**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 – 33**
**Pores and Porosity -A Revisit**

[FL] welcome to this lecture 33 titled pores and porosity a revisit; you have already seen some of these concepts and material earlier on the earlier on in this course, which is part of the course on hydration porosity and strength of cementitious materials. What we will do today is basically a revisit of the concepts in pores and porosity, relevant to cement pastes and try to extend that idea to concrete.

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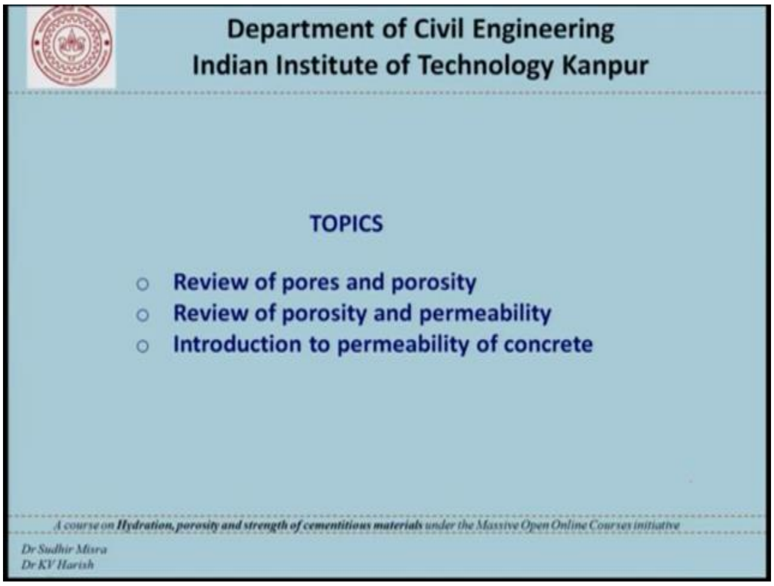


So, as far as the topics are concerned for the day, we will review the idea of pores and porosity review porosity and permeability and briefly introduce the topic of permeability of concrete which is a stage beyond the paste systems that has been talked about extensively in this course so far.

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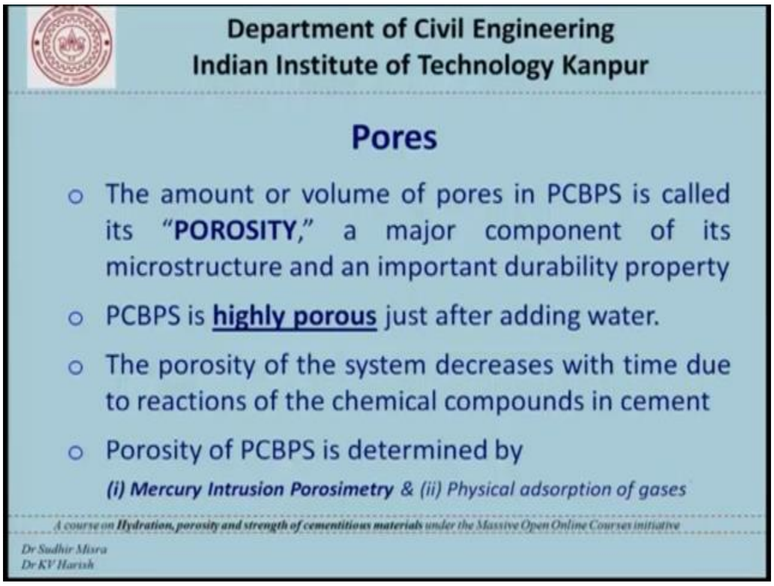


Now, what you already done is a definition of pores, which is that it is the amount or volume of pores in PCBPS which is Portland cement based paste systems is called the porosity and the major component of its microstructure and an important durability property.

We will see how these things come to life how they acquire a meaning in our discussion on durability of concrete structures; the PCBPS is highly porous just after adding water and that pores get refined as hydration proceeds. The porosity of the system decreases with time due to reactions of the chemical compounds in cement which is the process called hydration you also seen that porosity of these systems can be measured using mercury porosimetry and physical adsorption of gases, and we will stick to our discussion on mercury porosimetry once again in this discussion today.

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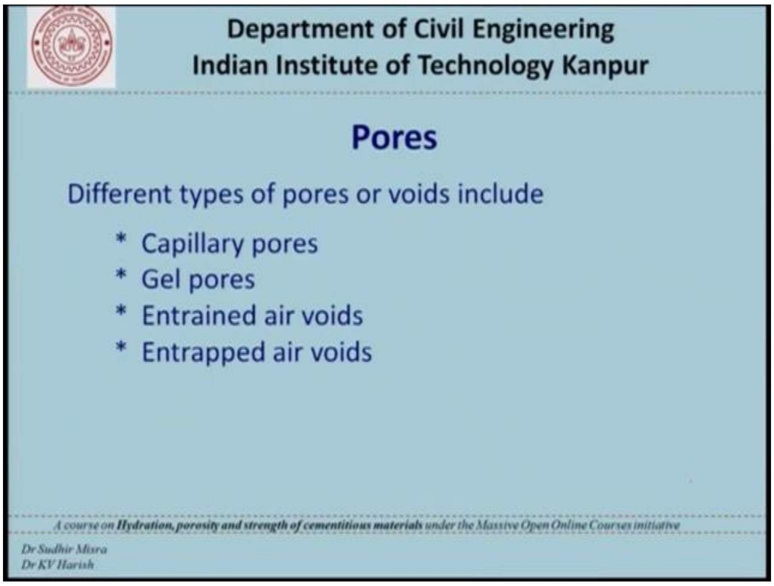


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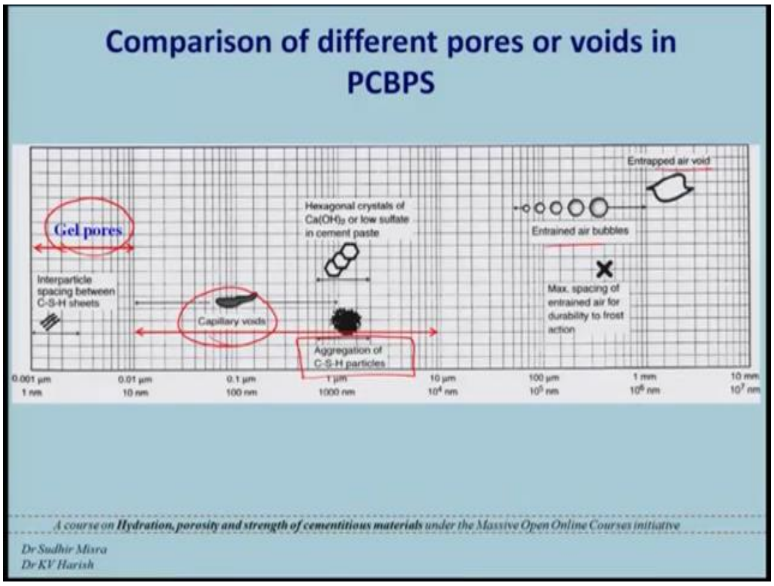


