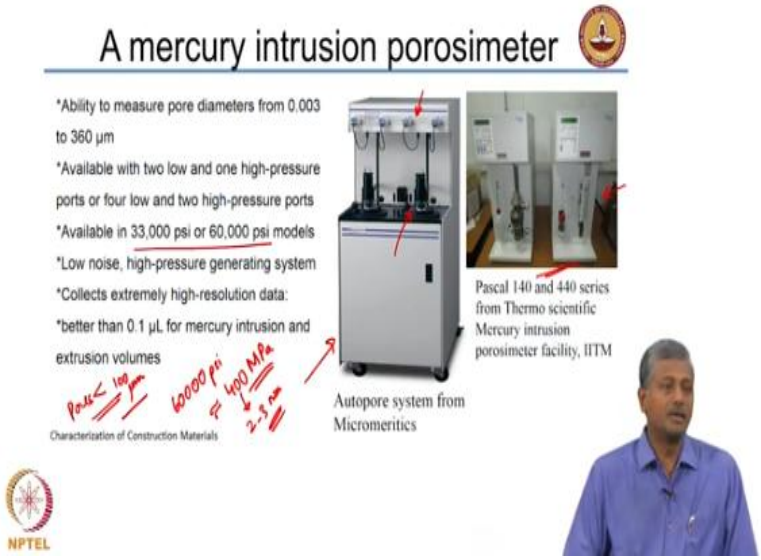
Characterization of Construction Materials
Prof. Manu Santhanam
Department of Civil engineering
Indian Institute of Technology, Madras

Lecture -60
Working of Mercury Intrusion Porosimeter - Part 1

(Refer Slide Time: 00:12)

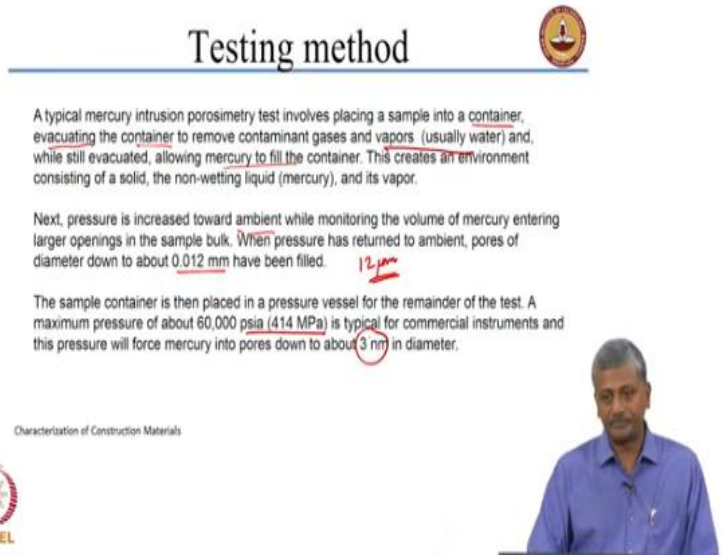


So hello everyone, we were talking in the last lecture about what the principle of mercury intrusion porosimetry is. As we discussed that it's a simple fact of actually pushing a non-wetting fluid into the pores of a porous material and the higher the pressure that we apply to push this in, the likely chance of encountering smaller diameters of pores is there. So as a result of this with incremental pressures you are filling smaller and smaller porosities and that helps you get an estimate of the pore size distribution.

Most mercury intrusion porosimetry equipments have two chambers: one is the low pressure chamber; the other is the high pressure chamber. The low pressure chamber is where we are trying to intrude the mercury into the porous material in the larger pores - up to atmospheric pressure; we pressurize up to atmospheric pressure and make the mercury great enter the larger pores. And in the high pressure chamber we are going above the atmospheric pressure and going up to pressures, in some cases, as high as 400 MPa and that corresponds to a pore size of about 2- 3 nm.

