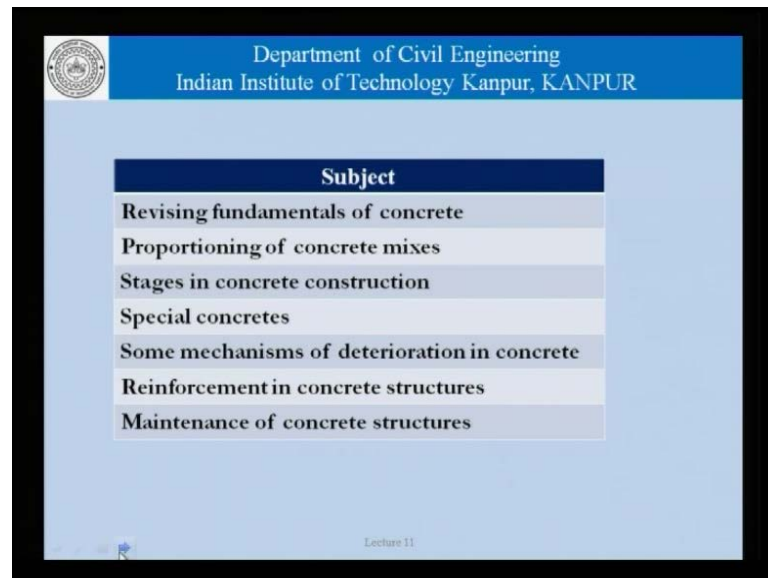


**Concrete Engineering and Technology**  
**Prof. Sudhir Misra**  
**Department of Civil Engineering**  
**Indian Institute of Technology, Kanpur**

**Lecture - 11**  
**Porosimetry – Measuring Pores in Concrete**

(Refer Slide Time: 00:20)



Subject
Revising fundamentals of concrete
Proportioning of concrete mixes
Stages in concrete construction
Special concretes
Some mechanisms of deterioration in concrete
Reinforcement in concrete structures
Maintenance of concrete structures

[FL] and welcome to this lecture on concrete engineering and technology. In this series of lectures, we are trying to revise fundamentals of concrete; talk about proportioning of concrete mixes, stages in concrete construction, special concretes, deterioration in concrete structures that we see around us, reinforcement of concrete structures and their maintenance. So, as part of the discussion on revising the fundamentals of concrete, in the last discussion, we were talking about pores and porosity in concrete. And we had for convenience, divided the discussion into origin of pores and porosity; nature and characterization of pores, and finally measurement of porosity in concrete. Now, out of a three, we had more or less completed the discussion on the origin of pores and their nature and characterization.

(Refer Slide Time: 00:43)

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**Pores and porosity in concrete**

- Origin of pores and porosity in concrete
- Nature and characterization of pores in concrete
- Measurement of porosity in concrete

Lecture 11 4

(Refer Slide Time: 01:14)

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**The volume after a reaction becomes smaller than the volume before a reaction.**

$$\text{C}_2\text{S} + 4.3\text{H}_2\text{O} \longrightarrow \text{C-S-H} + 0.3\text{CH}$$

Mass (g)	172.17	77.49	227.51	22.23
Density (g/cm <sup>3</sup> )	3.28	1.00	1.90	2.24
Volume (cm <sup>3</sup> )	52.5	77.5	119.7	9.9

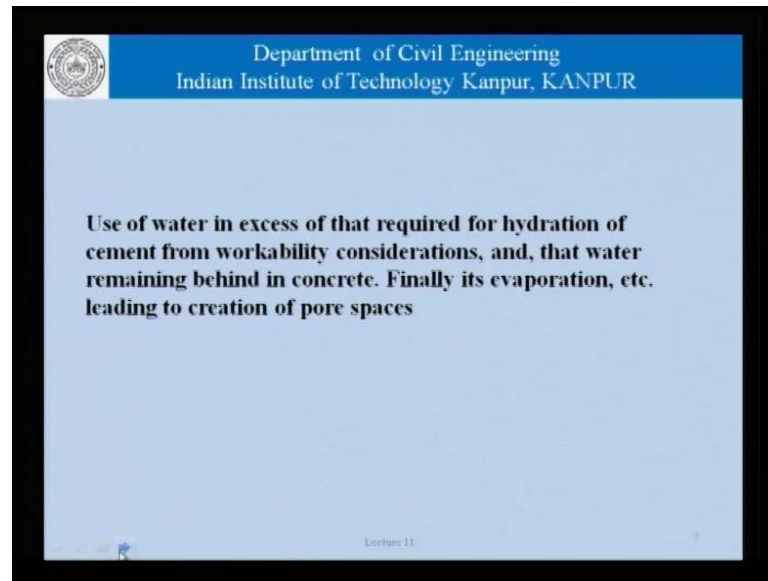
↳ 130.0 ←      ↳ 129.6 ←

→ 0.4 (Δ0.4%) ←

Lecture 11 6

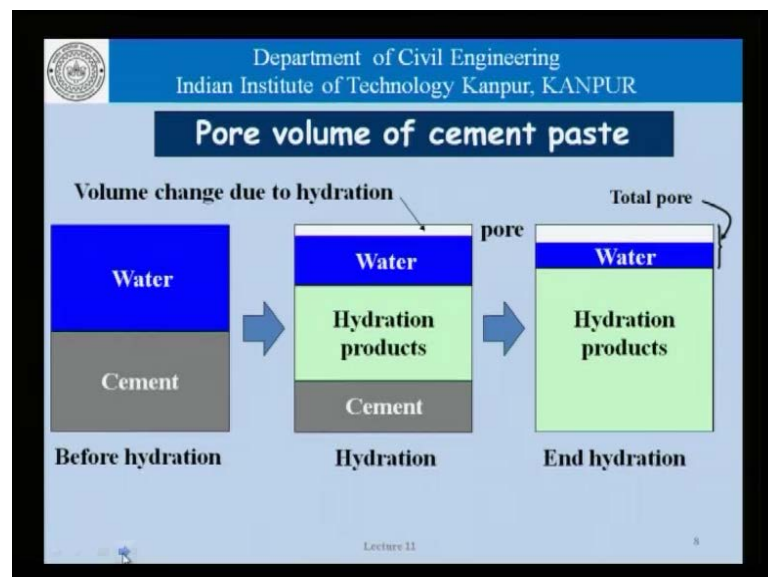
And before we proceed further, we can just quickly recapitulate as to what went on at that time. We talked about the fact that, the volume of the products as far as hydration is concerned is slightly lower than that of the reactance. And that is one of the reasons why we have blank spaces or blank pores or voids within the concrete system.

(Refer Slide Time: 01:42)



Another reason was the fact that we use excess water compared to that which is required for hydration of the cement. And that excess water once it remains in the concrete matrix after the hydration has been completed tends to escape through evaporation and so on if the structure is exposed to the atmosphere. And in any case, the space that is occupied by water is susceptible to finally becoming void space.

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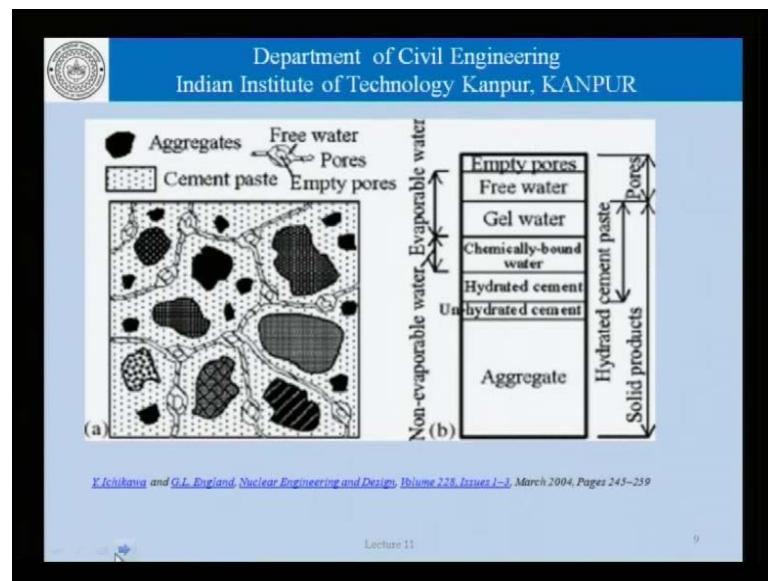


Even in cases where the structure is under water and is not likely to be dried up, the volume of voids occupied by water surely is not solid hydration products. And at the end

of it, is one form of porosity. At best, we can call it concrete, which is saturated with water as far as the pores are concerned. This is the diagrammatic representation, which we saw last time of water and cement hydrating, going for an intermediate stage, and finally, the end of hydration. Here we have of course, shown complete hydration of cement and there is no cement left. But, there is always a possibility that we talked about last time that, some cement may still remain at the end of the hydration process.

