we find is that, the unhydrated cement grains decreases because cement is reacting and forming hydration products. So, parallely you will also see hydration products slowly increasing. And likewise you also see that the water that you had initially starts hydrating and forming hydration products, and the capillary pore water slowly decreases.

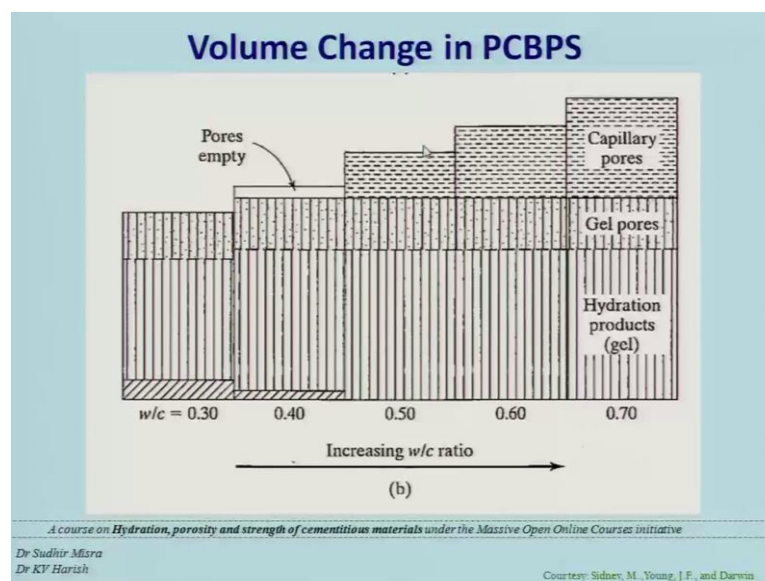
And, in addition you also see that the hydration products have gels and you also have gel pores in the hydration products. So, the gel pores also start increasing slowly, and at a

matured state see in this case it is 100 percentage hydration you see that the Portland cement based paste system may contain some capillary pores. It may contain gel pore it may contain hydrated products. And remember this is alpha equal to 1 that why you do not find any unhydrated cement grain.

And this is the theoretical case in actual case typically you will have something like this where in you see that at an alpha equal to 0.75, you have unhydrated cement grain hydrated product gel pore and capillary pores. And remember that in the previous lecture we have seen evaporable water and non evaporable water. So, if you basically heat a cement paste to say 100 to 105 degrees Celsius the water that basically escapes out of the system is largely the water that is present in the pores. And also the water that is present in the gel pore.

Remember that the gel pores contain 3 types of water. Inter layer water small misa pore water micropore water and so that is it. So, you have 3 waters that are present in gel pores. The chemically combined water is available actually in the hydration products. So, when you heat the sample to 100 to 105 degree Celsius if water is present in the gel pores and if water is present in the capillary pores basically escapes. And that is together called as evaporable water which we have already see in the previous lecture.

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Now, another volumetric representation that is very important is that what has happened to the hydrated system, when the water cement ratio changes from say 0.3 to 0.7 the

reason why 0.3 to 0.7 is chosen primarily because in conventional practice we typically used water cement ratios between 0.4 to 0.6 below 0.3 it is generally called as very low workability and greater than 0.7. It is called as very high workable concrete. So, usually we do not use such concretes and also the system that you have here is a matured system.

So, if you go to the previous figure what we have shown in this representation it is not a matured system, in the sense that alpha is slowly increasing with respective time and it is trying to reach complete hydration. So, in the system that is shown in the second representation it is actually a matured system which means what is the nature of the system at alpha equal to 1 at water to cement ratio equal to 0.3 that is what is shown here likewise what is a matured system at alpha equal to 1 and water to cement ratio equal to 0.4.

So, basically the comparison here between different water cement ratios is basically a matured system. So, which means that alpha is basically one in all the case. So, with increase in the water to cement ratio what you find is that you have some unhydrated cement grain, you may have hydration products and you may have gel pores. So, if you increase the water cement ratio what happens is the unhydrated cement grain basically decreases and at some level you may attain 100 percentage degree of hydration, or in other words alpha could be equal to 1.

In likewise if you see the hydrated products compared to a lower water cement ratio higher water cement ratio has more volume of hydration products. So, what we can generally say from this representation is that if you increase the water cement ratio, the degree of hydration increases because the unhydrated cement grains are decreasing and at some state it becomes 1. Now if you go the gel pores what we find is even while increasing the water cement ratio from 0.3 to about 0.7 to find that the gel pore is not decreasing or increasing it remains constant.

Whereas to the capillary pore is increasing when you increase the water to cement ratio. So, if you take high water to cement ratio system, here representing water to cement ratio equal to 0.7, you find that more capillary pores are present compared to 0.3 water cement ratio. Likewise, hydration products are also generally higher compared to this case, but the gel pores are consistently the same. So, irrespective of whatever may be the amount

of water or cement that you add initially the amount of gel pores that is present in the Portland cement based system is constant. This is a very important thing one has to remember. And the question of whether water is present in the capillary pores or not and water is present in the gel pores or not is again a function of alpha and water to cement ratio. So, these things are already discussed in the previous lecture. So, I request you to again get back to those slides to understand what is mentioned.

Now, what these 2 representations have shown there is an approximate idea is of what is increasing and what is decreasing. Now the question comes is can we find out approximately what are these values, and is there any formula that can come out which can interrelate all these factors. So, power has made lot of derivation using mass balance equation and he has come out with different equations. So, we will not get into the derivation, but we will directly go into the equations that power has developed.

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Powers set of most important equations

Particular	ID	Formula	Unit
Non-evaporable water	w_n	0.24α	%
Evaporable water	w_e	0.18α	%
Vol. of hydration product (%)	V_{hp}	0.68α	cm^3/g
Gel porosity	w_e/V_{hp}	26	%
Capillary pore volume	V_c	$w/c - 0.36*\alpha$	cm^3/g
Volume of unhydrated cement	V_u	$(1-\alpha)*V_{sv}$	cm^3/g
Volume of paste	V_{paste}	$w/c + V_c$	cm^3/g
Capillary porosity	P_c	V_c/V_{paste}	%

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Now, the set of equations that he has developed is as follows. Non evaporable water he found it as 0.24 times alpha. Evaporable water he found it as 0.18 times alpha; likewise volume of hydration product gel porosity capillary pore, volume of unhydrated cement, volume of paste and capillary porosity. So, he found out formulas for all these things and some are empirical in nature and some are confirmed for experimental works, but largely the formulas are empirical as well as theoretical in nature. All these formulas are

important for people who are taking quizzes or exams. So, you may have to remember all these formulas and remember that these formulas are not complex formulas

So, these are very simple formulas and are also very important when we go to the next stage to understand; what is the minimum amount of water that is required in the cement paste for the Portland cement based paste system to be fully hydrated and other things. So, let us go into each of this formula. Now the ids are actually shown here. So, I am directly going to the formula. W_n which is 0.24 times alpha W_e is 0.18 times alpha, volume of hydrated product is 0.68 times alpha, W_e divided by V_{hp} gives the gel porosity it is 26 percent. This value is very important primarily because we have seen in the volume representation that gel pore volume does not increase substantially and it is constant all throughout.