You should also be aware that there is an upper limit for the pore size. Generally if you have pores greater than 100 µm, you may not be able to actually pick those using MIP, because you do not really need any pressure to push the mercury into pores which are larger than 100 µm. So MIP is suitable only for pores less than 100 µm. So please remember when you have to actually determine pore size, there are macro techniques as we discussed earlier, based on simple water absorption principles, of course, that does not determine the actual pore size but at least determines what the rate of absorption is. However, if you want to get pore characteristics of less than 100 µm in diameter you need to adopt techniques - either microscopic techniques which can probably get you down to about 1 µm or some tenths of microns, but if you want to get in the nanometer size range, you are talking about using mercury intrusion porosimetry.

(Refer Slide Time: 02:26)



So the method obviously is to have your sample which is broken up into very small fragments, which is then put inside a sample holder. So you have the container or sample holder which needs to be then evacuated. That means we place it in the chamber and evacuate. Why do we need to evacuate is because whatever gases are there inside the chamber, even air, for instance has to be removed and it also helps in actually completely removing the air from within the pores which are accessible from the surface. And of course, if there is any water vapour present, it is done to also evacuate that water vapor. So vacuum has to be first applied and then we allow mercury to fill the container. So it is not intruding the sample yet, it just fills the container around the sample and then we pressurize the mercury to enter the sample.

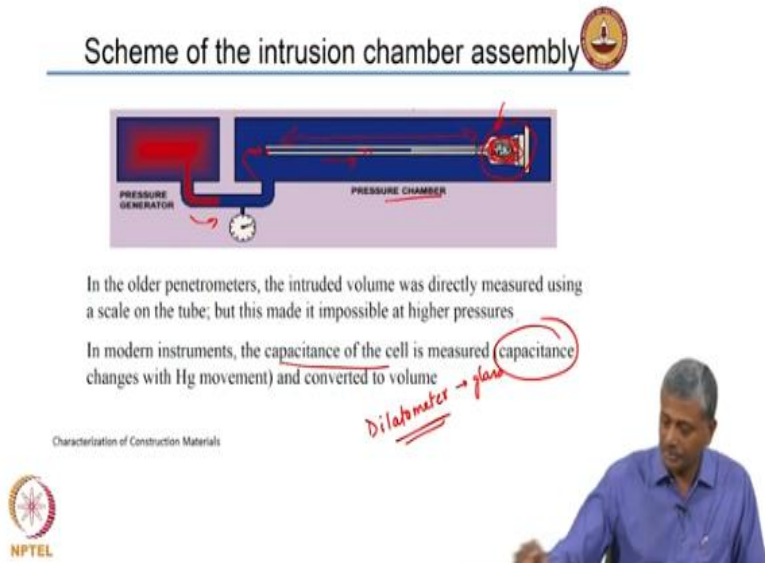
So, pressure is generally increased towards ambient, while monitoring volume of mercury entering the larger pores. When the pressure has returned to ambient, the pores to a diameter of about 0.012 mm (about 12 µm), so even up to ambient pressures, that is 1 bar, you fill up about 12 µm sized pores. So if you want to go finer than this, you have to transfer it to the high pressure vessel. So the high pressure vessel can go all the way up to about 400 MPa that corresponds to roughly about 3 nm size pores. Now in most porous materials, we do not really want to go beyond 3 nm, because beyond this the kind of pressures that are exerted will be too high and as it was asked earlier, the high pressure of the mercury intrusion may also result in damaging your sample to some extent.

And we will talk later about the fact that you are pressurizing the mercury. So you are in fact going to be compressing the mercury also, at higher pressures there is more compression of the mercury. There is also going to be compression of your sample. So you need to ensure that, that factor is accounted for when you are actually calculating the volume intrusion into the sample, that means you want to actually only calculate the amount of volume intruding the sample. And not the change in volume because of the compression of the mercury as well as the sample, we will talk about that again later.

(Refer Slide Time: 04:53)

So this is a typical experiment, where you have this sample holder which is going to be loaded into this high pressure vessel or chamber. Now, the pressurization is done with the help of hydraulic oil and that is what exerts such high pressures to push the mercury into the chamber.