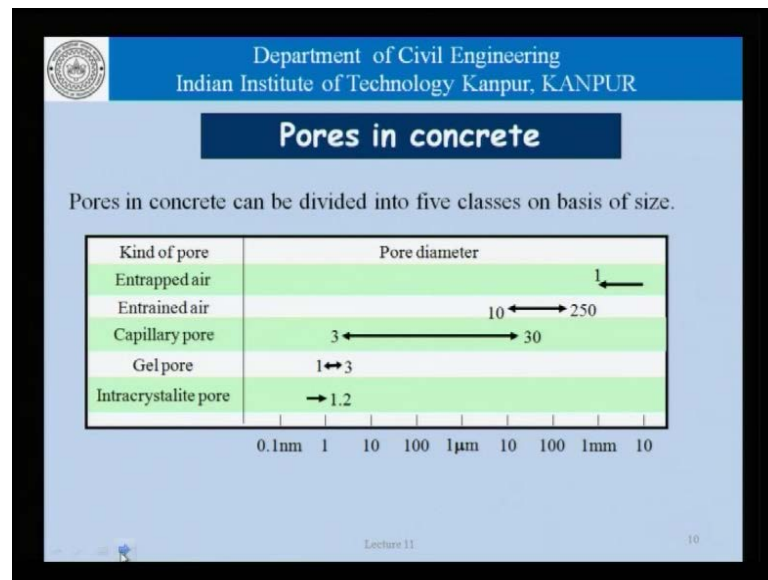
In any case, this space here which is occupied by water or the pore space generated on account of dimensional changes or the volume changes on account of hydration products being slightly less in volume compared to the reactance; this is space is what is contributing or causing the porosity in concrete. And this space increases as more water is being added, that is, as the water cement ratio is increased. And that is partly the reason why the strength goes down as water cement ratio is increased. It is the increase in pores space that causes this decrease in the strength.

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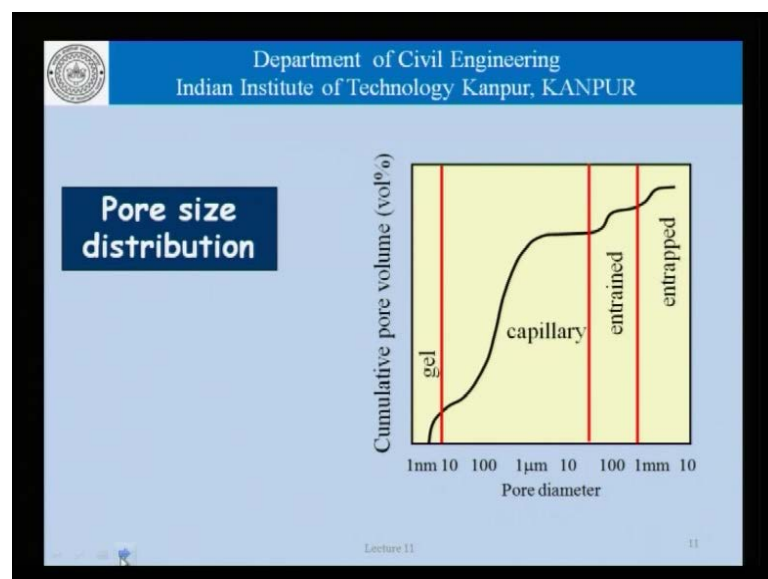
And then we had looked at some of these models, which have been proposed in terms of looking at the pores spaces. And as far as pores spaces are concerned, we have talked about chemically bond water, gel water, free water and empty pores. And all of which essentially, is one form of porosity or the other.

(Refer Slide Time: 04:15)



We had also looked at five class classification of pores in concrete based on sizes – entrapped air, entrained air, capillary pores, gel pores and intracrystalite pores. And depending on the nature of these pores, their original genesis, their sizes are quite different. And the pore sizes in concrete could range from 0.1 nanometer to about a millimeter and so on. So, there is a huge range of pore sizes as far as concrete is concerned.

(Refer Slide Time: 04:50)



And, this here is the pore size distribution of the different kinds of pores – entrapped air, entrained air, capillary pores, gel pores and so on. And, we had constructed or considered an illustrative example, where pores of different sizes, different in number and contributing to porosity.

(Refer Slide Time: 05:00)

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**Illustrative example**

$D_1 < D_2 < D_3$

Take a pore structure (A), as shown. Model pores are cylindrical – with and associated diameter and volume.

Concrete could have pores of varying diameter.

Lecture 11 12

(Refer Slide Time: 05:17)

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**Illustrative example**

1. Total pore volume in both cases =  $V_1 + V_2 + V_3$
2. In A, the large sized pores occupy the large volume.
3. In B, the largest volume is occupied by medium sized pores
4. In A, the small sized pores occupy the least volume.
5. In B, the large pores occupy the least volume

$D_1 < D_2 < D_3$

**A**

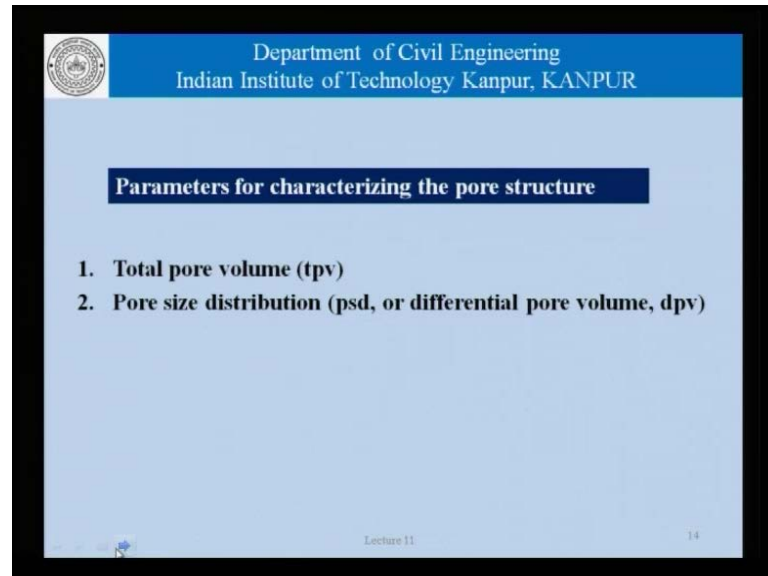
**B**

Lecture 11 13

And, we had talked about a situation, where if these pores were to be analyzed in terms of their contribution to a total pore volume in the system, there could be two cases: A

and B; where even though the total volume could be very much the same, the actual distribution as far as the contribution from larger pores could be different.

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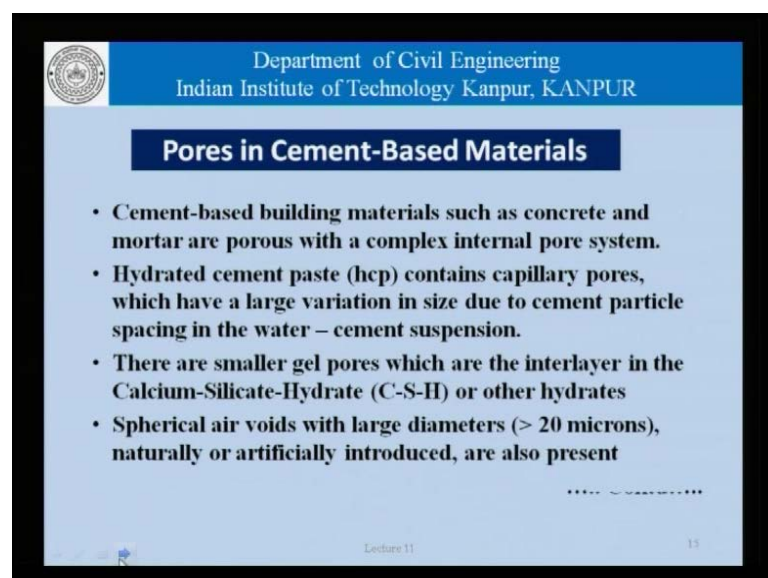
**Parameters for characterizing the pore structure**

1. Total pore volume (tpv)
2. Pore size distribution (psd, or differential pore volume, dpv)

Lecture 11 14

And, we had talked about the fact that parameters that characterize pores size distribution as far as concrete is concerned. The both commonly used parameters are the total pore volume and the pore size distribution, which is often represented as the differential pore volume; that is, how much is the volume of pores of certain sizes or different sizes.

(Refer Slide Time: 06:01)



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**Pores in Cement-Based Materials**

- Cement-based building materials such as concrete and mortar are porous with a complex internal pore system.
- Hydrated cement paste (hcp) contains capillary pores, which have a large variation in size due to cement particle spacing in the water – cement suspension.
- There are smaller gel pores which are the interlayer in the Calcium-Silicate-Hydrate (C-S-H) or other hydrates
- Spherical air voids with large diameters (> 20 microns), naturally or artificially introduced, are also present

Lecture 11 15

Now, to summarize as far as pores and cement based materials are concerned, cement-based building materials such as concrete and mortar are porous with a complex internal pore structure. Hydrated cement paste – hcp consists of capillary pores, which have a large variation in size due to cement particle spacing in the water-cement suspension. We should remember that, at the end of it, the paste is nothing but a suspension of cement particles in water. Of course, it is not a suspension, which is of fluid consistency; very often it is a dough-like consistency. But, it is the suspension nonetheless. So, depending upon the characteristics of these cement particles as they are suspended in water, we have different kinds of pore systems that evolve.