So, that 26 percent is a very important value. And capillary pore volume V_C is equal to water to cement ratio minus 0.36 times alpha. Remember these are empirical relationships. So, these formulas are empirical in nature and you cannot expect a dimensional homogeneity in all these formulas. So, V_C is equal to water to cement ratio minus 0.36 times alpha and V_u volume of unhydrated cement is equal to 1 minus alpha into V_{sv} . So, what is V_{sv} it is the specific volume of cement which is equal to 1 divided by specific gravity, remember that. So, the value of specific gravity of cement is 3.15.

So, whatever is one divided by 3.15 comes that is V_{sv} and volume of paste is water to cement ratio plus V_C and capillary porosity P_C is given by V_C divided by V_{paste} . So, V_C divided by V_{paste} . And the unit is are also provided here some are in percentage and some are in centimeter cube per gram, assuming that you are taking one gram of cement then the whatever is the volume that you get that is in centimeter cube. And if you carefully look into the formulas you will also find that pretty much alpha comes for each of the equation that is a very important thing. So, that is one of the important thing in powers model that the degree of hydration is directly related to all these parameters; so volumetric parameters. So, there is a direct correlation of the degree of hydration with all these parameters.

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Gel to space ratio

- Gel/Space ratio (X) is an **important microstructural parameter** that governs the properties of PCBPSs
- Capillary and gel pores are related to the gel/space ratio

$$X = \frac{\text{volume of gel (including gel pores)}}{\text{volume of gel} + \text{volume of capillary pores}} = \frac{0.68\alpha}{0.32\alpha + w/c}$$

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So, coming back to gel by space ratio which we saw in the previous lecture, so the gel by ratio X which is given by volume of gel divided by volume of gel plus volume of capillary pores can be obtained by using the respective equations, and you will finally, get 0.68 into α divided by 0.32 into α plus water to cement ratio. Which means the gel by space ratio is a direct function of α , which is degree of hydration and the direction function of water to cement ratio. This is a very important and a significant parameter which was found by power.

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Relationship between strength and gel/space ratio

$$\sigma'_c = AX^n$$
$$\sigma'_c = \begin{cases} 235 X^3 & \text{MPa} \\ 34,000 X^3 & \text{lb/in.}^2 \end{cases}$$

where
A – constant representing the intrinsic strength of the cement gel (i.e., the strength at $X = 1.0$)
N – constant having values in the range of 2.6 to 3.0, depending on the characteristics of the cement

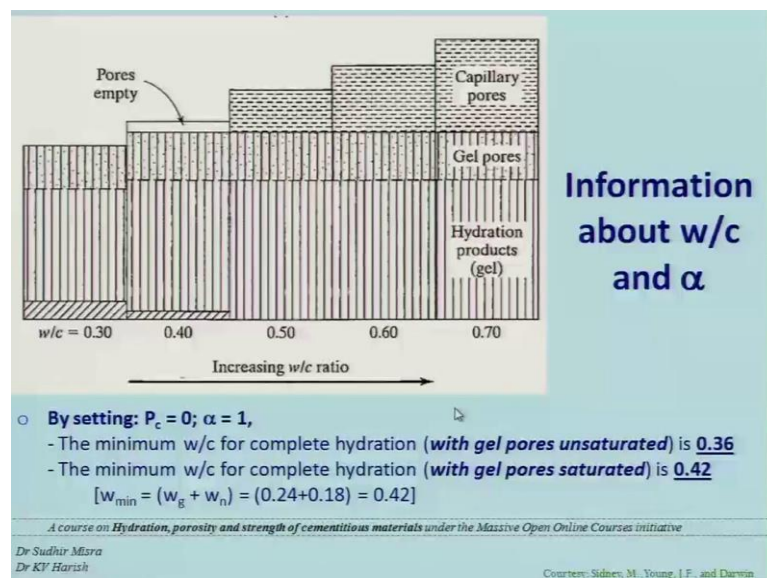
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Courtesy: Sainey, M., Young, J.F., and Darwin

Now. So, what power did he take? He took 3 mixtures and what he did was he cast a cement mortars, he cast a 50 mm specimens or 2 inch cube specimens. And these 3 mixtures he varied the gel to space ratio by varying the water to cement ratio. So, and then he plotted gel to space ratio in the X axis and the strength that he obtained in the y axis. And he typically got data points indicated by these symbols the round symbol as well as the cross symbols and also the triangles. And he plotted a curve and the equation is approximately $\sigma \propto X^3$.

Remember carefully that this strength of the cube here is expressed in lb per inch square. And this is into 10 power 3 which means this is not just ranging from 0 to 18, it is 0 to 18 into 10 power 3 lb per inch square. If we have convert it in to m P a then this 3400 sorry 34000 has to be converted to 235. So, 34000 is in lb per inch square and if you convert it into m P a it is 235. So, the same equation is provided here. And if you want to make this constants common, then the constants a and n are used. So, when he tried different mixtures what he found is that the constant n typically varied from 2.6 to 3 within a narrow range. And a typically is the constant representing the intrinsic strength of the cement gel, that is strength at $X = 1$.

So, this is a very important equation and derivation which was obtained by power. So, what is basically related is that the microstructural parameter gel by space ratio is related to the strength of the cube.

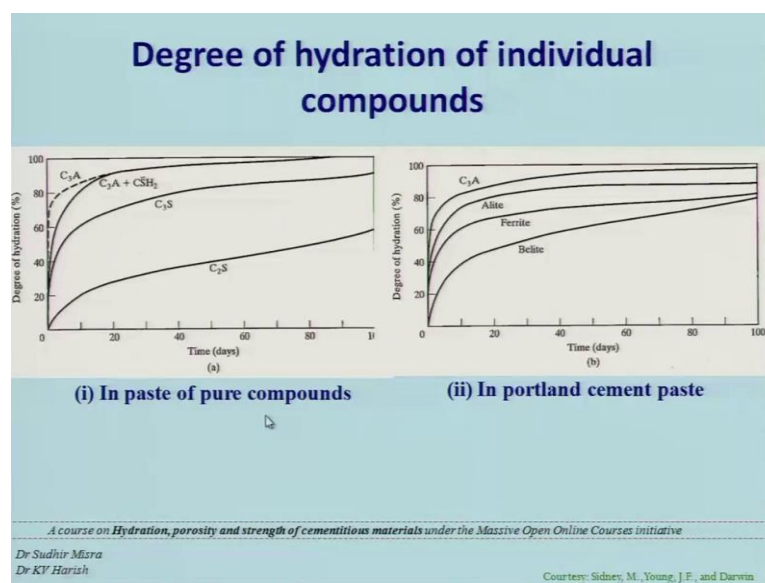
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So, another important thing which power has reached in cement hydration system is that he provided more information about approximate water to cement ratio for complete hydration. So, if you get back to the formula for capillary porosity which is V_C divided by V_{paste} . So, what power did is that he said P_C equal to 0 and α equal to 1. And he found out what is the minimum water to cement ratio for complete hydration. What do you mean by complete hydration? You want unhydrated cement paste to be 0 in the system. So, and for that you have 2 different cases. You want water in the gel pores or you do not want water in the gel pores. If you want water in the gel pores, then the value is 0.42. If you do not water in the gel pores which are unsaturated it is 0.36.