You also known that pores in cement paste can be classified as capillary pores, gel pores entrained air voids and entrapped air voids and they vary in size from one nanometer or a few nanometers to write down to 10 millimeters. Well 10 millimeters could be an exaggeration, but you can easily find something which is more than a millimeter and if you see the inside of a concrete as a slice you will easily be able to identify at least a few of those pores which could be maybe two millimeters or three millimeters, and easily visible to the naked eye. We have the gel pores in this range here capillary pores in this range here and then we have this aggregation of c s h particles and entrained air bubbles and entrapped particles of air, and entrained air well and entrapped air is what we seek to minimize through the process of compaction.

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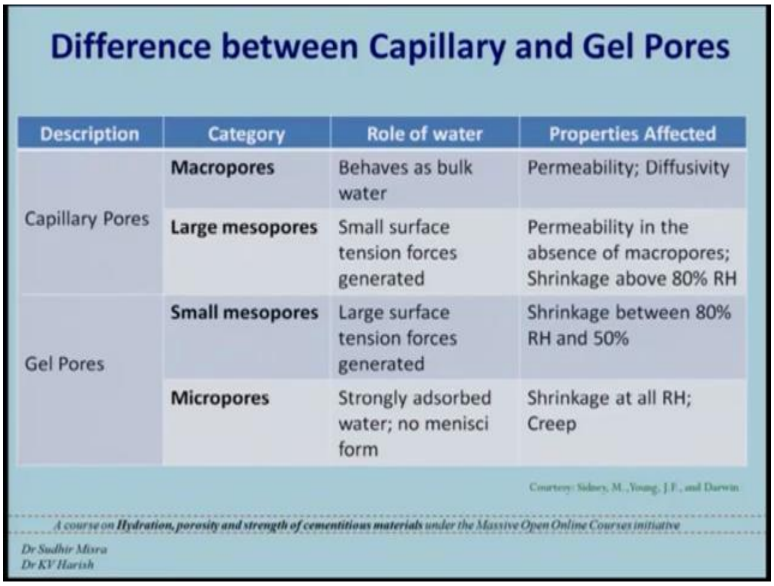


| Description | Category | Role of water | Properties Affected |
|---|---|---|---|
| Capillary Pores | **Macropores** | Behaves as bulk water | Permeability; Diffusivity |
| | **Large mesopores** | Small surface tension forces generated | Permeability in the absence of macropores; Shrinkage above 80% RH |
| Gel Pores | **Small mesopores** | Large surface tension forces generated | Shrinkage between 80% RH and 50% |
| | **Micropores** | Strongly adsorbed water; no menisci form | Shrinkage at all RH; Creep |

We have also talked about the difference between capillary and gel pores and what is the role of water in their formation and their behavior and also the property is the effect; we have also seen how these pores and porosity is measured.

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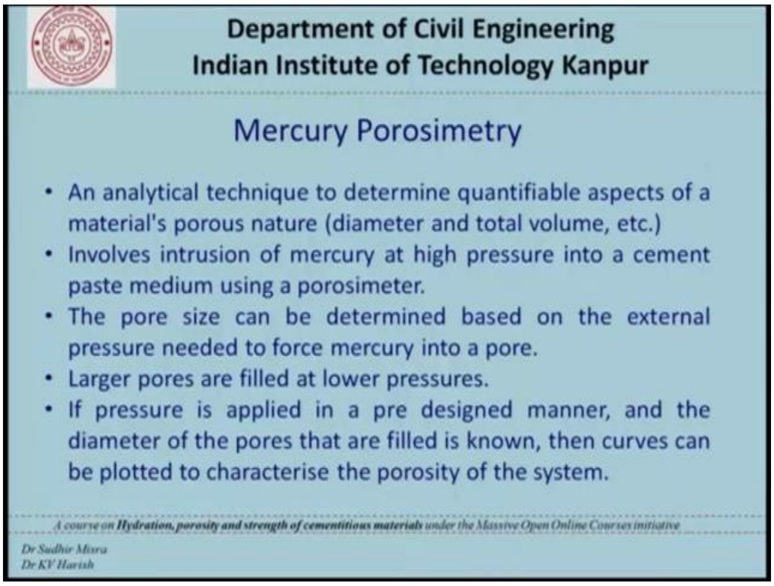


And mercury porosimetry was a technique which was introduced which is an analytical method to determine quantifiable aspects of a materials porous nature, which is the diameter of the pores and the total volume. It involves intrusion of mercury at high pressure into a cement paste medium using a porosimeter, and the pore size can be determined based on the external pressure that is needed to force the mercury into a pore, larger pores are filled at lower pressures and if the pressure is applied in a pre designed manner and the diameter of the pores that are filled at a given pressure is known, then the curves can be plotted to characterize the porosity of the system.

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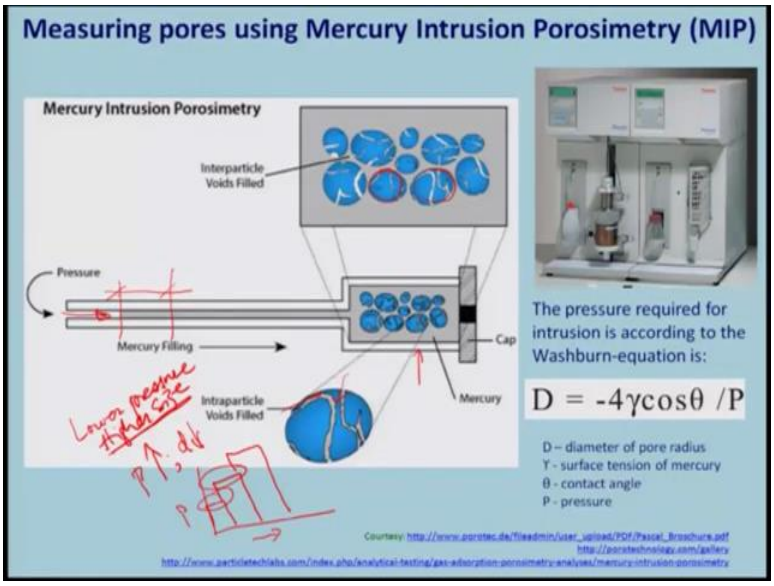


So, we have done all this before and we have also seen how mercury intrusion porosimetry really works. As you can see here these are the small samples or specimen that we take, they are not of the same size they are usually broken off from a paste sample, filled into this a specially designed container which is filled with mercury and what we try to do is apply pressure here and want a mercury to fill into these voids or into these pores or pore space within the sample.