If we use chemical admixtures to break the flux that form of the cement particles in the suspension, the characteristics of hydration change and so does the pore size distribution. So, these are the kind of things that we need to remember when we talk about pores, porosity and the pore size distribution of concrete. There are smaller gel pores, which are interlayered in the calcium-silicate-hydrate or other hydrates. There are spherical air voids, which are larger in diameter naturally or artificially introduced. Artificially introduced air, which is entrapped air, tends to be larger particles; whereas, entrained air is smaller particles.

(Refer Slide Time: 07:46)

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### Pores in Cement-Based Materials

..... Contd.....

- In the neighborhood of the aggregates a (more) porous interfacial transition zone is present.
- Presence of pores is at the root of almost all durability related problems, which can arise out of ingress and movement of deleterious ions or materials through the pore space

CO<sub>2</sub>, Cl<sup>-</sup>  
water ↓

**Concrete is not as solid  
as we may like to believe.**

Lecture 11 16

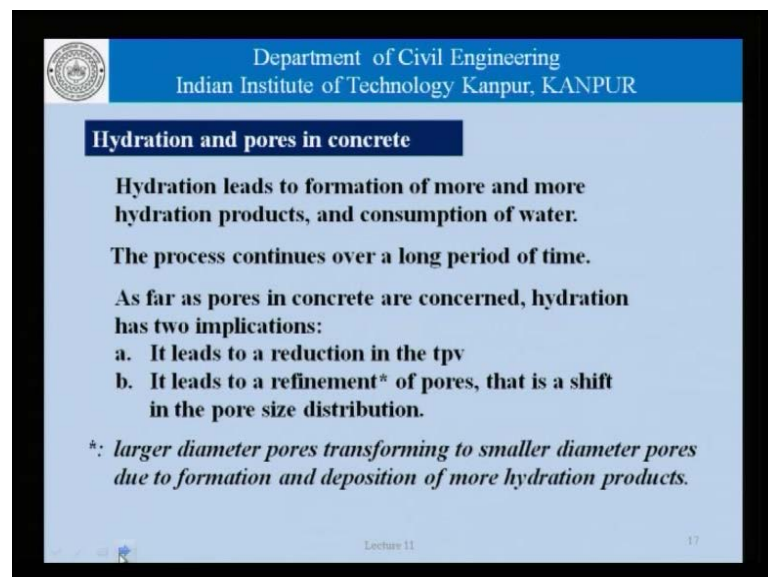
And, if we continue the discussion; in the neighborhood of the aggregates a more porous interfacial transition zone is present. This is something which we have talked about on



several occasions that, if we look at an aggregate, if we look at a concrete closely, there is aggregate particles sitting here, which is surrounded by cement paste. And the properties of the cement paste in the immediate neighborhood of the aggregate, especially at the bottom of aggregate, where the bleeding water from the paste tends to accumulate. And the properties of the portion here, which is the main cement paste or the main body cement paste – they are slightly different. And if these properties are different, they manifest themselves in the changes in the pores size distributions or the pore structure in these two places.

Presence of pores in the concrete is at the root of almost all durability related problems, which can arise out of ingress and movement of deleterious ions or materials through pore space. And this includes materials such as carbon dioxide, chloride ions, water and so on. So, it is all... So, it is the movement of these ions through the pores that cause most of our durability problems. And therefore, it is important that, as concrete engineers, we understand the characteristics of the pores in the pore size distributions within the concrete. At the end of the day, concrete is not as solid as we may like to believe.

(Refer Slide Time: 09:32)



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**Hydration and pores in concrete**

Hydration leads to formation of more and more hydration products, and consumption of water.

The process continues over a long period of time.

As far as pores in concrete are concerned, hydration has two implications:

- It leads to a reduction in the tpv
- It leads to a refinement\* of pores, that is a shift in the pore size distribution.

*\*: larger diameter pores transforming to smaller diameter pores due to formation and deposition of more hydration products.*

Lecture 11 17

Now, how does hydration come into picture as far as changes in porous and pore size is as concerned? Hydration leads to the formation of more and more hydration products and the consumption of the water. So, if there is a system, where hydration is stopped

intermediate, then there is more water available to evaporate. And therefore, the porosities will be higher. The process continues over long period of time. And that is the reason why the pore sizes and the pore distributions – they evolve over a longer period of time as far as more cements are concerned. As far as pores and concrete are concerned, hydration has two implications. It leads to a reduction in the total pore volume.

So, as more hydration products are formed, they are deposited within the system; and the total amount of space available for pores becomes lesser. So, the total pore volume changes; it reduces. And the second thing that happens is the refinement of pores; that is, a shift in the pore size distribution. Refinement essentially refers to larger diameter pores being transformed into smaller diameter pores due to formation and deposition of more and more hydration products.

So, one way of looking at this discussion could be to think in terms of a cylindrical pipe with reactive walls. So, basically, as more and more hydration takes place, because the walls of the pipe are reactive, hydration products will continue to be formed and the diameter of the pipe reduces. So, there are two things that happen. One is the diameter reduces, and therefore, the total free space or the pore space in the pipe reduces. And that has the implication in terms of also changing the size distribution of pores.

(Refer Slide Time: 11:40)

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One concept that we should finally include in our discussion is **connectivity** of pores in concrete.

This is central to an understanding of any porous material.

It is the connectivity that facilitates movement of material within the porous material

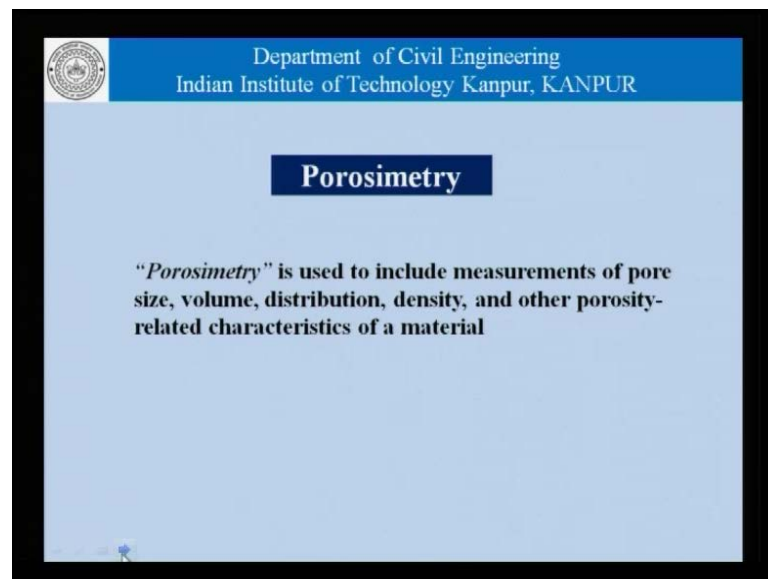
Lecture 11 18

One... Other concept that is very important as far as pores and porosity in concrete is concerned is that of connectivity of these pores. As far as durability related problems are

concerned, it makes a difference whether the pore system in concrete is continuous and connected or it is discontinuous. Only in the event that the pore system is continuous and connected, can the deleterious materials such as carbon dioxide, chlorides and so on, move freely from one place to another as far as concrete is concerned, as far as hardened concrete is concerned? If the pore system was discontinuous, then the freedom or the free movement of this deleterious material is highly restricted; and we have less problems even if the total pore volume was the same. Now, this (( )) concept of connectivity is very central to our understanding of any porous material. And as I discussed or explained just now, it is the connectivity that facilitates movement of material within the porous material.

Now, having completed the discussion of the origin and the nature and characterization of pores, we come to the discussion on measurement of porosity in concrete. Now... And that is the central theme as far as our discussion on the subject today is concerned.

(Refer Slide Time: 13:12)



Porosimetry is used to include measurements of pore size, volume, distribution, density, and other porosity-related characteristics of a material. So, as far as the pores in a porous material, is concerned, it could be characterized by size, volume, distribution, the density, and so on and so forth. So, any method that helps us better understand these characteristics of a pore system, is porosimetry.

(Refer Slide Time: 13:49)

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**Illustrative example**

Consider a pore system as shown, with diameters ranging from  $d_1$  to  $d_4$ .

In a 2-d representation, the area (and therefore the length,  $l_1$  to  $l_4$ ) represents the volume fractions of the different sizes, and the total area represents the total volume of pore space.

$d_4 < d_3 < d_2 < d_1$

Lecture 11 22

And, one example that we have is mercury porosimetry. And that is the method that we will talk about today. Now, let us consider an illustrative example as shown here. Consider a pore system as shown with diameters ranging from  $d_1$  to  $d_4$ . So, we have pores of diameters  $d_1$  here,  $d_2$ ,  $d_3$  and  $d_4$  such that obviously,  $d_1$  is the largest diameter and  $d_4$  is the smallest. Now, if this was the solid phase and this here represented the porous space, there is this model of the pore system of this particular sample or specimen whatever we may call it.