(Refer Slide Time: 05:20)



Now, this is a brief layout of the pressure chamber or into which the sample holder or sample container is kept. The sample container is also called a dilatometer. It is made with glass. And it has got a capillary tube on one side and on the other side it has a cylindrical sample holder. So you put your porous material sample inside the sample holder and in the beginning of the experiment you will fill up the entire tube as well as the entire container which is inside with mercury. So that is your zero volume intrusion case. So under evacuation, under vacuum you fill up or flood the entire tube and the chamber with mercury.

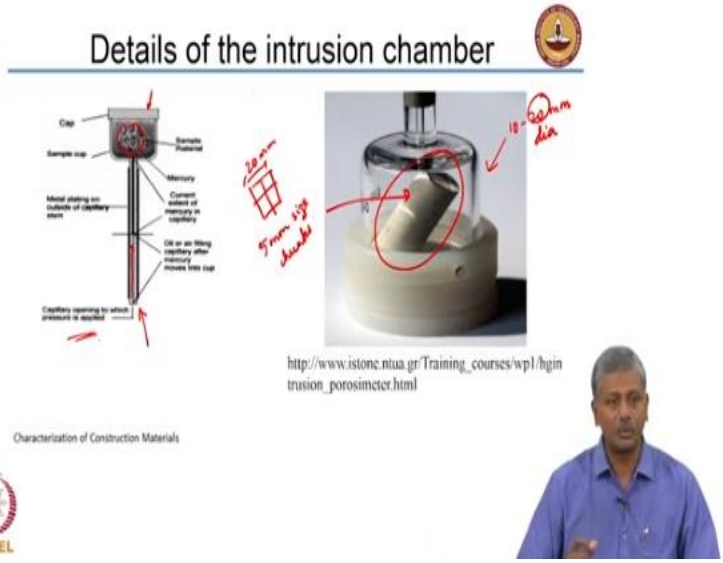
Then you are going to be generating the pressures which will push the excess mercury that is outside, into this chamber. So as the mercury gets pushed, more and more mercury starts entering the sample here, so there will be a decrease in level of the mercury in the capillary tube. So in the older generation penetrometers, all you had to do is actually remove the capillary tube and measure the penetration directly by graduations on the tube, but that is a cumbersome process, because you can imagine that you need to remove this, clean it and then place it back in the other chamber - it is a lot of work. So, modern instruments take advantage of electrical measurements to convert this into the volume intrusion.

So what the modern instruments do, is the capacitance of the cell is measured, obviously the capacitance will change, as the mercury dips inside this tube. As the mercury level changes

inside the tube, the capacitance value will change; for instance if the original mercury was here when it shifts to this location (intermediate location), you have an air-filled tube so the capacitance is going to be changing for the tube and that is what is getting measured in the system and translated into the amount of volume of mercury actually entering the sample. So volume intrusion today is measured using capacitance and this capacitance is converted to the volume of mercury that is intruding the pores.

Capacitance: It is just an electrical property to be measured in this case - capacitance is the measure of the ability to actually store charge, so as the volume inside the capillary tube changes, you have a change in the composition of the air inside the capillary tube. Now you only have air present inside, so obviously there will be a change in the charge carrying capacity of this tube, so it is much easier to measure in this case and you essentially convert that into the overall volume of mercury that is intruding into the sample. The chamber is vacuumized and then you are filling Hg in, that is, flooding with mercury under vacuum and then you apply the pressure which penetrates the sample pores.