So, how he arrived at 0.42 is that the value that he got from evaporable and non evaporable water content. He basically added those 2 things because α equal to 1; so 0.24 into α plus 0.18 into α . Since α equal to 1 it gives 0.42. So, the bottom line in this explanation is that, if you want complete hydration then it is achievable under 2 conditions. One is unsaturated the other one is saturated and approximately between a water to cement ratio of 0.36 to 0.42. Remember all the derivations that were obtained by power is only theoretical. In practical case this could be different and it could be substantially different. Now we come to the next stage to understand what happens to the degree of hydration of the individual compounds.

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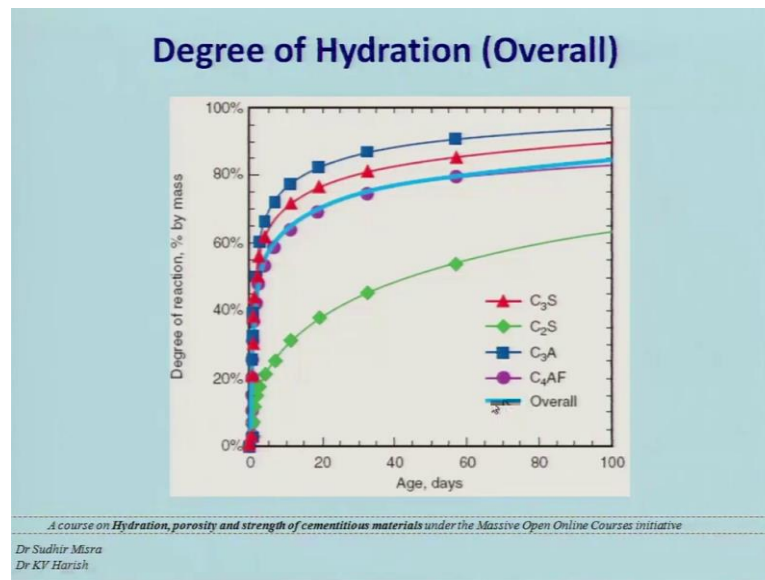


Now, what you have seen in the previous volumetric representation is that how was the degree of hydration ranging basically between 0 to 1, but that is for entire Portland cement as a whole now if you take individual compounds and again when we say individual compounds you have 2 case one is pure compounds the other one is the impure compounds which we generally find in Portland cement waste. So, here in this figure there are 4 curves that are given one is for C 3A the other one is for C 3A with gypsum the other is for C 3S the other one is for C 2S remember that C 4A f is not given.

So, if you do not have gypsum in the system, then the degree of hydration is very quick for C 3A. And if you have gypsum it is relatively slower and likewise if you see C 3S, it is also steeper, but not to the level of C 3A with or without gypsum and if you take C 2S it is relatively lower. And you also find that there is initial steepness that you can see with respect to degree of hydration, and after some time the degree of hydration flattens this also you may also have to think this from the angle of through solution and topo chemical modes of hydration. So, at the initial stages it is high primarily because it is in the through solution process. Because hydration is in the through solution process at a later stage it is in the topo chemical mode.

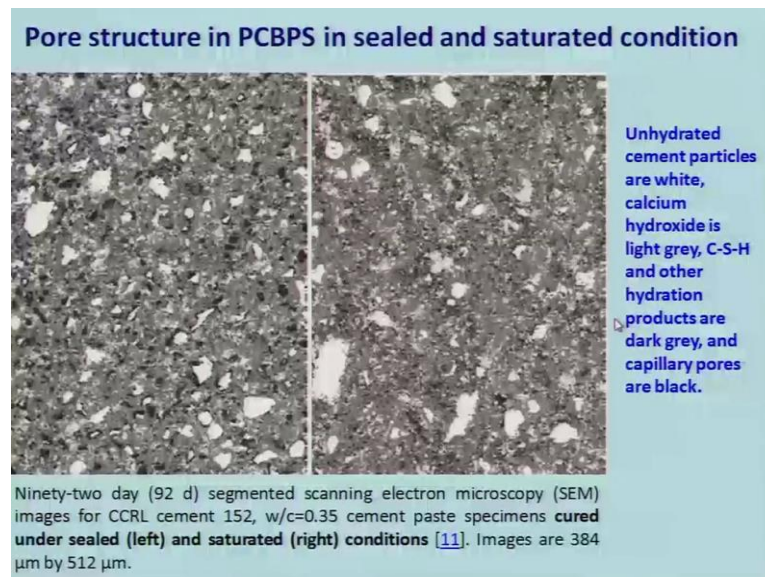
Now, similar things can also be obtained for the compounds that have impurities like in our Portland cement paste. And individually you find that you get these type of trends. Remember that the same values for C 2S and belite you will not get. Primarily because you have impurities here; likewise C 3S and alite will not be similar. Likewise, C 3A and C3A here will not be similar primarily because it is contains impurities, but the trends will be similar that is very important. Which means compared to the C 3A the rate of hydration or degree of hydration of C 3S and C2S are lower. The same thing is reflected here also compared to C 3 the alite and belite rate of hydrations are lower.

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And what is shown in this figure is that you have C₃S C₂S C₃A C₄AF and overall how was the degree of hydration changing. So, what you find is that the overall value somewhere comes in between the C₃A C₃S C₂S and C₄AF. So, the overall curve you get in between these 4 curves.

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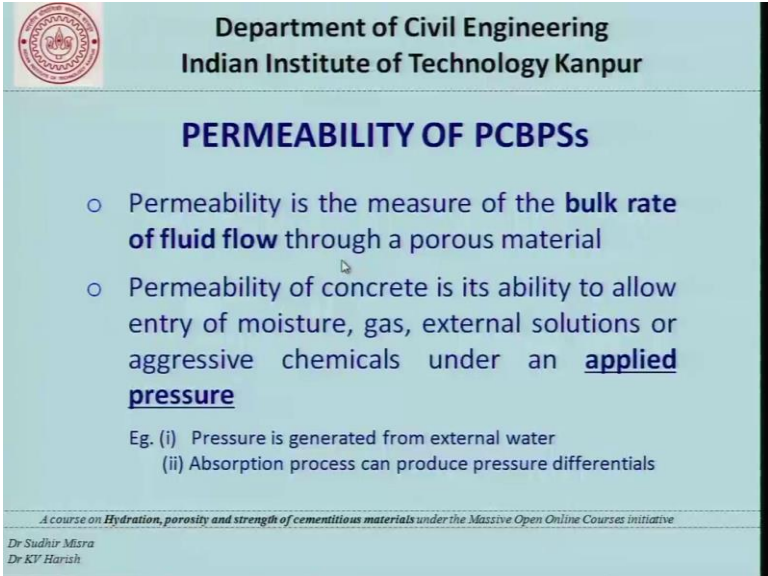



Now, how does the structure hydrated system looks in a scanning electron microscope? Is what is shown here? So, there are 2 figures in one figure what is shown is a sealed condition, which power did for his investigation. And the other one is a saturated

condition. So, what you generally find is that the sealed condition has some larger pores compared to the saturated condition. So, this is one factor which indicates that powers formulas and other things need not be fully taken for the saturated condition. So, some of his formulas can be acceptable and remember that those are acceptable only for the sealed condition. When it comes to the saturated condition which we normally use it in the field and in the lab some things are different. So, what is shown here is basically the pore structure?