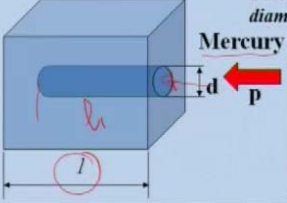
Now, in a 2-d representation, the area and therefore, the legs; now, if we have diameters  $d_1$  and if we have the pores measuring  $d_1$  in diameter over a length  $l_1$ ; we have pores of  $d_2$  over a length  $l_2$ ;  $d_3$  for  $l_3$ ; and  $d_4$  for  $l_4$ . The total area here, that is, this entire area – this essentially represents the porosity of the pore system. Through the back door without explaining it too much, I have slipped in couple of concepts here; I have slipped in the concepts that, the pores are different in number. If we look closely at this picture, there are these lines shown here, which essentially represents let us say the number of pores. And their total lengths have been lumped at one place. The second thing which I have done is that, I have put the largest diameter pores close to the end. And as we go inside, the pores have been taken to be of smaller and smaller diameters. Now, the importance or the implications of this model or this assumption will come out later as we talk more.

(Refer Slide Time: 15:59)

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### Principle of Mercury Porosimetry

The relation between mercury pressure and pore diameter can be defined the following equation.



**Mercury**

$$p \cdot \pi (d/2)^2 = \gamma \cos \theta \cdot \pi d$$
$$\therefore d = 4 \gamma \cos \theta / p$$

where,  
 $\gamma$  : Surface tension of mercury  
 $\theta$  : Contact angle of mercury and sample

**Assumption: Pores are cylindrical**

Measure both pressure and volume of mercury intruded in the sample, the pore diameter can be calculated using by this equation.  
As a result, the pore volume with a certain diameter can be obtained.  
When a pore diameter is small, high pressure is needed.

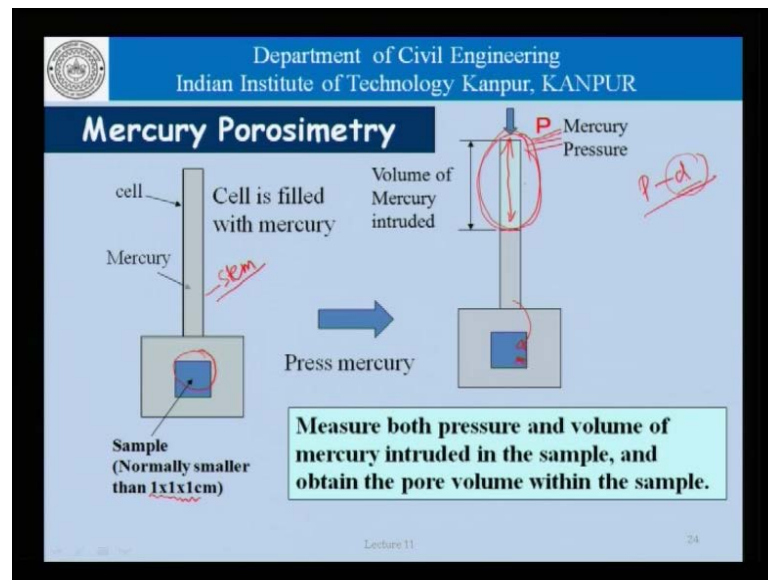
Lecture 11 23

The principle of mercury porosimetry; and that is the method that we are talking about is that, mercury is forced into a pore measuring a diameter  $d$  over the length  $l$  assuming that this is the total length of the solid. Now, this here shows the force equilibrium that we have. And finally, we have a relationship, which says that, the diameter of the pores that is being filled with mercury is inversely related to the pressure that is applied from outside. If we remember this, I think we will follow the discussion a lot more easily. Mercury is being forced into this pore; and the pressure that is required to force the mercury into the pore system is inversely proportional to the diameter.

So, if we somehow are able to get a relationship between the diameter intruded and the pressure required, then we would be able to study the pore size distribution in material such as this. We have made another assumption that, the pores are essentially cylindrical in nature. And that is the assumption that we also saw in the previous slide when we talked in terms of diameters of different pores –  $d_1$  to  $d_4$  – all arranged in a certain manner.

Now, if we are able to measure the pressure and the volume that is intruded, we would be able to calculate the diameter of the pore in the system. And as a result, the pore volume with certain diameters can be obtained. And as we have said, when the pore diameters are small, higher pressures are required to cause intrusion of mercury.

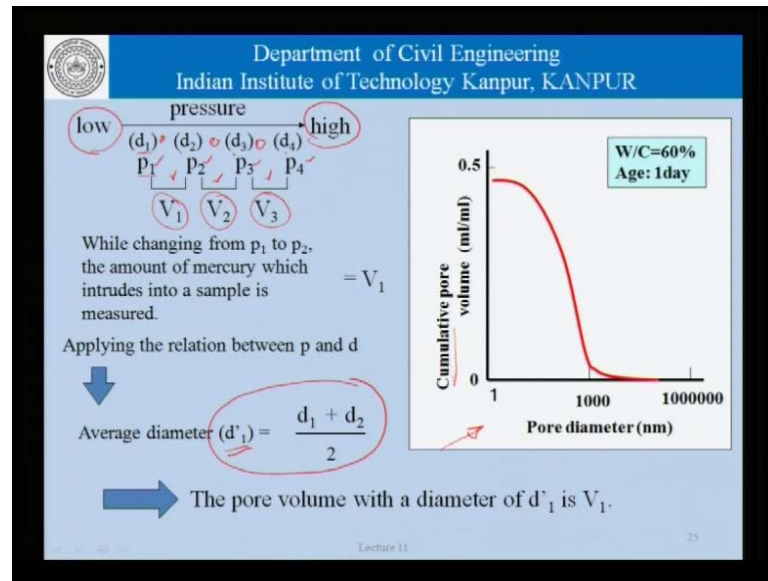
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Now, if we remember this part, let us look at how the system actually operates. What we do is, we place samples of concrete pieces, which are measuring less than a centimeter by a centimeter by a centimeter. So, they are really small pieces. We put them into this cell, what is also called a penetrometer. Fill this with mercury, which has a long stem. So, this is the stem of the penetrometer. We will take a look at the picture later on. And once the cell is filled with mercury, we apply pressure. And as pressure is applied, the mercury will tend to intrude into the concrete samples or pieces.

And the amount of mercury that goes into the concrete piece will obviously come from here; that is, this length will reduce. So, this is the sample which is filled with mercury. And at a certain point in time, after pressure has been applied, this amount of mercury has actually intruded into the sample. And now, we can relate what pressure did we use to cause this intrusion. And since we know the pressure-diameter relationship, we know that, this volume corresponds to the volume of pores having a diameter  $d$ . So, this principle is the one that is used throughout the measurement of concrete pores using mercury porosimetry.

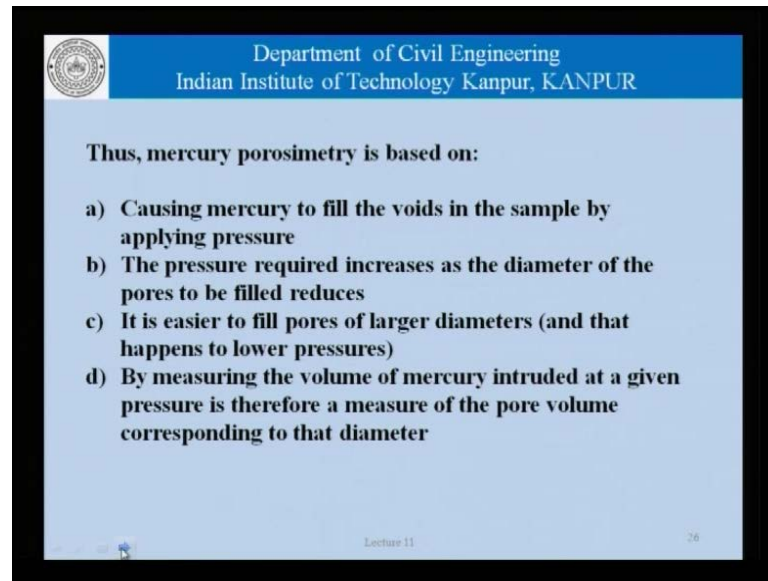
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What really happens is that, from a low level of pressure, we go to high level of pressure from  $p_1$  to  $p_2$  to  $p_3$  to  $p_4$ . And at each of these steps, we note the volumes  $v_1$ ,  $v_2$ , and  $v_3$ , which correspond to the diameters that we have here. Now, from the equation that we have, we know that, at a pressure  $p_1$  holds for diameter  $d_1$  would be filled; for a pressure  $p_2$ , the pores of diameter  $d_2$  will be filled and so on.