Obviously, at lower pressures we would expect the higher size or large diameter pores to be filled and consequently as the pressures are increased we would expect the lower diameter pores to be filled and that was the intent when we said that if we increase the pressure. So, if we plot the time and pressure we increase the pressure keep it at some point then increase the pressure again and keep it the increase the pressure again then at each pressure step if we know the volume of intrusion that happens and that we can measure from a change here, we will know how much is the pore volume corresponding to those diameters of pores.

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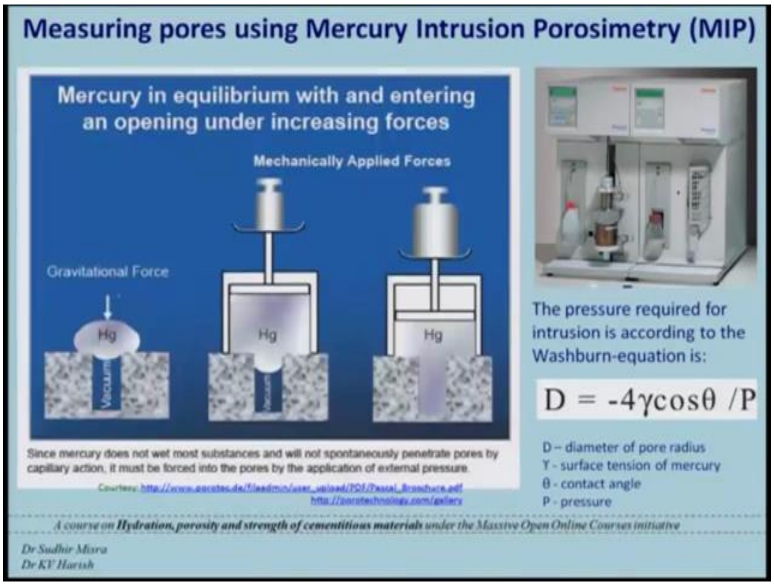


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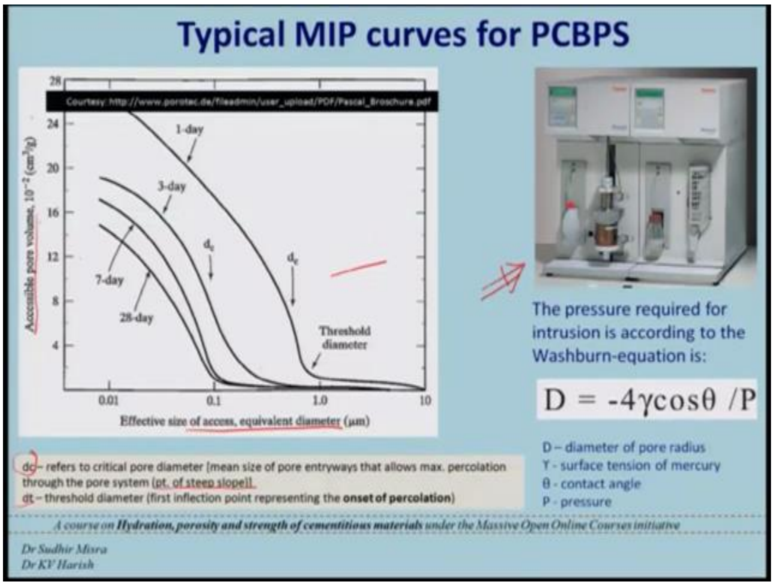


This principle we have already done and this is just another explanatory slide and finally, what we get is this a typical MIP curve for Portland cement based paste systems. We have already seen this and this here is the equivalent diameter or the effective size of access and here we have the accessible pore volume or the total pore volume intruded, and this picture here is that of a commercially available mercury porosimeter.

In this diagram here d c refers to a critical pore diameter which is the mean size of pore entryways that allows maximum percolation through the pore system that is the point of steep slope, and d t is the threshold diameter which is the first inflection point representing the onset of percolation.

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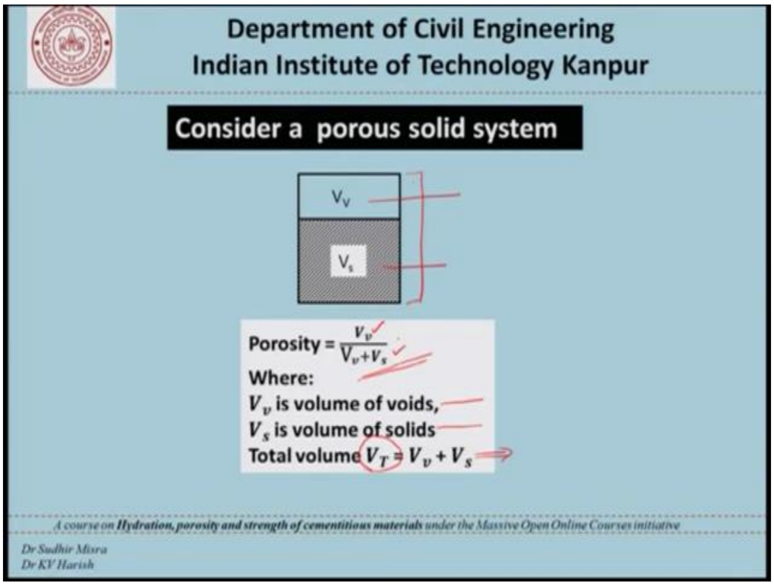


So, this is what we had seen before; now let us take a look at the whole idea of porosity once again. If we consider this to be a porous solid system where this is the volume of voids V v, V s is the volume of solids the total volume of the system is V v plus V s which is the total volume. So, we can define porosity as the volume of voids to the total volume.