So, when we say pore structure, we basically say what is the distribution of pores in the Portland cement based paste system. How the pores are distributed all through the system? In this type of diagram usually the unhydrated cement particles are shown in white color, the typical scanning electron microscope image will look like this where unhydrated cement particles are white in color the pores are usually black in color and the grey regions are usually the hydrated products.

(Refer Slide Time: 24:46)



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PERMEABILITY OF PCBPSs

- Permeability is the measure of the **bulk rate of fluid flow** through a porous material
- Permeability of concrete is its ability to allow entry of moisture, gas, external solutions or aggressive chemicals under an **applied pressure**

Eg. (i) Pressure is generated from external water
(ii) Absorption process can produce pressure differentials

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Now, coming on to the next topic and very important topic which is permeability and porosity of Portland cement based paste systems, we will see how permeability and porosity are related at a later stage. Now what is permeability? Permeability is the measure of the bulk rate of fluid flow through a porous material. Permeability of concrete is its ability to allow entry of moisture gas external solutions or other aggressive chemicals under an applied pressure.

And if you practically see cases where permeability will be an issue some examples are shown if you take a dam or other cases, you see that huge water is on one side of the dam and remember that we are talking about a concrete dam. So, the water is usually present for a longer time in the dam. So, it may take and the hydrostatic pressure of water will provide the pressure that is required for water to penetrate into the dam. So, here where the example one indicates the case that happens in a dam pressure is generated from external water. Sometimes you may also have absorption process that can produce pressure differentials.

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Comparison of permeability of cement paste

Effect of Age of Cement Paste on Its Permeability
Coefficient $w/c = 0.51$)

Age (days)	K_p (m/s)	
Fresh paste	10^{-5}	Independent of w/c
1	10^{-8}	
3	10^{-9}	
4	10^{-10}	Capillary pores interconnected
7	10^{-11}	
14	10^{-12}	
28	10^{-13}	
100	10^{-16}	Capillary pores discontinuous
240 (maximum hydration)	10^{-18}	

Courtesy: Sidney, M., Young, J.F., and Darwin

Now, we would generally like to know what will be the permeability of cement paste at an early stage right from the fresh paste to about say more than 28 days is a permeability more or less and how it is increasing and all those things. Because we have already seen this for the porosity, because in the previous lectures we have seen that the porosity at the fresh state is extremely high, and it has decreased it is decreasing rapidly at some point when the calcium silicate hydrate gel and ettringite are getting formed. And it decreases steeply when the calcium silicate hydrate gel goes rapidly.

And finally, at a matured state the porosity is very low. So, now, what happens to the permeability at the fresh state the permeability is of the order of 10^{-5} meter per second, and say at about one day this reduces to 10^{-8} . And likewise say about 3 days it has reduced to about 10^{-9} . So, usually 10^{-8} to

about 10^{-13} indicated at 28 days those are extremely low permeability. And usually at these levels water typically cannot enter the Portland cement based paste system.

So, what is the information that you have to take from the levels of permeability that are discussed here is that when it is fresh the permeability is 10^{-5} . The Portland cement based paste system achieves say initial or final setting time, at that point the permeability is of the order of 10^{-5} to 10^{-8} meter per second. So, at that levels itself it is very difficult for external water to get into the Portland cement based paste systems. And more information is also provided for example, for ages beyond say 28 days the permeability goes very low 10^{-13} to as low as 10^{-18} . And likewise one more information is that at these ranges say from 10^{-5} to 10^{-13} , the capillary pores that are present are interconnected to each other.

With curing age what happens is the capillary pores become discontinuous. We will talk about interconnectivity of pores at a later stage, but as of now what you have to know is with period of curing the permeability it decreases substantially and one more information is that this 10^{-5} to about 10^{-13} is the range irrespective of what the water to cement ratio is. So, this investigation is primarily done for make sure having a water to cement ratio of 0.51.

So, even if you use lower water cement ratio or a higher water cement ratio, this range of permeability you will typically find with any Portland cement based paste systems. The exact values maybe different, but the levels 10^{-5} to 10^{-13} will essentially remain the same.

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PERMEABILITY OF PCBPS

- Substantial pressure is required to make water penetrate through PCBPS just after its final setting time
- Permeability of PCBPS usually refers to its “**water permeability**” although in many cases, it can refer to permeability of other solutions/gases

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So, now getting back to some other things in permeability, substantial pressure is requiring to make water penetrate through Portland cement based paste system, just after it is setting time. So, like what we have seen here is that just after setting time the permeability is minus 5 to minus 8 meter per second. So, it becomes very difficult for water to simply penetrate. So, you need very high pressures in order to make the water permeate into the system. Permeability of Portland cement based paste system usually refers to it is water permeability. In a general sense permeability of concrete is usually refers to it is water permeability. Although in many cases it can refer to permeability of some solutions likes chlorites or some gases like oxygen or hydration sulfide.

We have seen that there is a factor that we have used in this table call K_p . So, K_p represents the coefficient of permeability and the explanation of that is provided here.

(Refer Slide Time: 31:07)

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PERMEABILITY OF PCBPSs

- The flow of water through cement paste obeys Darcy's law for flow through porous medium. The rate of flow of water (v) is determined as

$$v = K_p \frac{h}{x}$$

where h = head of water (hydraulic pressure), x = thickness of the specimen, K_p = Permeability co-efficient (is not a constant & depends upon the w/c and age of the paste)

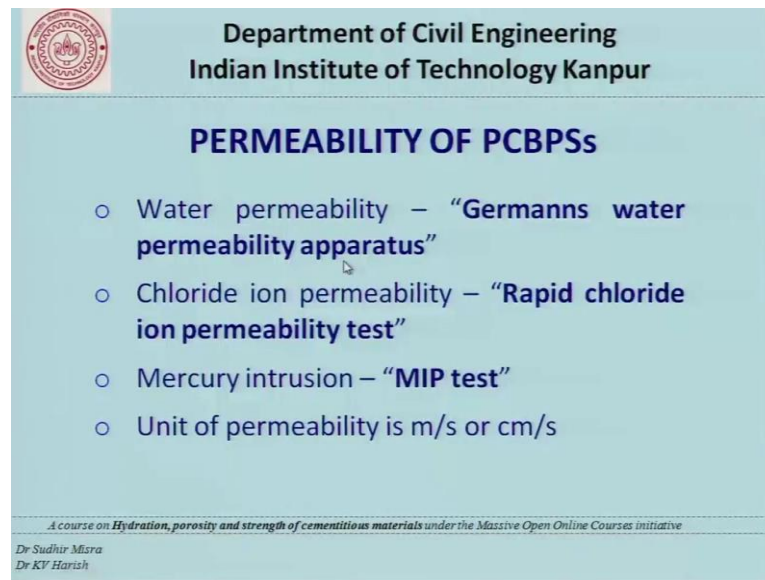
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So, the flow of water through cement paste obeys Darcy's law for flow through porous medium. So, the formula is given by $v = K_p \frac{h}{x}$, and v is the rate of flow of water which is nothing, but permeability measured in meter per second and K_p is the coefficient of permeability h is the head of water and x is the thickness of the specimen that is taken up. Remember that K_p permeability coefficient is not a constant and it depends upon the water to cement ratio and age of the paste. So, if you get back to the table to see that this factor is dependent on water to cement ratio. When I said independent of water to cement ratio, I mentioned that the levels at which you get which means the orders 10^{-5} to 10^{-13} are independent of water to cement ratio here. We are talking about in this case we are talking about the magnitude.