Now, as we increase the pressure from  $p_1$  to  $p_2$ , all the pores between  $d_1$  and  $d_2$  will be filled. It is difficult to find out how much is the volume corresponding to a diameter between  $d_1$  and  $d_2$ . So, what we get here is an average diameter of that; that is, an average diameter corresponding to the average of  $d_1$  and  $d_2$ . And if this exercise is repeated over the different pressure steps, we know the corresponding average diameters. And these results are often represented in a diagram like this; which we will study in a little greater detail, which plots the cumulative pore volume or the total pore volume with respect to the pore diameter.

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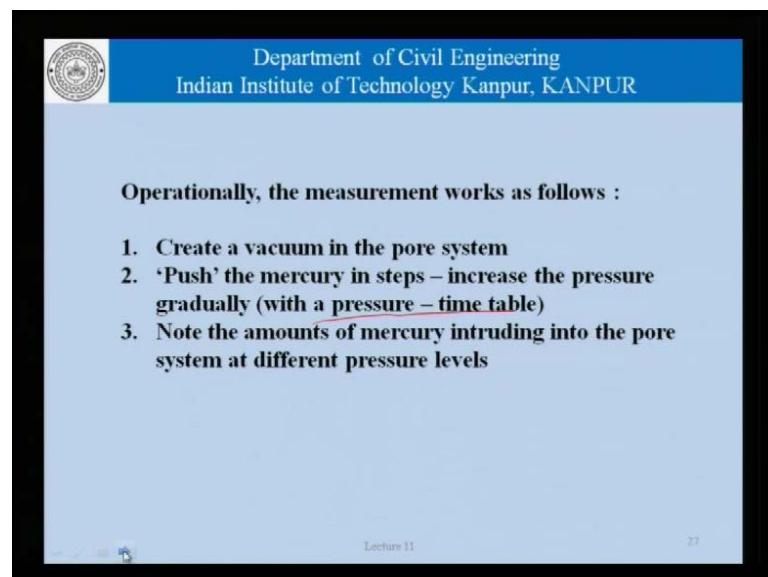
Thus, mercury porosimetry is based on:

- Causing mercury to fill the voids in the sample by applying pressure
- The pressure required increases as the diameter of the pores to be filled reduces
- It is easier to fill pores of larger diameters (and that happens to lower pressures)
- By measuring the volume of mercury intruded at a given pressure is therefore a measure of the pore volume corresponding to that diameter

Lecture 11 26

The principle of mercury porosimetry therefore is causing mercury to fill the voids in a sample by applying pressure. The pressure required increases as the diameter of the pores to be filled reduces. It is easier to fill pores of larger diameters; and that happens at lower pressures. By measuring the volume of mercury intruded at a given pressure level, this is therefore, a measure of the pore volume corresponding to that diameter.

(Refer Slide Time: 21:50)



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Operationally, the measurement works as follows :

- Create a vacuum in the pore system
- 'Push' the mercury in steps - increase the pressure gradually (with a pressure - time table)
- Note the amounts of mercury intruding into the pore system at different pressure levels

Lecture 11 27

And, operationally, the system works as follows. Create a vacuum in the pore system; without creating a vacuum, it is not possible to get intrusion of mercury the way we



would like it to happen. Push the mercury in steps – increase the pressure gradually with a pressure-time table. So, we increase the pressure in several steps; and that can be defined in terms of a pressure-time table that, has to how much time should the machine stand at a given level of pressure. We note the amounts of mercury intruding into the pore system at different pressure levels.

(Refer Slide Time: 22:34)

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Analogous to how we do a compression or tension test. In this case, we increase the load gradually, and see the response in terms of deformation.

Similarly in the case of porosimetry, the pressures is increased as an independent variable and the response in terms of mercury intrusion is recorded (at each step).

Lecture 11 28

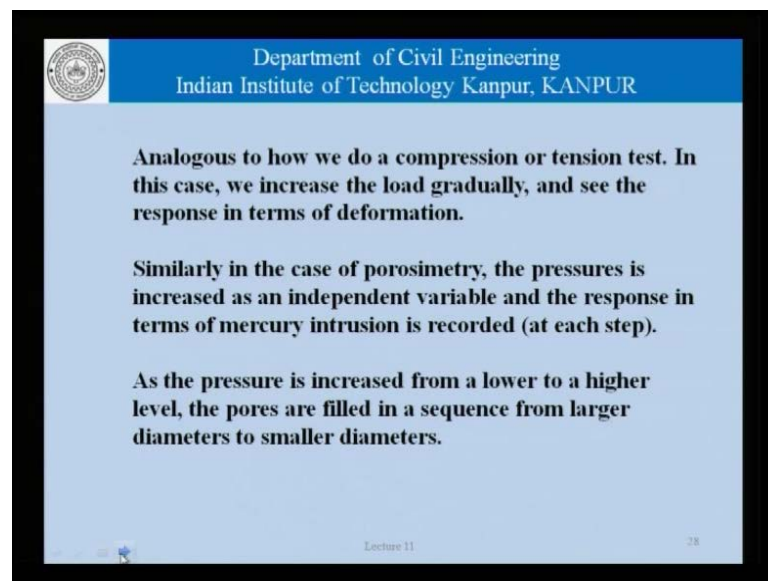
Now, this discussion is pretty similar to how we do a compression or a tension test. In which case, what we do is to increase the load gradually and we see the response in terms of the deformation of the specimen. What we really do is we have a cube or a cylinder or whatever it is; we increase this force; we keep increasing this force as a function of time and monitor the response of this specimen. How we change the force determines whether we are trying to do a force-control or a displacement-control test. But, apart from that, at the end of it, it is a variation of the applied force with time. And that is something which we are imposing upon the specimen of concrete and monitoring its response in terms of strengths. So, we do something similar here.

In the case of porosimetry, the pressure is increased as an independent variable. And the response in terms of mercury intrusion is recorded at each step. So, what we really do is have a time and a pressure table. We can say that, for a certain amount of time, the pressure will be kept at a level of  $P_1$ ; after which it will be increased to a pressure level of  $P_2$ ; after some more time, it will be increased to a pressure level of  $P_3$  and so on.

These time steps can be constant or they may not be constant. They may be such that there is a feedback loop, which tells the machine that, go to the next pressure step only after the system has become stable; that is, no more intrusion of mercury is taking place at that pressure level. Now, this no more again can be a small number close to 0, which is predefined or predetermined and is fed into the machine as an input.

Once again, pressure in this illustration is not being continuously increased. It is being increased in steps. And you recall the discussion that we did earlier in couple of... And you recall the discussion we had a couple of slides ago when we said that, pressure is increased from  $P_1$  to  $P_2$ . And corresponding to  $P_1$ , we have all pores of  $d_1$ , which are filled up; corresponding to  $d_2$ , we have all pores, which we have... We have all pores of diameter  $d_2$ , which are filled up. And therefore, once we increase the pressure from  $P_1$  to  $P_2$ , all the pores in between  $d_1$  and  $d_2$  would be filled. And we will get a measure of the average pore size between  $d_1$  and  $d_2$ ; how much is that contributing to the porosity by way of how much is the differential intrusion of mercury during this pressure step.

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**Analogous to how we do a compression or tension test. In this case, we increase the load gradually, and see the response in terms of deformation.**


**Similarly in the case of porosimetry, the pressure is increased as an independent variable and the response in terms of mercury intrusion is recorded (at each step).**

**As the pressure is increased from a lower to a higher level, the pores are filled in a sequence from larger diameters to smaller diameters.**

Lecture 11 28

Continuing our discussion, as the pressure is increased from a lower to a higher level, the pores are filled in a sequence from larger diameters to smaller diameters. I guess now you understand what was the trick in arranging all the pores in the concrete in a sequence with the largest pores being placed closest to the surface, and then arranging them in descending orders of the diameter as we go inside the concrete.

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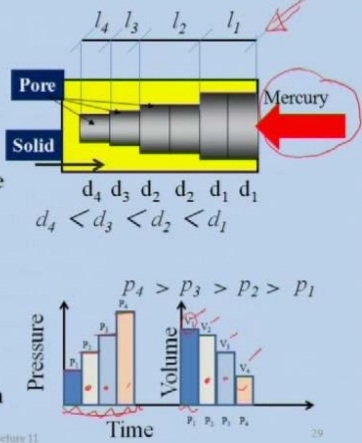
**Illustrative example**

Consider the pore system shown with mercury intrusion to occur as shown.

A volume ( $V_1$ ) fills at a pressure  $P_1$  (for pores with diameter  $d_1$ ).