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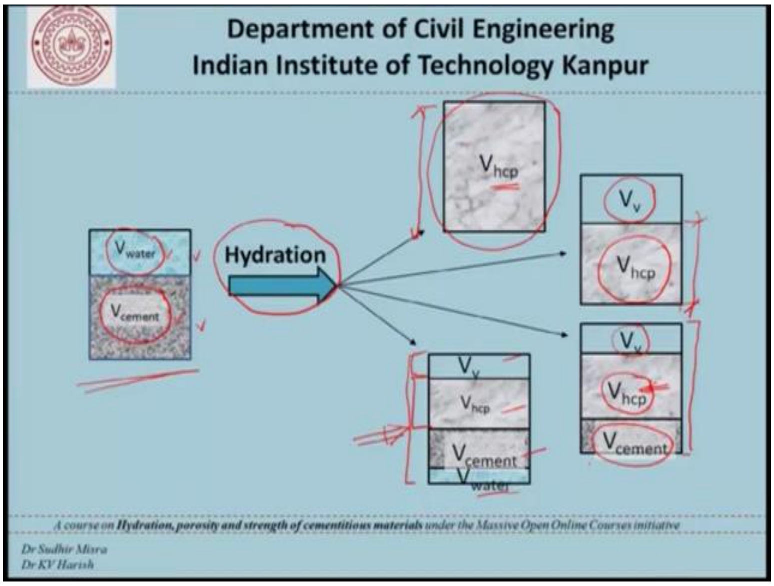


As far as hydration of cement and the porosity in cement paste systems is concerned this is where we start we have a certain volume of cement, we add a certain volume of water and we let the hydration proceed. Now as this hydration proceeds what we expect is HCP or hardened cement paste to be formed cement is consumed water is consumed and HCP is formed.

So, now if the HCP was an absolutely solid product and occupied the same volume as the volume of cement and the volume of water together this is what we will get, and this has no porosity. Now another situation is that the HCP occupies a slightly lower volume then the original volume and this volume which is left behind it becomes the volume of voids, another situation is given here where a certain amount of cement remains un hydrated a certain amount of hardened cement paste HCP is formed and then a certain amount of voids is also available to us or it is formed because the HCP does not occupy the same amount of volume or space as the original cement and water did. Here is another fourth variation where a certain amount of water and a certain amount of cement are both left out at the end of the hydration process, and we have a certain amount of HCP and a volume of voids.

So, as far as real life concrete is concerned the situation is somewhere in between this part and as far as real life concrete is concerned the situation is pretty close to something like this. Where we have a certain amount of water which is left we have a certain amount of volume of un hydrated cement some amount of HCP is which is formed, and there is a certain amount of volume and there is a certain amount of void volume in the paste. We must remember that HCP when we plot it like this and we say that there is a volume of voids like this it does not mean that the voids are sitting at one place and all the solids are sitting at one place. Before we carry this discussion further let us look at the idea of porosity from a slightly different point of view or slightly simplified point of view.

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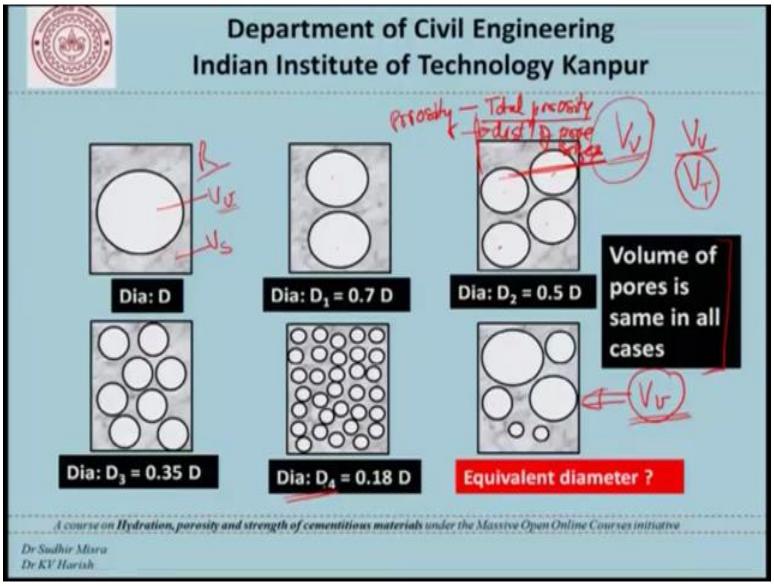


Let us talk in two dimensions and look at this picture where this is the volume of solids and this is the volume of voids. Now here what I have done is to schematically represent the voids through a circle, and this circle has a certain diameter or a certain radius. For the same volume of pores we can have one circle having this diameter or we could have two circles which will be smaller in diameter or we could have even four circles with even smaller diameters or six circles here on a large number of circles here with smaller diameters. In all these cases the total volume of pores is the same, what I am trying to say is that if this volume of voids is the same in all these cases then the porosity as we define it as the volume of voids to the total volume is really the same, except that it is obvious that as far as permeability is concerned or as far as the ease with which material can flow in and out of a porous system like this is concerned it is not really the same amount of convenience.

So, there is an issue that once we talk of porosity we should not only talk about the total porosity, which is defined as the total volume of pores to the volume of the material that is a total volume, but we should also include in our discussion some kind of a distribution of pore sizes this is something which is very very important in our understanding of the pore structure of cement pastes and therefore, that of concrete. Now as far as concrete is concerned do you think that hydration proceeds in a manner that pores of only a single size or a certain size are formed of course not; what we get as far as cement pastes are concerned is a distribution of four sizes which could be something like this, one large pore here another smaller pore here few smaller pores there and a few very small pores.

So, now in a situation like this we can of course, talk in terms of a total pore volume, but it is difficult to talk in terms of any diameter which represents these pores. Can we then talk about an equivalent diameter for these pores or this pore system that something which we need to think about and now we need to look at the graphs that we get the results that we have from the mercury porosimetry, once again a little more closely. Now getting back to our discussion of cement paste and it is hydration.