(Refer Slide Time: 07:44)



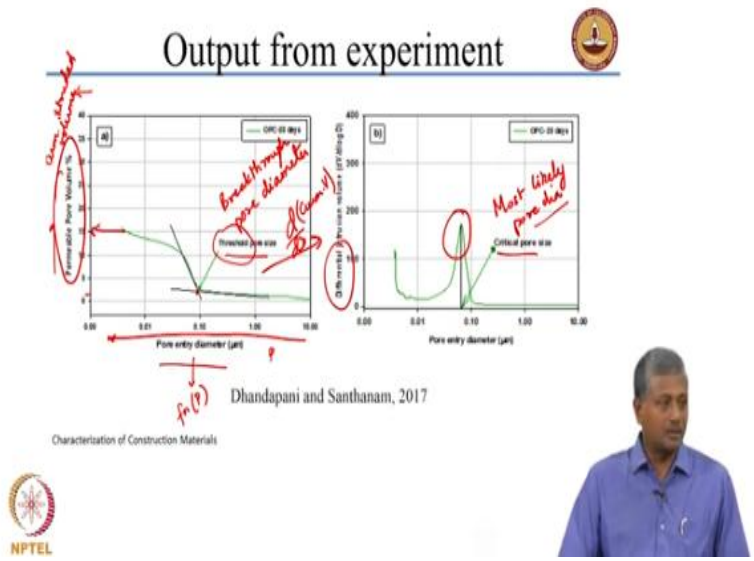
So again sample size is very important. This particular sample container as you can see from this diagram which is actually highly magnified, the sample container is only about close to 10 to 20 mm in diameter, mostly it will be around 20 mm diameter sample chamber, so it is a quite small sample chamber, and into the sample chamber you need to actually put in your sample.

So you need to ensure that your sample is first of all representative of what you are trying to measure. So what will we do if it is a concrete sample? You tend to avoid the aggregate and only choose the mortar fraction. And the mortar also, if you have a large chunk of, let us say about 20 mm size, you will actually break it down into several smaller chunks. So that now you have more exposure on the surface for the penetration to actually happen. You are not going to be changing the pore distribution because pores are much smaller than the size of the chunks that you are choosing. So, typically about 5 mm size chunks are good for putting inside the sample chamber.

Of course, this is a case where a cylindrical core has been taken through the sample and is directly put inside the chamber, but better to adopt very small size chunks because that increases the overall surface through which the intrusion can actually take place.

So again, this gives you an example (Figure on left) of the sample chamber or sample container. So you have the cap on one side, you have the sample sitting inside and you have the mercury trying to fill in through this tube. There is the capillary opening to which you apply the pressure to push the mercury into the sample.

(Refer Slide Time: 10:47)



So what is important is what you get out of this experiment? So as I said, all you have to do is simply pressurize the chamber and intrude mercury at greater and greater pressures which means

that mercury will start intruding smaller and smaller diameters of pores. So what you plot as a result of this experiment is the pore entry diameter versus the pore volume or cumulative intruded volume. That means how much volume of mercury is actually intruding the system. So, this (in graph in left) is not the original output that you actually get, you need to do some conversion to actually get the pore volume as a percentage, but what you have as the raw data available from the experiment is the cumulative intruded volume of the mercury into the system as a function of the pore diameter and obviously pore diameter as a function of the pressure. It is a function of the pressure that you apply in the system.

So as you apply a greater pressure, you are moving from a higher diameter to a lower diameter. So it is plotted in this way, so this is the direction of pressure (towards direction of decreasing pore size) that means more pressure implies lower and lower diameter, that is what you actually observe in this image. So now what is happening in this is that your system is very marginally filling up some of the larger pores which account to only about close to 2 to 3 % of your overall pore volume.

But at a particular point, what suddenly happens is that you have a sudden rise in the intrusion. There is a sudden rise in your mercury intrusion. So very often this sudden rise that happens from an almost asymptotic sort of a graph, it is called the *threshold pore size* or *breakthrough pore diameter*. The point of sudden increase in the amount of the mercury that is intruding is called the threshold pore size or breakthrough pore diameter. Now what does it mean physically? This breakthrough pore diameter is the largest size of pore that has to be overcome for a fluid to actually penetrate your solid; the breakthrough diameter is the largest pore size that needs to be overcome for the fluid to completely flood your porous sample.