So, magnitude basically comes before which means that for one paste, if you find for one Portland cement paste at say water to cement ratio of 0.3 if you find K_p value as 5×10^{-8} , for another water cement ratio which has lower you will have some other magnitude, but the permeability will be in the order of 10^{-8} .

(Refer Slide Time: 32:48)



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PERMEABILITY OF PCBPSs

- Water permeability – “Germans water permeability apparatus”
- Chloride ion permeability – “Rapid chloride ion permeability test”
- Mercury intrusion – “MIP test”
- Unit of permeability is m/s or cm/s

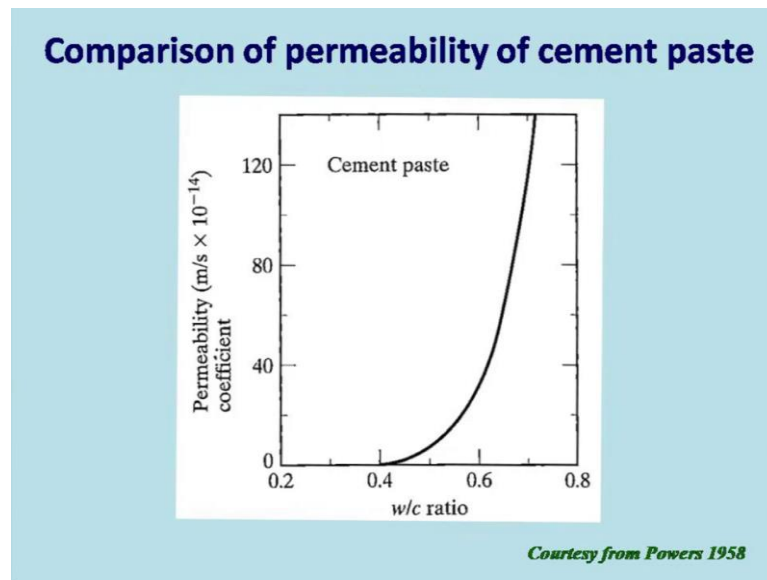
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Now, some more information about permeability water permeability is measured using Germans water permeability apparatus. Chloride permeability is measured using rapid chloride ion permeation test. I think this test is largely discussed probably in the first 3 lectures provided by Professor. Sudhir Mishra. So, you can probably get back to those lectures and find out how this test is done. As of now the Germans water permeability test is not important, but you may have to remember that this is for water permeability.

And likewise rapid chloride ion permeation test is for chloride ion permeability. And you also have mercury intrusion which we have already seen last couple of lectures. And remember that mercury intrusion porosimetry is primarily for understanding the porosity of the Portland cement based paste systems, but it can be extended to understand the permeability of the system also. And the unit of permeability is meter per second or centimeter per second.

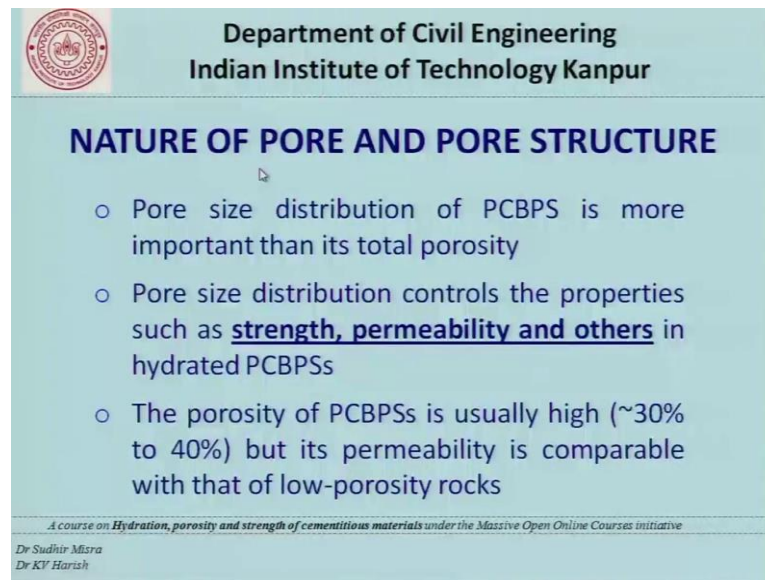
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So, a figure is shown here to understand what happens to the permeability of Portland cement paste with increase in the water to cement ratio. So, in the X axis you will have 0.2 to 0.8 and in the y axis you have permeability coefficient ranging from 0 to say about 120 or little about. And this is expressed in meter per second into 10 power minus 14. So, you have understand that these values are in 10 power minus 14 range.

So, what you find is that you find the exponential relationship between the permeability and as water to cement ratio increases, the permeability substantially increases. At an initial stage it is very slow, but later on suddenly it steeply increases especially if you take between 0.5 to say about 0.6 or 0.7 there is a steep increase.

(Refer Slide Time: 34:55)



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NATURE OF PORE AND PORE STRUCTURE

- Pore size distribution of PCBPS is more important than its total porosity
- Pore size distribution controls the properties such as **strength, permeability and others** in hydrated PCBPSs
- The porosity of PCBPSs is usually high (~30% to 40%) but its permeability is comparable with that of low-porosity rocks

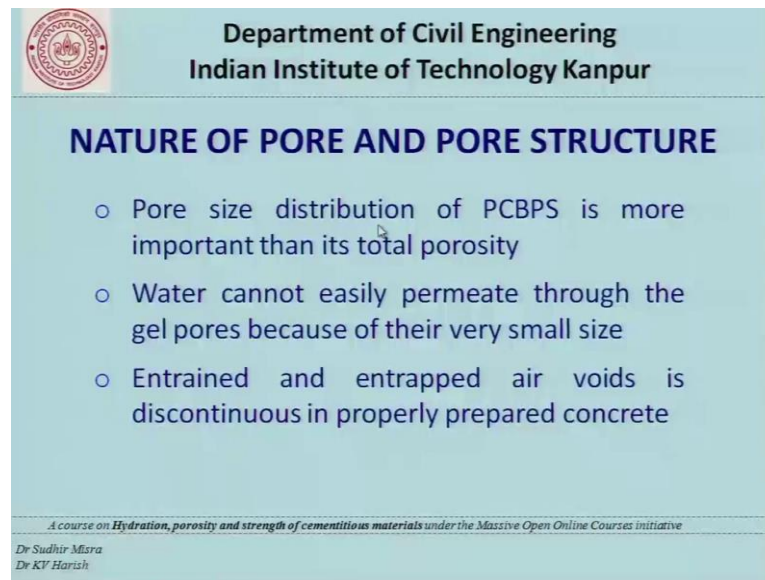
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Now, coming on to the next topics to understand the relationship between permeability and porosity, one should know the nature of pores and pores structure that exists in Portland cement based paste systems. So, pore size distribution is more important than the total porosity. Remember that we have discussed total porosity in the previous lectures when we discussed under different pores. So, the important thing that you have to know is pore size distribution is actually more important than total porosity. Pore size distribution controls the property of strength permeability and others in hydrated system.