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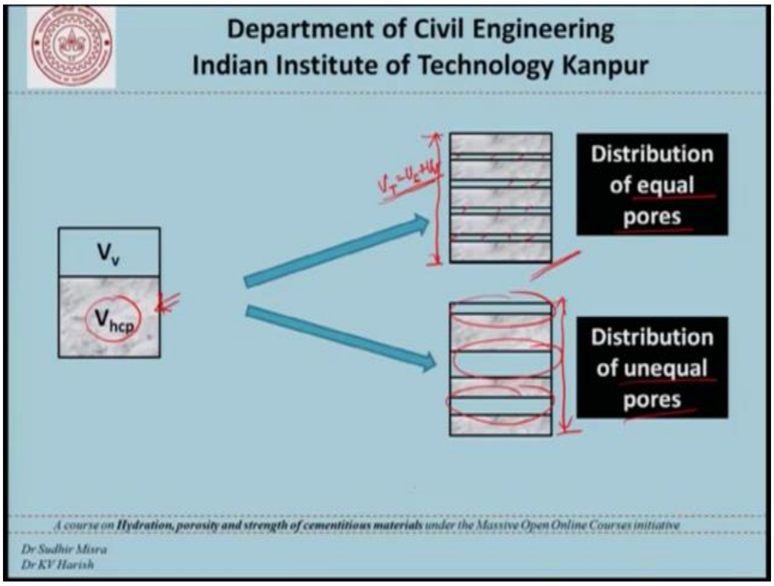


If this was the total volume of the solids and the pores being formed; obviously, all these HCP will not be lumped at one place, this here is just a diagrammatic representation of a situation which is given here where we are saying that pores of equal diameter are distributed all over the place in this HCP. The situation which I showed you earlier where the concrete or the paste system has unequal pores this is what that system represents where we have larger pores and smaller pores and maybe still smaller pores all of them distributed or located in different places as far as the HCP is concerned.

Now, this is something which we need to understand and keep in mind when we try to build a model or try to understand the importance of porosity in the context of paste especially when I take it to the idea of concrete.

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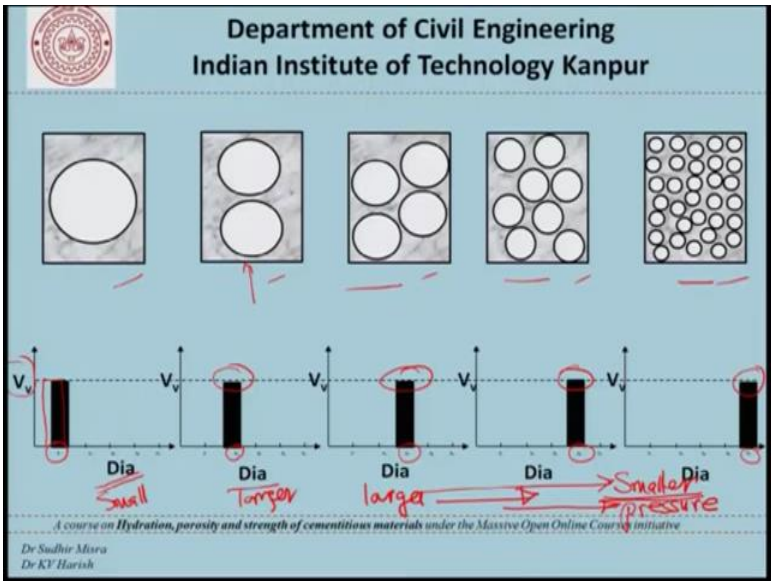


Now, in the situation like this which is the idealized form the larger pores smaller smaller and smaller and still smaller, if we do something like mercury intrusion porosimetry with these systems of pores, what we will get here is this which is V v which is the total pore volume at this diameter here we will have all the intrusion that happens. When it comes to this situation the same amount of intrusion happens except that this intrusion happens that D1 which is a smaller diameter than d and the relationship between d and D1 and so on can be worked out based on the geometry. Coming to this part and this part and this part in all the cases the total volume of penetration is the same, except that the diameter at which this is happening becomes smaller and smaller, which in other word means that if this was a real system the pressure at which this penetration was happening will keep increasing as the pore sizes become smaller and smaller, in this case total intrusion would be achieved at a small pressure this would be slightly larger than that this would be slightly larger than that value and so on and so forth and the pressure keeps increasing in this direction.

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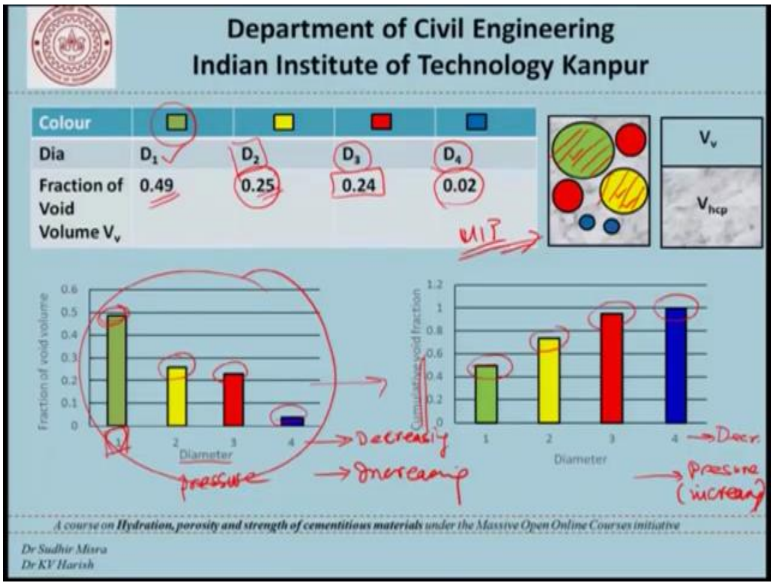


Now, let us look at the real situation again idealized in the case of concrete, that if we have a large pore here a smaller pore hear something smaller here and much smaller pores like this, then we know that this green colored pore having a diameter D1 contributes let us say 49 percent to the total porosity of the system the yellow guys this fellow he contributes 25 percent and has an equivalent diameter of or a diameter of D2, the pores with diameter D3 no matter what their number is contribute equally and the blue pores which are shown here contribute only 2 percent to the total porosity of the system. Now if this system was subjected to mercury intrusion porosimetry how would the results look like there is a diameter D 1 where we would get 49 percent of void fraction being filled at the smallest pressure.

So, if you plot diameter here which is decreasing this way and we can also plot pressure here which will be increasing this way. At this value here with the least amount of pressure we will be able to filling this green pore which will be 49 percent of the total pore. As the pressure is increased the yellow pores will get filled and that would add another 25 percent to this similarly the red pores would contribute 24 percent and these guys will contribute 2 percent and if this graph here is plotted on a cumulative pore volume basis, this is what we will get 49 percent again this is the diameter which is decreasing this way and we have pressure which is increasing. So, it is 49 then 60 something then 98 and 100.

So, this is how we need to understand the results from mercury intrusion porosimetry in the case or in a situation like the cement paste systems, where the problem is very complex and the pores are not of a uniform size.