So in a physical significance when we talk about concrete durability, we know that durability of concrete is intrinsically related to the permeability of the concrete. So in some ways the threshold pore size or the breakthrough diameter defines the amount of pressure that you'd need to actually infiltrate the system. That is why we find that in spite of extremely aggressive conditions, sometimes the penetration of moisture into the concrete is minimal, because the pressure generated by that water may not have been large enough to overcome this threshold

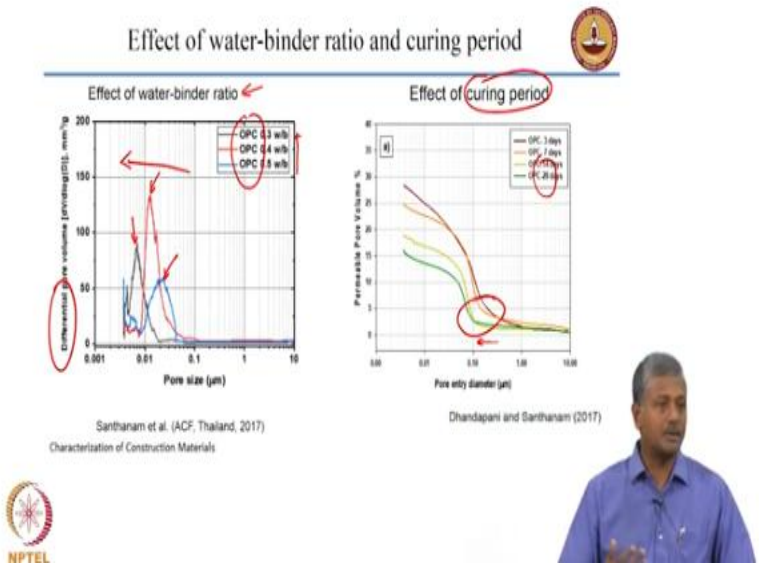
pore size. So it is the minimum pressure that you need to apply to flood your porous system with the fluid, so it has a direct connotation on your durability of the system. So the smaller the threshold pore size, the higher the durability of your system.

But threshold pore size does not indicate the most likely diameter of pores that is present inside the system and for that you need to plot the differential graph. So you take the same plot and do a differentiation (d/dD). You do a differentiation of this cumulative volume and get this differential intrusion volume plot, so all it does is actually measure the slope of this plot at any given point and the critical pore size or most-likely pore diameter, again, you will have several ways of actually representing these in papers, but some people call it most-likely pore diameter or you can say critical pore size, is where you get a peak in the differential intrusion curve. So that indicates that, most of the pores in the system are of that size. Your system is characterized by maximum porosity in that size. So it is like doing a frequency distribution of the pore size. So here is the pore size at which you get the maximum frequency of occurrence. So that is all it says.

One critical thing about how to actually determine the threshold, people have suggested various methods, you can actually directly pick out from the graph, as to the point at which there is a sudden increase. But very often what people say is, you can actually do this by drawing tangents for this curve and looking for the point at which the tangents actually intersect and marking that as a threshold pore diameter or breakthrough pore diameter. So from this experiment what are the values that we are looking at? One is this breakthrough pore diameter and the other is the most-likely or critical pore diameter. You can also get some estimate of the overall porosity of your system. That means the total intruded pore volume in the system corresponds to the overall porosity of the system. Now, please remember we are still only talking about porosity that is accessible to the mercury. They may be some discontinuous pores inside which may not be accessible at all. So we are still talking about accessible porosity.

So that is making physical sense, because in any case when permeability of concrete has to happen, it will happen only through the accessible porosity, the inaccessible porosity will not be playing a role in it at all.