The porosity of Portland cement based paste system is usually high and it is approximately 30 to 40 percent but, remember that despite having such high porosity the permeability of these mixtures are very low and comparable to the permeability of rocks.

(Refer Slide Time: 35:55)



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NATURE OF PORE AND PORE STRUCTURE

- Pore size distribution of PCBPS is more important than its total porosity
- Water cannot easily permeate through the gel pores because of their very small size
- Entrained and entrapped air voids is discontinuous in properly prepared concrete

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Pore size distribution is more important than it is total porosity as already mentioned. Water cannot easily permeate through the gel pores because of it is very small size. Remember that water to some extent can permeate through capillary pores, but not through gel pores. Because gel pores are smaller in size. Entrained and entrapped air voids if they are present in systems remember that entrained air voids are present in the system only when air entraining agents or and the entrapped air voids present. Usually present in the system in the order of 1 to 2.5 percentage and it could be more if the mixture is not properly compacted.

So, if these voids are present they are usually discontinuous and there is no continuity of the pores.

(Refer Slide Time: 36:52)

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NATURE OF PORE AND PORE STRUCTURE

- One critical factor that explains the nature of pores is **'PORE CONNECTIVITY AND CONTINUITY'**
- This factor basic relates arbitrarily the porosity of PCBPS with its permeability

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One important critical factor under this topic is pore connectivity or and continuity whether the pores are connected to each other or not the porosity and the permeability.

(Refer Slide Time: 37:09)

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PORE CONNECTIVITY AND CONTINUITY

- If pore continuity fully exists, system will be **porous and permeable**
- If pore continuity is fully absent, system will be **porous but impermeable**



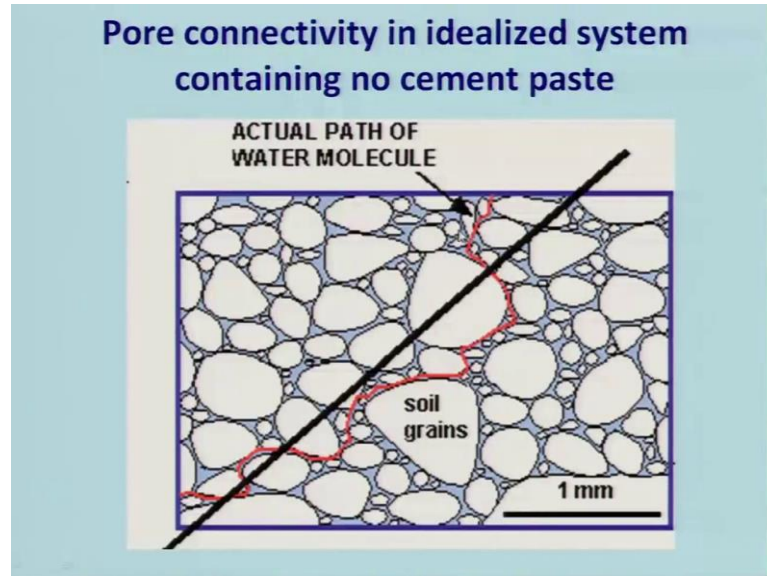
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So, to understand there are two more points which are important. If pore connectivity fully exists, then the system will be porous and permeable. If pore continuity is fully absent system will be porous, but impermeable. So, here what is shown is some hydrated particles which are shown in black color and in some of the cases you see that you have

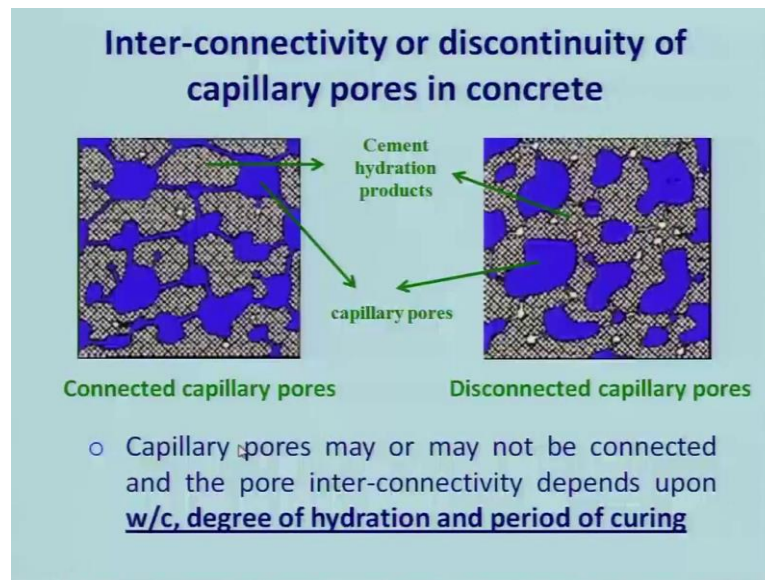
open pores which are connected to each other. Where as in some cases you have pores are which are disconnected to each other.

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If you take an idealized system where you have only aggregates. So, what you can see in the bluish portion is basically the water which can travel from one end to the other. So, remember that this the idealized system with no cement paste. So, we were assuming that there is no cement paste. So, water basically takes the path from connecting one void to another, and finally it goes to the other side. So, the pore connectivity is a very critical factor.

(Refer Slide Time: 38:19)



And so in this slide what is shown is that 2 systems are shown where in one system the capillary pores are connected and in the other system the capillary pores are disconnected.

So, here the capillary pore is indicated by the bigger water space. And the path that is connecting is actually the connectivity. And the hydration products are indicated in grey color. So, in this figure what you find is that the capillary pores are connected to each other. Where as in this figure what you find is that you have this capillary pores, but there is less connectivity. Why because the hydration compounds are already formed and this water is not able to reach this water. So, capillary pores may or may not be connected and pore interconnectivity depends on 3 factors. So, in the previous slides what we have seen is nature of more pores and pores structure and we have seen that pore connectivity and continuity is a very important factor and the pore connectivity is a function of water to cement ratio degree of hydration and period of curing.

(Refer Slide Time: 39:44)

Inter-connectivity or discontinuity of capillary pores in concrete

TABLE 18.3 Curing Time Required to Produce a Discontinuous System of Capillaries (Assuming Continuous Moist Curing)

<i>w/c Ratio</i>	<i>Curing Time (days)</i>
0.40	3
0.45	7
0.50	28
0.60	180 (6 months)
0.70	365 (1 year)
> 0.70	Not possible

Courtesy: Sidney, M., Young, J.F., and Darwin

Now, what is shown here is approximately if the water to cement ratio is changing from say 0.4 to up to 0.7, what is the curing time that you need in order to achieve a discontinuous system which means you want pores, but you do not pore to be continuous. And here it is assumed that continuous moist curing or wet curing is adopted.