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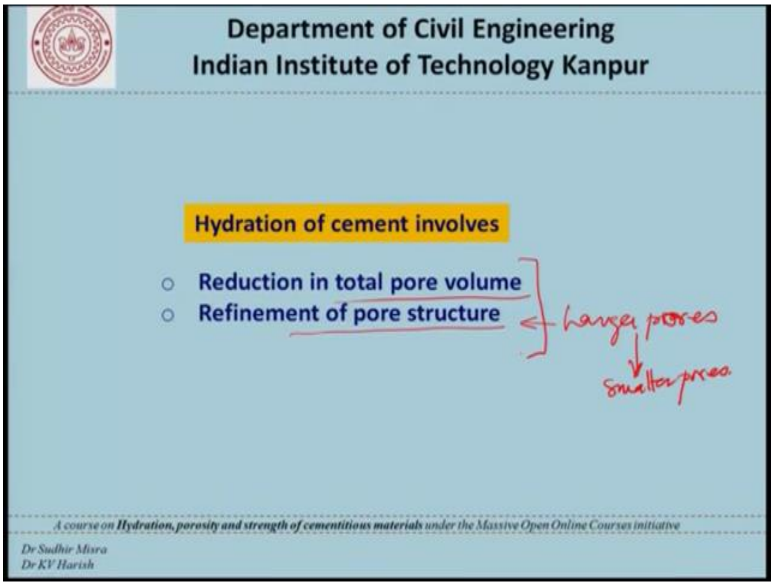


Now, as far as hydration of the cement is concerned it leads to a reduction in the total pore volume, and it also leads to a refinement of the pore structure which means that larger pores are transformed to smaller pores. So, this is how hydration moves forward as the concrete is cured as the cement systems are cured more and more hydration happens and so on.

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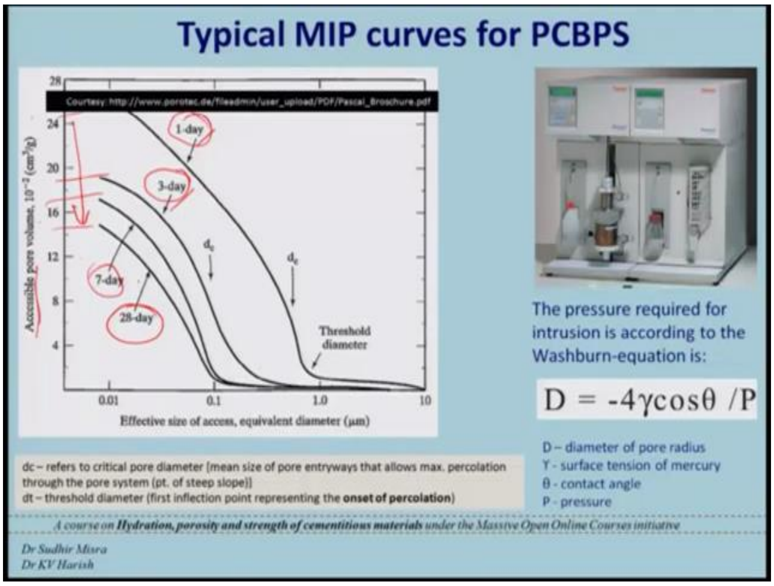


Now, let us go back and look at this graph once again, you will notice that these are the cumulative graphs which are available for a cement system or a cement paste system at different ages. So, it is one day 3 day, 7 day, 28 day and so on. As we can see the total volume that we are talking about is reducing as the ages increasing and that is what we mean when we say that continued hydration leads to a decrease in the pore volume, then the diameter at which the maximum inclusion takes place keeps shifting to the left and as we move to the left the diameters as is being shown here is decreasing. So, that is what we call refinement of the pore structure.

So, with this I hope we have a slightly better understanding and more insight into the pores and porosity of cement systems. Now let me give you food for thought just think about it.

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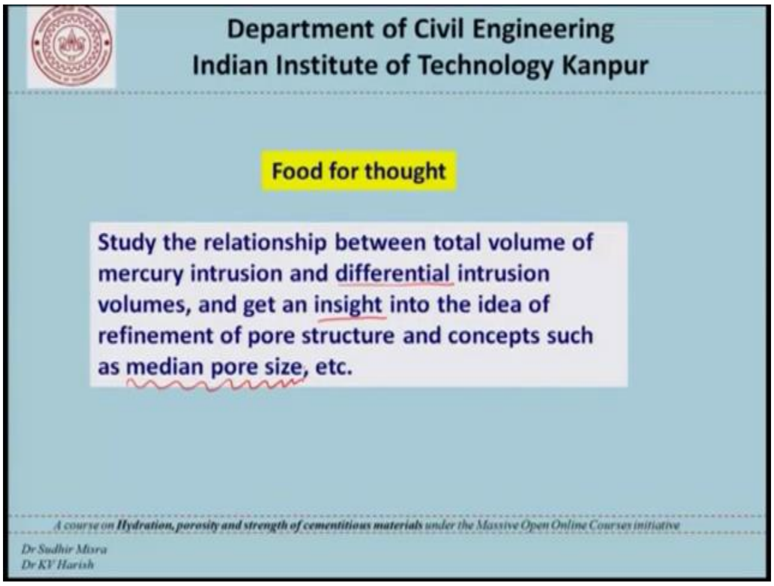


Study the relationship between the total volume of mercury intrusion and the differential intrusion volumes that is how much intrusion happens at a given pressure step; there are enough literature, the enough papers enough data which is available on the internet to be able to do this exercise on your own, just do that and then you will have an insight into the idea of refinement of pore structure and concepts such as the median pore size or a pore size which is such that 50 percent of the total volume of intrusion occurs before that.

We must remember this kind of discussion was at the back of our minds when we were talking about mineral admixture addition when we said that on account of the addition of supplementary cementitious materials and the pozzolanic reaction, the pores are refined more and more CSH is formed which then occupies the space which otherwise would have been occupied by just calcium hydroxide water and so on.

So, we have to understand and appreciate the idea of porosity the pores and the pore sizes in cement systems of cement paste systems and concrete in that perspective, and then try to understand and decide what is the use and why should we use pozzolanic material fly ash blast furnace slag silica fume and so on. So, if you read literature which compares the pore size distributions a total pore volume at a given age for cement systems not having silica fume and having silica fume, you will be able to appreciate the kind of discussion that we just had in terms of the total volumes that we have and so on.