In the following pressure step, once the pressure is increased to  $P_2$ , another  $V_2$  of mercury would intrude the pore space completely filling the pores having a diameter  $d_2$ , and so on

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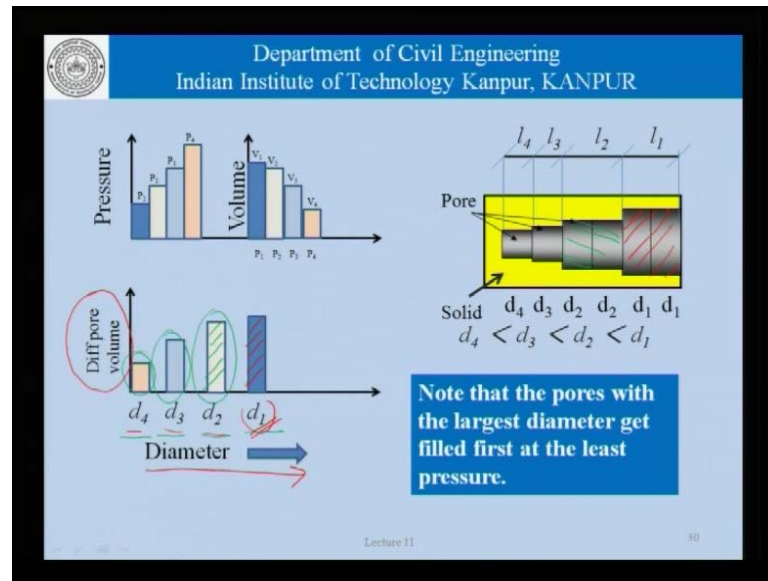


Lecture 11 29

This is the model that we were talking about. And now, we say that, let us allow mercury to penetrate or intrude into this pore space. A volume  $V_1$  fills at a pressure of  $P_1$ . So, this is the pressure-time table that we are talking about. We are going to have pressure  $P_1$ ,  $P_2$ ,  $P_3$  and  $P_4$  for different periods of time. And we will watch how much of volume of mercury intrudes into the pore; and this being measured by the changes in the mercury level in the stem of penetrometer.

Now, if you look at this diagram, obviously, the volume of pores corresponding to the diameter  $d_1$ , which is the largest is very large. Let us say that, this volume intruded is  $V_1$ . Corresponding to this pressure step of  $P_3$ , the volume intrusion is  $V_3$ . And for  $P_4$ , it is  $V_4$ . Remember that, the volumes  $V_1$ ,  $V_2$ ,  $V_3$  and  $V_4$  are filled in this order; that is, first of all, we have  $V_1$ , then  $V_2$ , then  $V_3$  and then  $V_4$  as the pressure is being increased. But, the diameters that they represent, is the other way round; the  $V_1$  is getting filled first corresponding to the largest diameter and so on.

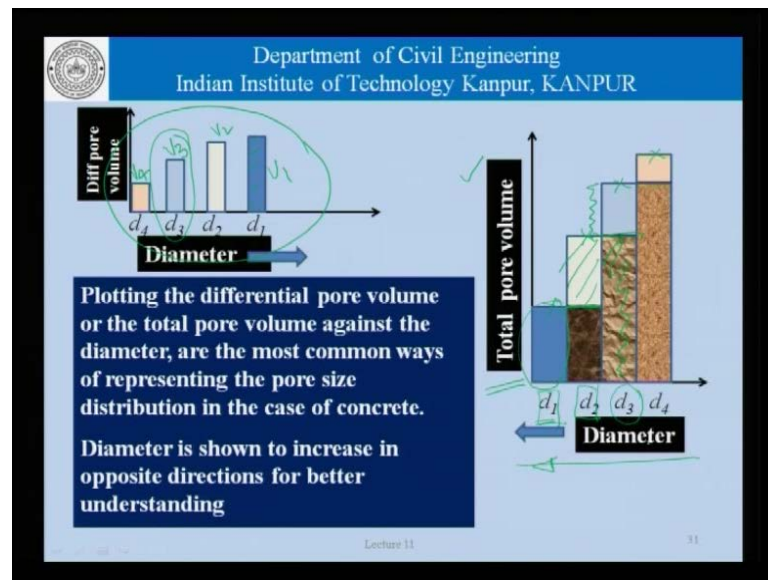
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This is another way of representing the data that we just saw. We have now plotted the differential pore volume  $d_1, d_2, d_3$  and  $d_4$ . Because  $d_1$  is the largest diameter; so it has been placed here. But, this amount of mercury or this volume was the first to intrude into the pores. And this is the volume corresponding to this space here. Similarly, corresponding to the volume of pores with  $d_2$ , they came next and filled up this space here. So, the order in which the pores are filled is the other way around. The order in which they are filled is  $d_1, d_2, d_3$  and  $d_4$ . And this is the differential pore volume; that is, the pore volumes that are getting filled at individual pressure levels and individual diameters.

Now, another way of representing this would be the total pore volume. This is the diagram that we already have; that is the differential pore volumes. We know that, corresponding to  $d_1$ , this is  $V_1$ ; corresponding  $d_2$ , this is  $V_2$ ; corresponding  $d_3$ , this is  $V_3$  and  $V_4$ . Now, if we plot the total pore volume that has been intruded, we will get corresponding to  $d_1$ , this is the pore volume. Once the pore volume corresponding to  $d_2$  gets added to it, the total volume that has intruded into the mercury is somewhere here. Out of which, this portion alone corresponds to the pores, which are between  $d_1$  and  $d_2$ .

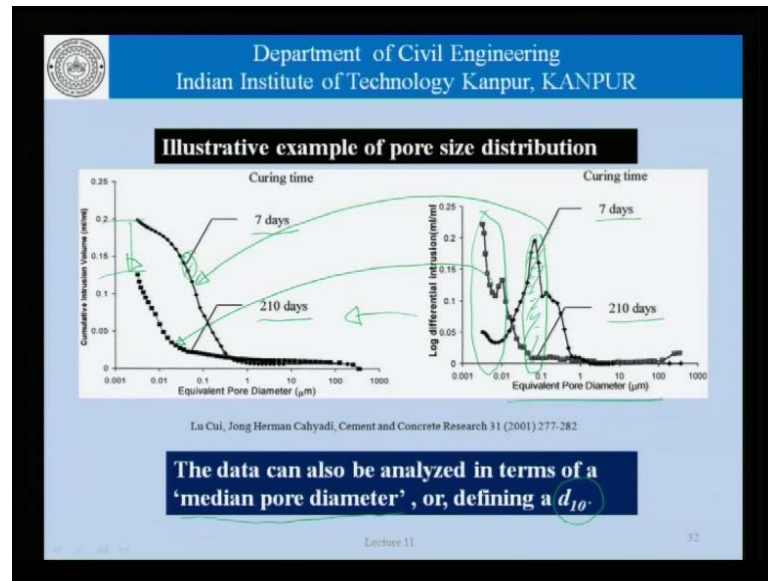
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Similarly, once we go to the next pressure step, this amount of mercury is already in the pores. And it is only this amount of mercury, which is getting added; that is, from here. But, the total amount of intrusion is here. Similarly, in the next step, the total amount of intrusion is here. Strategically, I have inverted the diameter direction here. So, the  $d_1$ , which is the largest diameter, has been placed closest to the origin. So, the diameter in this case is increasing this way. And that is the traditional way. The diameter of pores is increasing this way. And that is one of the ways that very often you will see when you look at pore size distributions being represented or being talked about as far as mercury intrusion porosimetry and its applications in concrete engineering is concerned.

Here is an example of a real pore size distribution of concrete; and we have an equivalent pore diameter. The differential pore volume in terms of milliliters per milliliter is often plotted on a logarithmic scale and is shown here; and we can find out that, corresponding to different diameters, what is the amount of pore space. What this picture here, which is for 7 days shows that, there is large amount of volumes; the maximum differential pore volume occurs at this pore size. But, this does not give us an idea of the total pore volume.

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Now, compared to the pore size distribution in terms of the differential pore volume at seven days, if we look at a matured cement paste or a concrete, which these authors are talking about; we see that, there is a complete change in the pore size distribution of the material. The peak that we saw here simply does not exist when we are talking about a mature paste; that is, all these pores here have now become filled with hydration products.

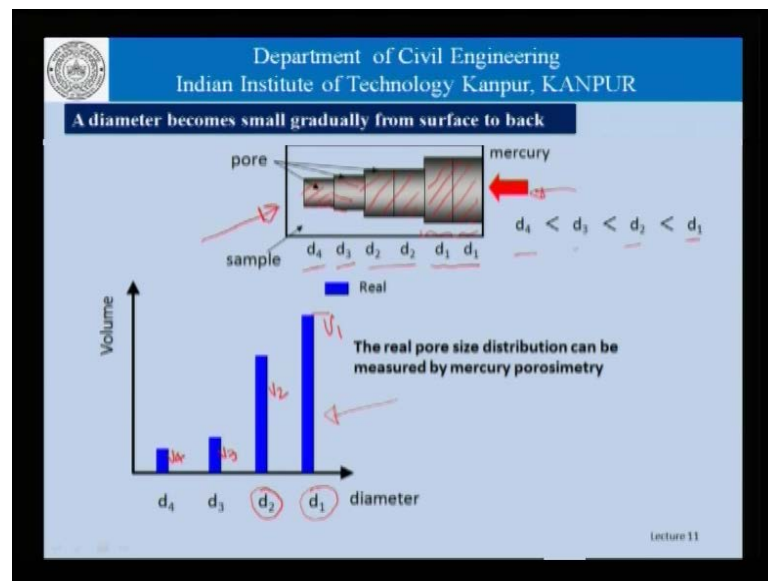
Now, if we look at the cumulative intrusion volume or the total pore volume, what we are talking about; we find that, these are the reported values at 7 days and 210 days. So, this 7-day differential pore volume corresponds to this total pore volume; and the 210-day differential pore volume here corresponds to the 210-day total pore volume results as shown here. So, we see that, this peak or this distribution, which can be seen at this point here has vanished; and also, the total pore volume has reduced. And this is what we were talking about when we said that, as we have more and more hydration occurring in the cement paste and the concretes, the total pore volume changes, it reduces. And also, the pore size distribution changes, refinement occurs; that is, larger sizes of pores vanish and we get smaller and smaller sizes of pores.