So, for a water to cement ratio of 0.4 it takes only 3 days to achieve a discontinuous system. For higher to water cement ratio it reaches it needs up to 365 days to achieve a discontinuous system. Now the question arises do we need continuous system or discontinuous system. If you get back to the slide if you have a continuous system what basically happens is that any solution or chemicals basically passes from one end to the other. So, we prefer to have a non continuous or discontinuous system. So, that water or external agents do not permeate through the Portland cement based paste system. So, that no chemical reactions or other things happens inside.

So, the goal is primarily to achieve a discontinuous system. So, that we can say that the Portland cement based system may have porosity, but the permeability is substantially lower. So, what you what you see is that if you increase the curing time, it needs up to 180 days to achieve a discontinuous system and remember that if the water to cement ratio is higher than 0.7, which is generally consider to be a very high water to cement ratio range. Typically getting a discontinuous system becomes impossible.

(Refer Slide Time: 41:45)

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Relationship between porosity & permeability of PCBPS

- Permeability of system can be related to its porosity **only if the capillary pores are continuous or inter-connected**
- The size of interconnected capillary system is measured in terms of **effective/critical pore access diameter (d_c)** determined by MIP

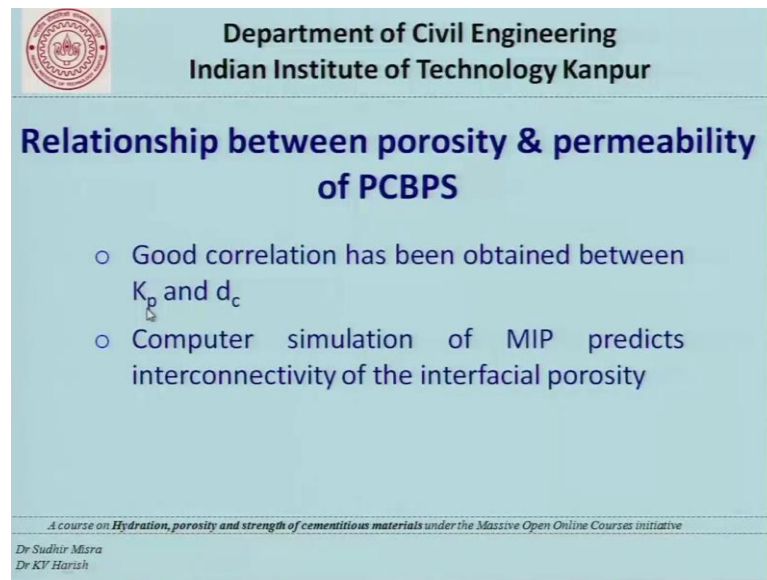
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Now, getting on to the relationship between porosity and permeability of Portland cement based paste system. And remember that porosity is already discussed extensively and hence we will not get in to that. Permeability of system can be related to it is porosity only if the capillary pores are continuous or interconnected. Now immediately you could think to yourself why not the permeability of the system can be related to porosity through the gel pores.

Remember that the gel pores have smaller pores and hence water cannot easily diffuse into the system. So, it is largely the capillary pores which define the porosity of the system. So, the permeability and porosity can be related only if the capillary pores are continuous or interconnected. The size of interconnected capillary system is measured in terms of effective or critical pore access diameter which can be obtained from mercury intrusion porosimetry. So, couple of lectures before we have already seen how to determine d_c .

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Relationship between porosity & permeability of PCBPS

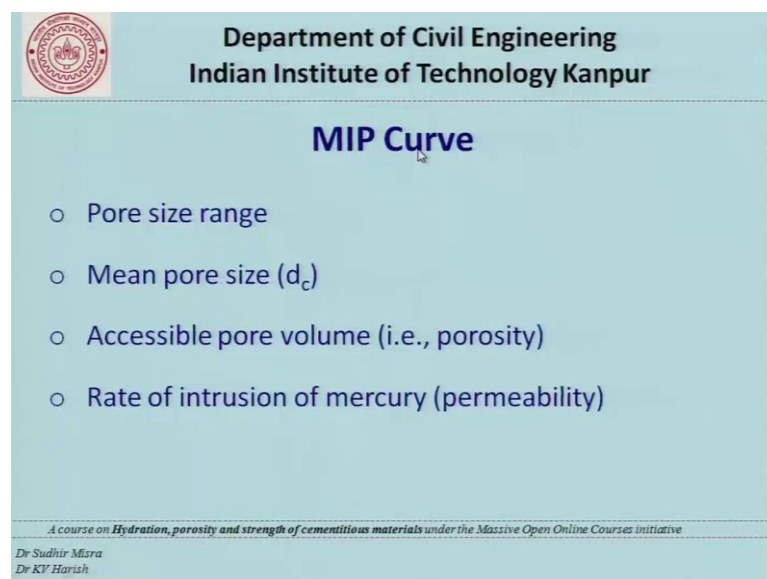
- Good correlation has been obtained between K_p and d_c
- Computer simulation of MIP predicts interconnectivity of the interfacial porosity

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So, we will again go through some of the figures to understand the connection between permeability and porosity. And past studies have shown that there is a good correlation that exists between K_p which is a coefficient of permeability and d_c . So, K_p is considered as a permeability factor or coefficient of permeability and it has good relationship with d_c which is actually the porosity factor. And computer simulation of mercury intrusion porosimetry predicts the interconnectivity of the interfacial porosity.

(Refer Slide Time: 43:39)



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MIP Curve

- Pore size range
- Mean pore size (d_c)
- Accessible pore volume (i.e., porosity)
- Rate of intrusion of mercury (permeability)

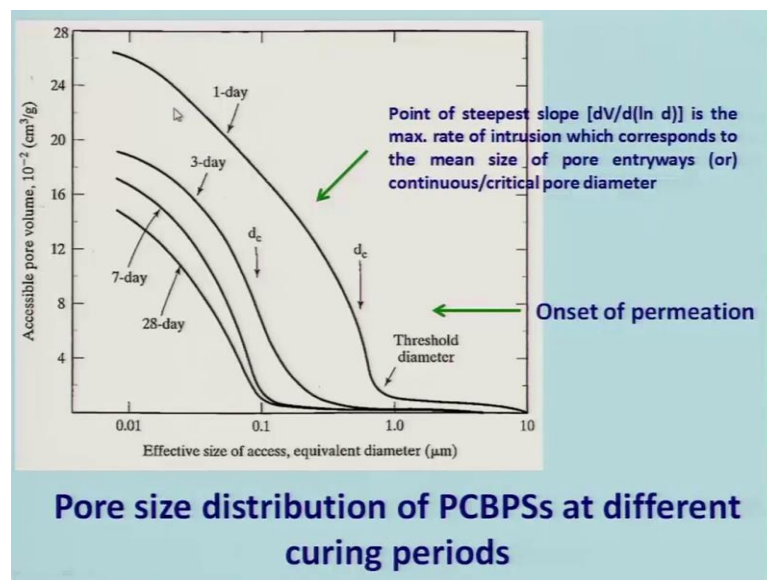
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So, now some more explanation about mercury intrusion porosimetry curves are provided, in the explanation that we saw couple of lectures before under mercury intrusion porosimetry, we saw that the pore size ranges could vary and we saw how to determine d_c and also pore volume and others. Now in addition to all these 3 we should also understand that MIP can also be used to understand the permeability through a factor called rate of intrusion of mercury. So, whatever mercury that enters into the sample it is usually the accessible pore volume.