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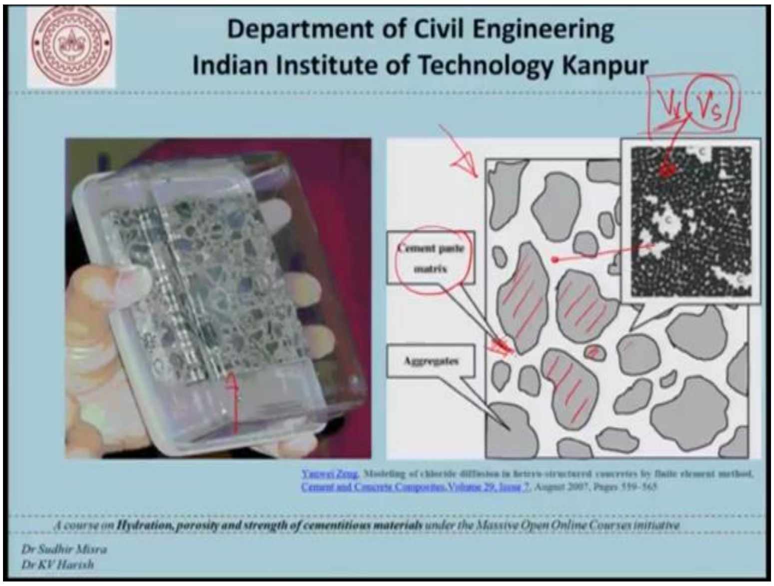


Now, let us try to understand this whole idea of concrete. Concrete is surely not only paste, as we can see here which is just a simple slice of concrete we have seen this picture before this is idealized here we can have all these as aggregates that is these are the inert pillars in a concrete matrix, and we have cement paste here this white portion here is all cement paste now. So, cement paste itself has what we have been talking about a solid phase and a part which is voids. So, far we have been concentrating and discussing extensively only this part here, as far as concrete is concerned which is the real material for engineers the situation is vastly complicated and we should try to understand this system.

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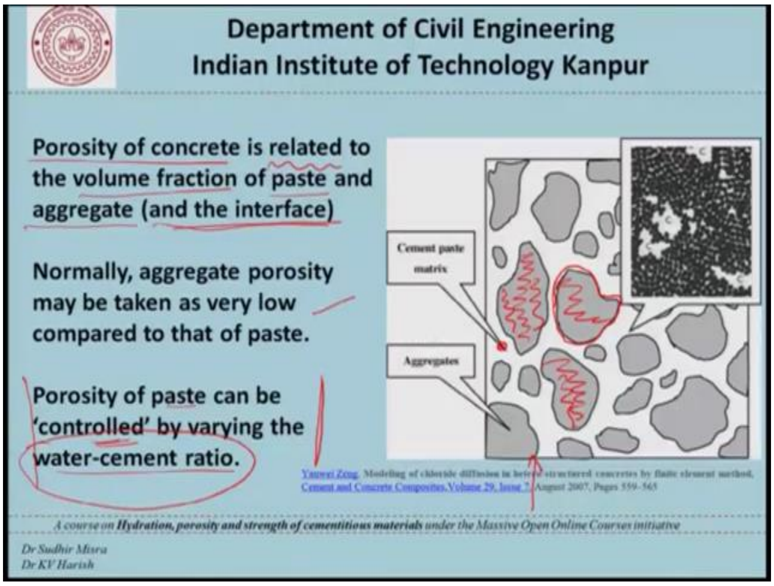


Now this system is more complicated and we can talk in terms of porosity of concrete only in terms of the fact that it is related to the volume fraction of paste and the aggregate and then the interface; what this really says is that if we look at the volume fraction of the paste phase in this picture, as far as the porosity of this concrete is concerned this will be related to how much of it is aggregate and how much of it is paste. And it will also be related to whether we want to treat it the porosity or the ease with which the material can move through these things which is called the interface.

Also we must remember that normally aggregate porosity may be taken to be very low compared to that of paste. So, we essentially assume that the porosity of the aggregate phase here is much lower, after all aggregate is basically rock concrete indeed is a man made rock, but as far as the natural rock which is the aggregate is concerned that porosity is substantially lower compared to the porosity of the (Refer Time: 27:32). Also once we agree with this it becomes obvious that the porosity of the paste can be controlled by varying the water cement ratio, because we have already seen that if we increase the amount of water we are basically increasing the water over and above that required for hydration and that is the water that is going to be evaporated and lost leaving behind pore spaces.

So, the porosity of the paste can really be controlled by controlling or varying the water cement ratio given the fact that the aggregate porosity is small we can say that the porosity of the concrete itself can be controlled if we control the water cement ratio and that is what is conventional wisdom. So, even without having gone through all this exercise we could have simply come to this conclusion and that is what most of the time the codes and the specifications and common practice is, if we want less firm ability we want less porosity we try to control reduce the water cement ratio. And that is what is the bottom line when we are using chemical admixtures, especially super plasticizers where the effort is that we get the same amount of workability without having to use that much water.

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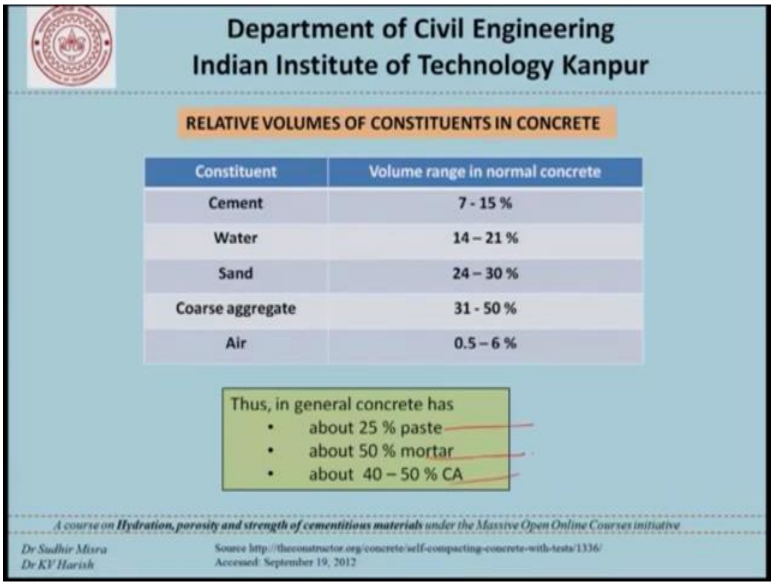


Now, this picture here shows you the relative volumes of the constituents in concrete cement varies from 7 to 15 percent water 14 to 20 percent, sand is about 24 to 30 coarse aggregates 31 to 50 and about half a percent a 6 percent of air depending on what kind of chemical admixtures we use and therefore, we have about 25, 27 percent of paste about 50 percent of mortar, and 50 percent of coarse aggregate now with this background and 50 percent of coarse aggregate.