Now, what is the importance of these smaller sizes of pores or the larger sizes of pores as far as the strength is concerned, as far as property such as shrinkage or durability is concerned, is something, which we need to be aware of. What are the implications of

using mineral admixtures such as fly ash or silica fume on the pore size distribution? Because they ultimately take part in the hydration or they fill the pore spaces and cause changes in the pore structure. Now, what changes they cause? If that needs to be studied quantitatively, we need to use the techniques such as the mercury intrusion porosimetry, what we are discussing now. Of course, we have been talking about the total pore volume and the differential pore volume.

We can also talk in terms of a median pore diameter or a concept such as  $d_{10}$ ; the median pore diameter is the diameter corresponding to which 50 percent of the pore volume is higher than that diameter. We can talk in terms of a  $d_{10}$ , which is the diameter, which is such that 10 percent of the volume is finer than that or coarser than that, whichever way we want to define it. So, even though the total pore volume and the differential pore volume are the principle measures or parameters for characterizing concrete porosity, there could be other measures once we have this data in hand.

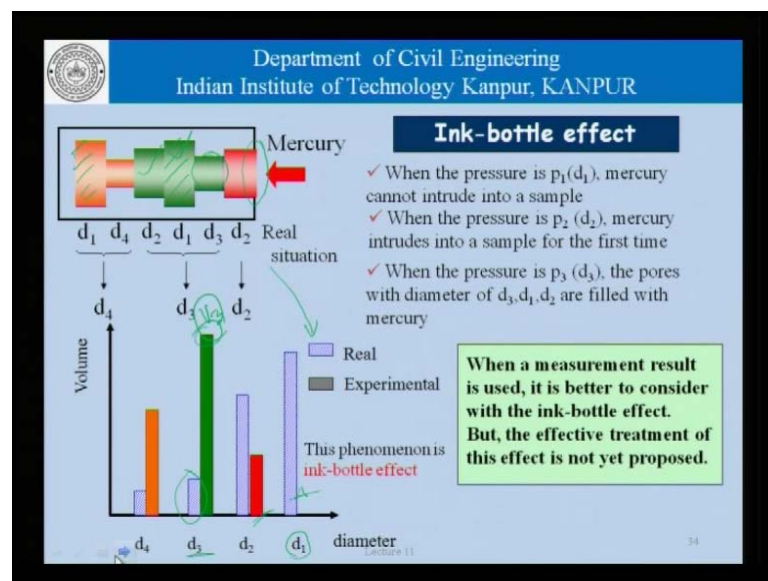
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Now, before we look at the details of mercury intrusion porosimetry and how the data is interpreted, let us look at a simplified picture or a schematic diagram, which shows pores or cylinders of different diameters let us say  $d_1$ ,  $d_2$ ,  $d_3$  and  $d_4$ , which are arranged in this manner such that of course,  $d_1$  is greater than  $d_2$ , which is greater than  $d_3$ , which is greater than  $d_4$ . The lengths here can be used to determine the volumes of the pores corresponding to a particular diameter. Now, with this example, what we will get is

something like this; that pores having a diameter  $d_1$  have a certain volume; let us call it  $V_1$ . Similarly, pores having a value  $d_2$  have a volume  $V_2$ ; similarly,  $V_3$  and  $V_4$ . Now, in this case, it is important to note that, mercury is being forced into this pore structure, which is arranged as shown here from the surface and first fills this volume, then fills this volume followed by this volume, and finally, this volume as the pressure is increased. This does not happen in real life.

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Now, if we have a system, which is something like this; and that is the more realistic distribution as far as concrete is concerned. There is no way that we have a system, where all the coarse pores are at the surface. And as we go within the concrete, the pores become finer and they are waiting for us to measure the diameters and measure the amount of volume and so on; that does not happen. And that is what is called the ink-bottle effect. Now, if you remember, an ink bottle looks something like this.

So, this diameter here in the ink bottle is smaller than the diameter at the bottom. And as far as mercury pores are concerned, this diameter here is larger than this diameter here. So, this picture essentially looks like an ink bottle. In a manner of speaking, the larger diameter pores are hidden behind smaller diameter pores. And now, what we are trying to understand is what are the implications of this phenomenon in terms of the mercury intrusion porosimetry.

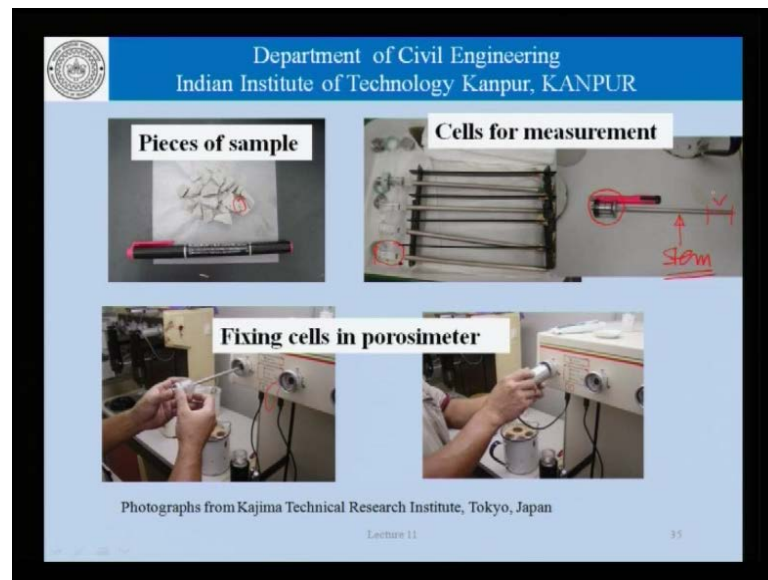


Now, this somehow is the real situation as far as the pore volumes are concerned. We have a substantial amount of pores corresponding to  $d_1$ . There is this pore of  $d_1$ ; there is this pore of  $d_2$  and so on. So, there is a large contribution of pore volume corresponding to a size  $d_1$ . However, when pressure  $p_1$ , which corresponds to  $d_1$  is applied, the mercury cannot intrude in the system, because the surface through which the mercury has to intrude has a diameter of  $d_2$ . So, the pores with the diameter  $d_1$  are really hidden behind. And therefore, the intrusion is 0. Only when the pressure applied is increased to a pressure  $p_2$ , which corresponds to a penetration diameter of  $d_2$ , the mercury intrudes into the sample for the first time and we get a value something like this. The mercury still does not penetrate into the next level, which is having a diameter  $d_3$  smaller than  $d_2$ ; and therefore, requires a higher pressure.

Now, if we increase the pressure there, what happens is that, not only this portion of the mercury gets filled, but this portion as well as this portion also get filled, because the pressure required to fill the volume of pores corresponding to that diameter is actually smaller. So, we are applying a pressure higher than that, and therefore, the mercury will simply flood into the pore space corresponding to  $d_1$  and  $d_2$ . And what we will get is this amount of mercury intruded the pore sample when the pressure was  $p_3$ ; and roundly tell us that the amount of pores corresponding to a diameter  $d_3$  is this value, let us say,  $V_3$ . Whereas, the actual pores of this size are only  $d_3$ . And the same thing is happening when we go to  $d_4$ ; the large pore of  $d_1$  behind  $d_4$  is also getting filled up. This phenomenon as I discussed, is the ink-bottle effect.

And when a measurement result is used, it is better to consider the ink-bottle effect. But, an effective treatment of this effect is not yet known. There are some researchers, who are trying to understand this issue and trying to address it by saying that, we have a cyclic test; that is, we increase the pressure once and then we reduce the pressure and see how much mercury actually comes out. Those are some of the ways that people are trying to address this issue of ink-bottle effect as far as concrete structures are concerned.