So, if you take derivative with respect to time of this, you typically land up getting rate of intrusion of mercury which is an indication of the permeability of the system.

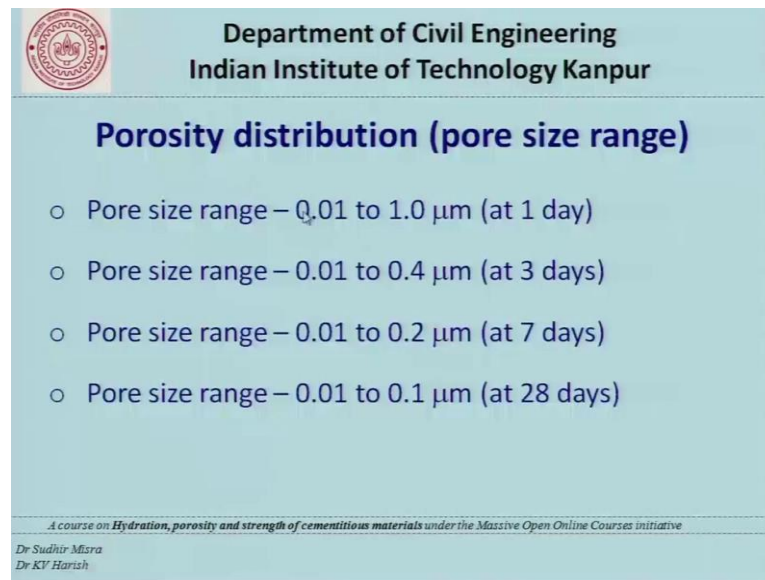
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Now, coming on to this figure which we have already discussed couple of lectures before you have equivalent diameter that is taken in the X axis and your accessible pore volume taken in the y axis. And you typically have 4 different curves and the first one represents the one day cure specimen second one is a 3 day third one is a 7 day and 4th one is a 28 day. You also know that this d_c represents the point of steepest slope. And it is the maximum rate of intrusion which corresponds to the mean size of pore entry ways from this range to this range. And likewise the threshold diameter is threshold diameter represents the onset of permeation.

Now, how can we understand this curve much better especially from the view of especially from the view of curing time?

(Refer Slide Time: 45:34)



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Porosity distribution (pore size range)

- Pore size range – 0.01 to 1.0 μm (at 1 day)
- Pore size range – 0.01 to 0.4 μm (at 3 days)
- Pore size range – 0.01 to 0.2 μm (at 7 days)
- Pore size range – 0.01 to 0.1 μm (at 28 days)

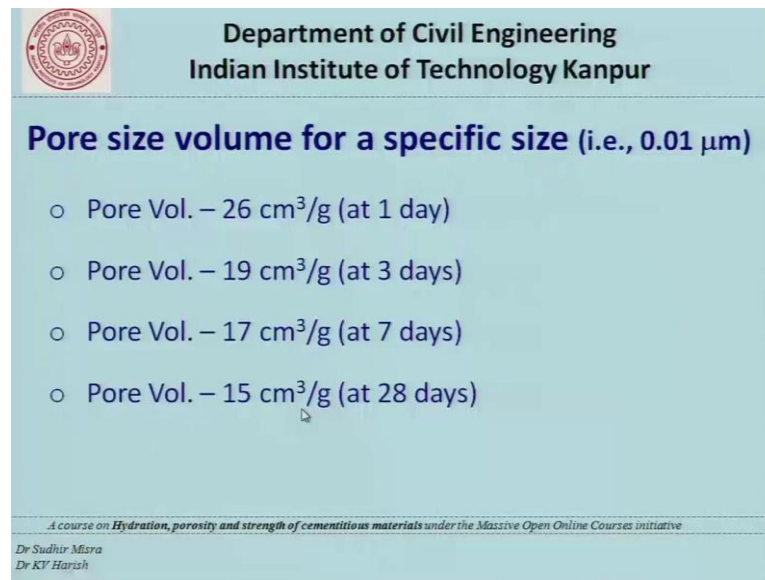
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Now, if you compare say one day 3 day 7 day and 28 day curve, you find that the pore size range is between 0.01 to 1 micron meter at one day and it is up to 0.01 to point 1 micron meter at 28 days. Typically, you find that the smallest pores are available in all the at all the curing ages 1 to 28; however, the bigger pores you see that it is decreasing with age. So, if you take at one day it is 1 micron meter and it reduces to point 1 micron meter at 28 days.

So, that is indication that when the period of curing is increasing or when time is increasing the pore sizes become smaller and smaller.

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Pore size volume for a specific size (i.e., 0.01 μm)

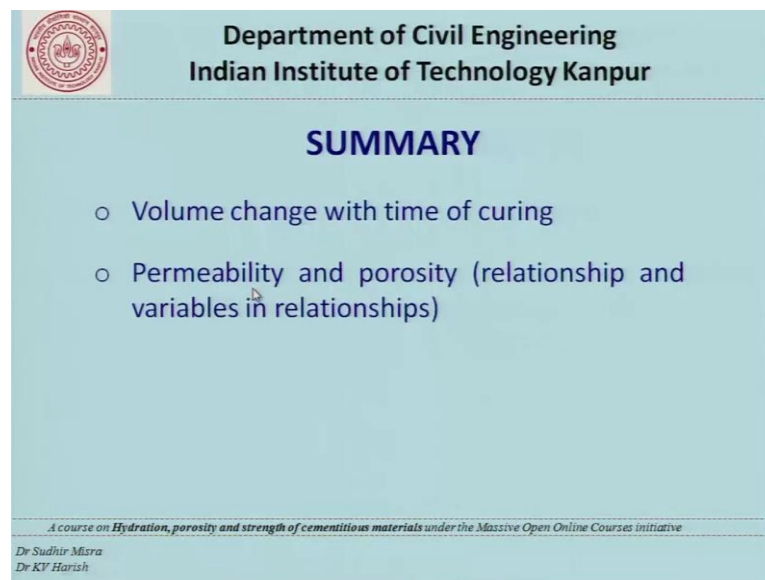
- Pore Vol. – 26 cm^3/g (at 1 day)
- Pore Vol. – 19 cm^3/g (at 3 days)
- Pore Vol. – 17 cm^3/g (at 7 days)
- Pore Vol. – 15 cm^3/g (at 28 days)

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Likewise, the pore volume also decreases for each one of the cases. So, for the first one it is 26 centimeter square per gram and it decreases to 15 centimeter cube per gram.

(Refer Slide Time: 46:41)



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SUMMARY

- Volume change with time of curing
- Permeability and porosity (relationship and variables in relationships)

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So, in summary what we have seen is what are the volume changes that are happening with time of curing, and what is permeability of concrete what is coefficient of permeability what are the important factors which connect permeability and porosity primarily, what we have seen is pore structure nature of pores pore connectivity and all those things. And all those factors are functions of water to cement ratio time of curing

and degree of hydration. And also finally, we have seen that permeability and porosity can be related only when the capillary pores are connected to each other. If it is not connected it is difficult correlate permeability and porosity. With this, I am completing this lecture.

Thank you.