(Refer Slide Time: 17:16)



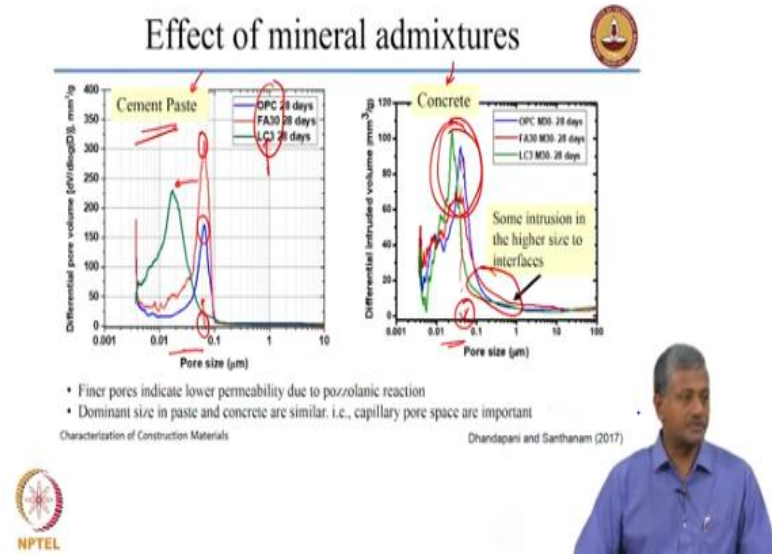
So let us now take a look at what happens to the cementitious systems when you do minor changes to the composition. One is obviously the effect of water-binder ratio. We know that very well that when you reduce the water-binder ratio, you tend to reduce the porosity of the concrete system. But what is more interesting is you also get a reduced size of the pores.

So what is not plotted here is the overall porosity, but what is plotted is a differential graph. So, you get the critical size and you can clearly see that as the water-binder ratio reduces, the pore size or most likely pore size (critical pore size) also significantly reduces and that is something which we expect again because we know that to produce a more impermeable concrete you need to reduce the water-cement ratio. Of course this is only in systems which have Ordinary Portland cement; if you start working with systems which have fly ash or slag or other substituting ingredients, you may get an entirely different pore structure, which I will show you an example of later.

What about the effect of curing period? We know very well that as you cure more and more, the system gets less and less porous and also less permeable, and where this is getting indicated is by doing a comparison of the threshold pore diameters, you see that at later ages, that is 14 and 28 days, your threshold diameter or the breakthrough diameter is shifted to smaller values, when you cure the system for a longer period of time. So higher curing implies lower

threshold pore diameter; that means with increased curing, the resistance to permeation of water and other aggressive chemicals will also improve with time.

(Refer Slide Time: 19:19)



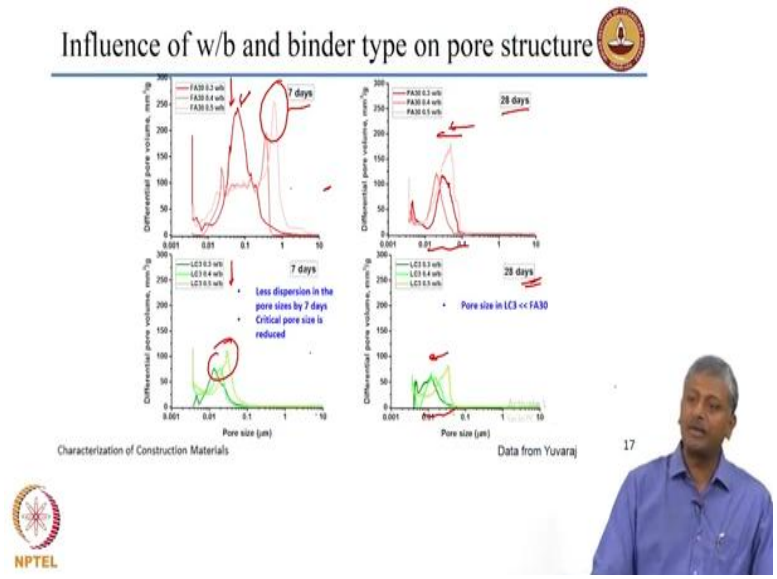
Now the most interesting characteristics that MIP seems to bring out are the differences in the ways that systems with mineral admixtures actually tend to behave. So here there is an example of both paste and concrete. Of course, in paste you only have the hydrated cement paste, the unhydrated particles and possibly some porosity. In concrete you also have to account for the presence of aggregate, probably interfaces between aggregate and paste that may contribute to higher porosities and so on. But again, the total porosity is not what is being shown here, the size of the pores is being shown in this case.