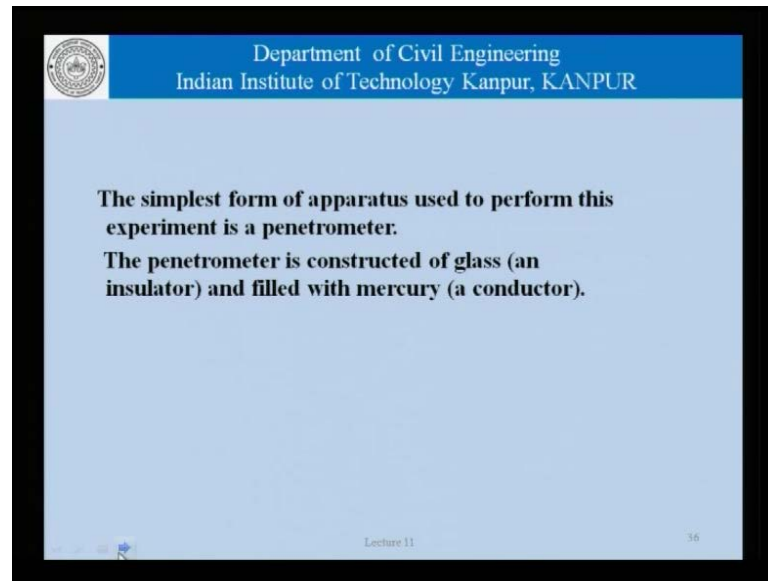
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These here are pictures of the porosimetry being actually carried out; which we can see that, there is some pieces of samples and which are quite small. And these samples or these small pieces are put in these cells or penetrometers; and that whole system is sealed; and we have this as the... After the cells in the penetrometers have been sealed, we put them inside this machine, seal this part, and we are ready to carry out the test. And once the test has been carried out, we remove these penetrometers. And what we see here is a penetrometer with mercury present in this cell. And this is the stem that we talked about. And the amount of movement of mercury that takes place in the system is what we are talking about when we talk of the differential pore volumes and so on.

To describe the apparatus in text, the penetrometer is constructed of glass, which is an insulator and fill with mercury, which is a conductor. And, the stem is a capillary that acts as a reservoir for the analytical volume of mercury. It is plated with a metal, which is conductor. And the two conductors, that is, mercury inside and the metal plating outside are separated by glass and they form a coaxial capacitor. Now, as the pressure forces the mercury out of the capillary and into the sample, the mercury inside decreases and so does the capacitance. So, it is the change in this capacitance that we monitor to understand how much is the length of mercury that has intruded, which is related to the volume of mercury that has intruded.

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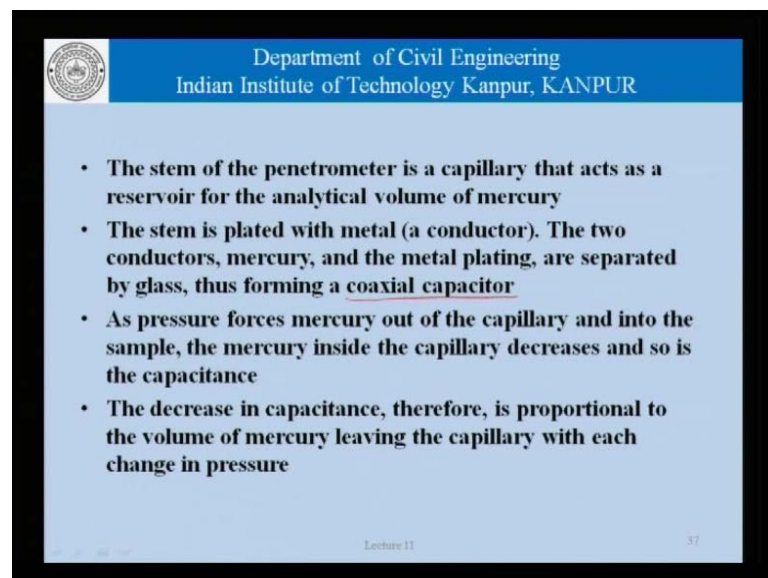


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The simplest form of apparatus used to perform this experiment is a penetrometer.  
The penetrometer is constructed of glass (an insulator) and filled with mercury (a conductor).

Lecture 11 36

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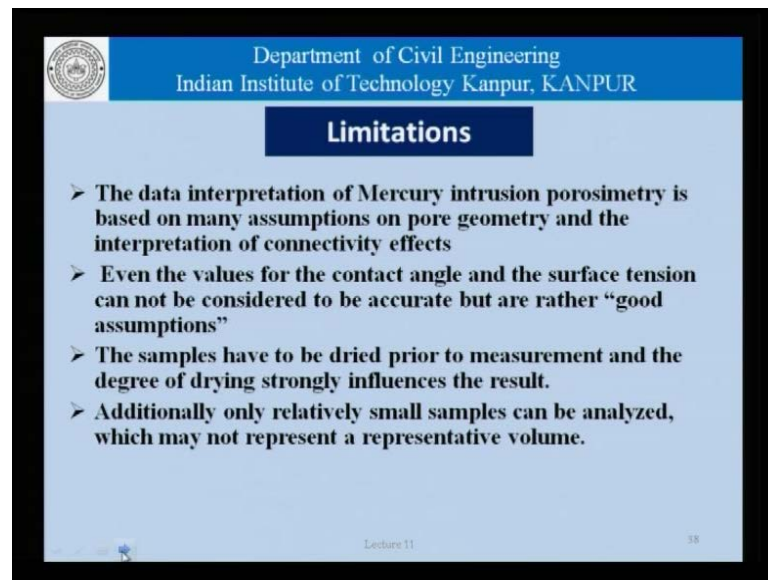
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- The stem of the penetrometer is a capillary that acts as a reservoir for the analytical volume of mercury
- The stem is plated with metal (a conductor). The two conductors, mercury, and the metal plating, are separated by glass, thus forming a coaxial capacitor
- As pressure forces mercury out of the capillary and into the sample, the mercury inside the capillary decreases and so is the capacitance
- The decrease in capacitance, therefore, is proportional to the volume of mercury leaving the capillary with each change in pressure

Lecture 11 37

There are obvious limitations to the test. The data interpretation of mercury intrusion porosimetry is based on many assumptions on pore geometry and the interpretation of connectivity effects. Even the values for the contact angle and the surface tension cannot be considered to be very accurate. But, they are just good approximations. The samples as far as concrete is concerned have to be dried prior to measurement and the degree of drying strongly affects the results.

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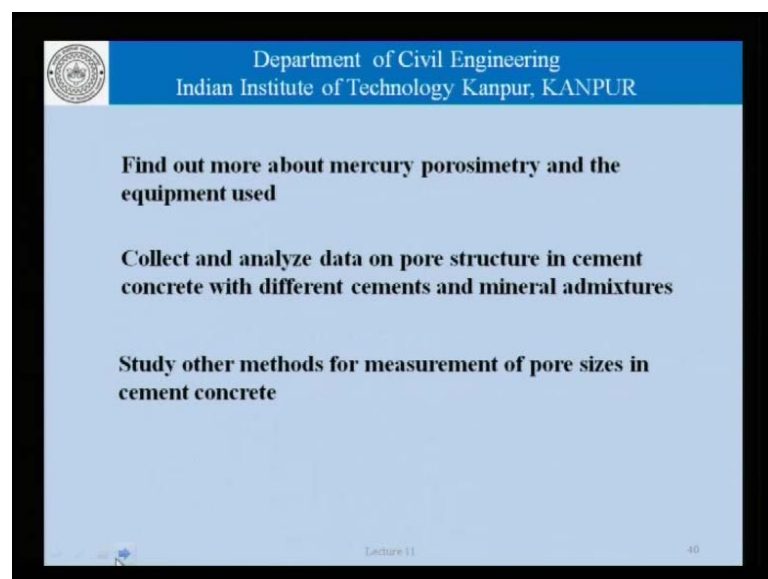
### Limitations

- The data interpretation of Mercury intrusion porosimetry is based on many assumptions on pore geometry and the interpretation of connectivity effects
- Even the values for the contact angle and the surface tension can not be considered to be accurate but are rather “good assumptions”
- The samples have to be dried prior to measurement and the degree of drying strongly influences the result.
- Additionally only relatively small samples can be analyzed, which may not represent a representative volume.

Lecture 11 38

And only very small samples can be analyzed and they may not necessarily be truly representative in terms of the volume is concerned. See we can imagine that, we are trying to characterize concrete using samples, which are simply too small, simply very very small. So, as far as research work is concerned; as far as understanding of certain principles in concrete engineering as concerned, mercury porosimetry is a very good tool, but its application in the field is a far cry.

(Refer Slide Time: 44:05)



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**Find out more about mercury porosimetry and the equipment used**

**Collect and analyze data on pore structure in cement concrete with different cements and mineral admixtures**

**Study other methods for measurement of pore sizes in cement concrete**

Lecture 11 40

Before we close our discussion, let us quickly go through some of the questions that we need to think about a little more. We could find about the equipment and the principles that are used a little more. We could collect and analyze data on pore structure in cement concrete with different cements and mineral admixtures, different ages, different curing conditions, whatever you have. And we could also study other methods for the measurement of pore sizes in cement concrete. With this, we come to an end of the discussion today.

Thank you.