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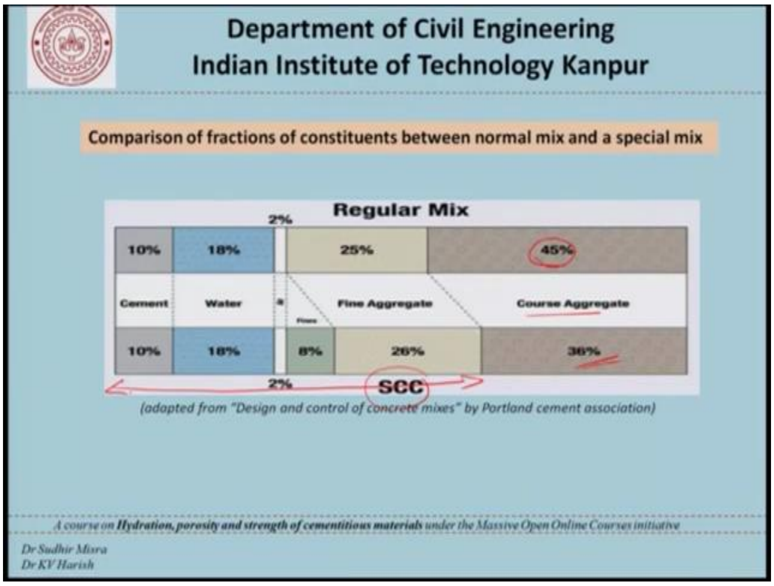


Of course when it comes to special concrete's like the self compacting concrete we find that the coarse aggregate content should be reduced or needs to be reduced from what say 40 to 45 percent to maximum of about 35 40 percent, and correspondingly there is an increase in the mortar content.

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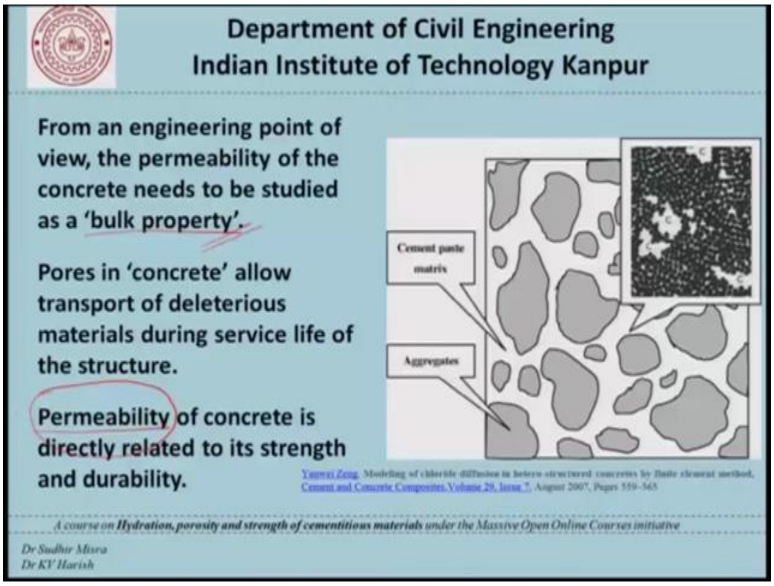


Now, with this background if we look at this picture once again it is easy to say that from an engineering point of view the permeability of concrete needs to be studied as a bulk property; whereas, the porosity of cement paste will help us understand the porosity of concrete, but when it comes to an engineering application we must also understand what is the permeability of concrete as such.

Pores in concrete allow transport of deleterious materials during service life of the structure these pores allow the ingress and transport of material like carbon dioxide or the chloride ions from the atmosphere or the environment in which the structure is located, and that causes durability problems and therefore, probability of concrete is directly related to its strength and durability meaning thereby that we mean what this means is that we need to understand and measure permeability of concrete directly as a bulk property of the concrete that we are using at a particular site in order to have an appreciation of its durability. The strength is a normal parameter which is measured and obtained using cubes or cylinders under standard conditions and so on and this measurement of permeability as a tool to have a better understanding of durability of the concrete is something what we will do in the next lecture.

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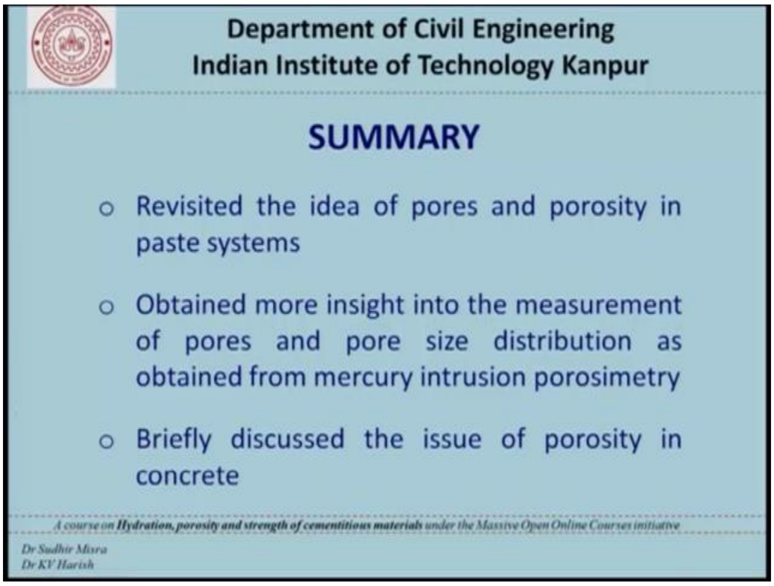


So, as far as our discussion today is concerned we revisited the ideas of pores and porosity in paste systems obtained more insight into the measurement of pores and pore size distribution, as obtained from mercury intrusion porosimetry and we briefly discussed the issue of porosity in concrete and the permeability in concrete and its relation to durability and so on.

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These are the reference materials which you can look up apart from the website and the information that is available on the internet there is an assignment that I have also given to you which is not going to be graded or submitted, but yes those of you who are more interested should try to understand a little bit more about the pore sizes and pore size distributions of different phase systems. And we will see you next time when we talk about the measurement of permeability in concrete.

Thank you.