So here for instance you have 3 different binder systems: one is made with OPC, one is with 30% fly ash (FA30) and the other is with limestone calcined clay cement (LC3). And you see here that, for OPC and fly ash, if they are cured to the same extent, you end up producing nearly the same critical pore size, i.e., the critical pore diameter is the same in the two systems for substantial level of curing (28 days curing). If you test the same systems at 3 or 7 days, there will be vast difference between OPC and fly ash, but in this LC3 system, you are now shifting your critical pore size to a smaller value which indicates that your pore system is getting finer and finer.

Do we see the same effects in concrete? Yes to some extent, we see the same effect in concrete with respect to OPC and fly ash, but here please remember you would not get the same degree of pore sizes, you may get slightly larger pore sizes, but overall in the paste region your pore sizes may be quite similar. The intrusion is high in this range from 0.1 to 10 μm, possibly because you have these interfacial transition zone effects that may intrude mercury into the ITZ also and that accounts for that extra intrusion because of the higher porosity of the interfaces. But as far as the paste is concerned, you still get the pore sizes in approximately the same range as you got for the paste system. So the paste in concrete gets fine porosity to the same extent as the regular cementitious paste itself, so irrespective of whether you choose a paste system or concrete system, your mercury intrusion porosimetry experiment is giving you a result of a consistent pore diameter.

Of course one thing you can see is, with respect to the cement and fly ash systems, the critical pore size is slightly lower in concrete as opposed to what you had in paste. Again, effects of packing are helping in the case of concrete; in paste you do not really find the effects of packing. In paste, you do not have particles of vastly different size ranges, so as you increase the range of availability of sizes, you have seen earlier in your particle packing algorithms that if you increase the range you get better packing in the system and in the concrete there are fines contributed by your sand also, which help to increase the degree of packing in your system, and that may be the reason why this marginal difference in your pore sizes from about 0.07 or 0.08 μm to 0.05 or 0.06 μm are being shown in the case of cement and fly ash systems.

(Refer Slide Time: 22:51)



Now here this is a combined influence of water-binder ratio and binder type on the pore structure. Once again the differential volume plots have been given here for the fly ash system at different water-binder ratios from 0.3 to 0.5, at 7 days and 28 days as opposed to LC3 systems at 7 days and 28 days. So what you see are the critical differences here? One critical difference that you observe is that the fly ash system responds in a large way to the increased duration of curing. From 7 days to 28 days, there is a significant reduction in the critical pore sizes indicated for the fly ash systems. Only at the low water-binder ratio system, you actually see a critical pore size that is already reduced to less than 0.1 μm. But in the case of the higher water-binder ratio systems, you still have pore sizes that are fairly large in the case of fly ash. But when you start approaching a higher degree of curing let us say 28 days for the higher water-binder ratio systems also, you are trying to push the critical pore sizes to a finer value. On the other hand, in the LC3 systems, even as early as 7 days, you already have most of your critical pores size values in the 0.0 into 0.1 μm range and that is further refined to slightly less than 0.01 μm pore size.

So what you are seeing here is the direct effect of the reactivity of the binder. So the faster the binder reacts, the faster the structure is attained and the finer the pores get at an early stage of curing itself, whereas, in the case of fly ash you need extended curing up to 28 days to achieve the same result.

Of course, this is only the porosity or pore size result from mercury intrusion porosimetry, what you need to also see are the corresponding effects that it has on the concrete durability. So a behaviour like this would indicate that a concrete with LC3, which is cured to 7 days will show definitely a greater durability as opposed to a concrete with fly ash at 7 days. But at 28 days there should be not much difference between the two systems because the pore sizes are almost identical in the case of fly ash and LC3 at 28 days.

Indeed, this is the case when you actually do concrete investigations that you can tie up these structural developments taking place at the micro levels to the actual performance of the concrete in a durability test. So very clearly the results indicate that this structural development is very well indicated by a good performance at the macro level.

.