Development and Applications of Special Concretes
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Lecture 08
Review of Normal Concretes: Pores and Porosity in Concretes.

Hello and welcome back to another lecture on development and applications of special concretes. Having completed the discussion on the review of proportioning of concrete mixes, today we will review our understanding of pores and porosity in concrete. And, that is still a part of the review of normal concretes that we are doing as a part of the foundation for the course on special concretes.

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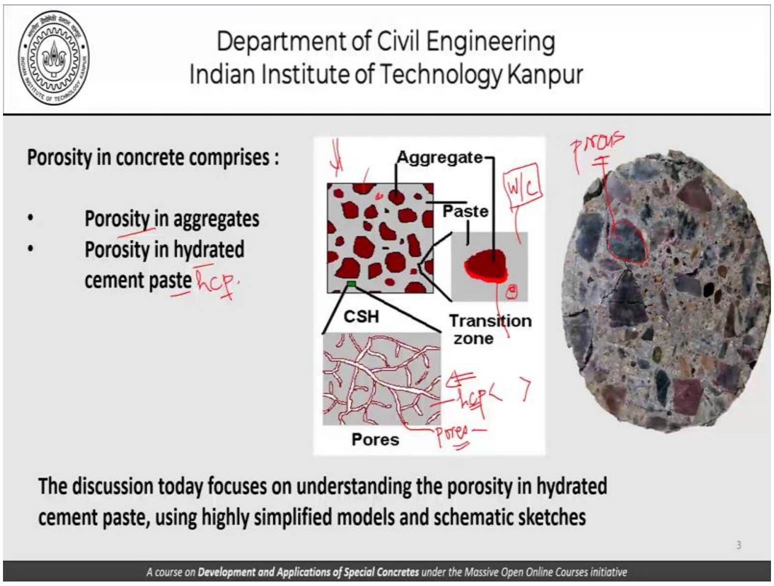

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Porosity in concrete comprises :

- Porosity in aggregates
- Porosity in hydrated cement paste hcp.

The discussion today focuses on understanding the porosity in hydrated cement paste, using highly simplified models and schematic sketches

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Now, this is a picture which we have been seeing all the time except that I have dropped all the descriptions assuming that you had enough of it and I think now you understand the model that we have been talking about but still, we look at this picture once again today to understand this idea of pores and porosity. So, what we are trying to do is we have modelled this concrete the way it is shown in this picture here.

We have these coarse aggregates sitting here and we have the mortar phase here. Now around this coarse aggregated mortar, we have talked about this transition zone and this is what we have called the main body mortar. Now if we look at a small part of this main body mortar here, the way it is expanded into this small inset. We have these solid hydration products which we can call as hydrated cement paste.

And we have these as pore spaces, of course it does not mean that there are channels of water running all over the place but what it really means is only the fact that in hcp, the kind of products that we have are more dense. And in the pore spaces, these hydration products have a lot more water in it. With that understanding and kind of assuming that all these pores are not necessarily of the equal size let us start our discussion today.

Porosity in concrete comprises of the porosity in aggregates and the porosity in the hydrated cement paste, which I have written it as hcp. Now, we have already told you that these aggregates are also porous except that the porosity of these aggregates is much lower compared to the porosity of the mortar that we create. We create means its man-made it is governed by the water-cement ratio.

When I talk of mortar, I am more or less always talking about cement paste in this context. And, the discussion today focuses on revising our understanding of the porosity and hydrated cement paste using highly simplified models and schematic sketches. So, even though we use the word concrete and cement paste quite interchangeably. We talk of the porosity in concrete but please remember that the porosity of concrete basically has these two components.

And most of the time, we are talking about the porosity which is in the hydrated cement paste, because this is what we control largely as far as normal concrete is concerned and it is this part which governs things like the strength permeability and so on. So, we are really interested in the permeability or the porosity the pore size distributions, whatever happens in this part, the hydrated cement waste, the porosity in aggregates is not something that we bother about all the time.

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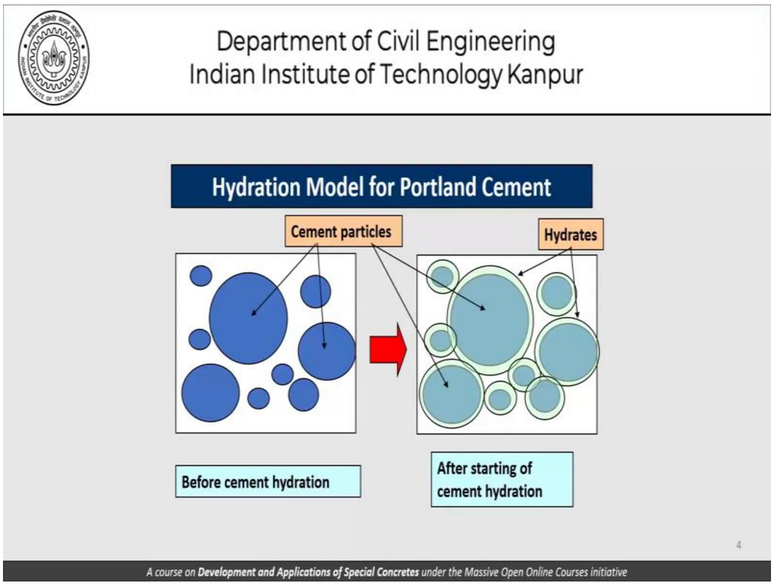
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Hydration Model for Portland Cement

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So, having said that let us start our discussion and look at the hydration model of Portland cement, what this hydration model really tells you, is that these are the cement particles. Of course, I have taken them to be spherical. But obviously cement particles are not spherical they are highly angular in nature but for the sake of argument its much simpler to draw perhaps its much simpler to take.

There is a certain amount of particle size distribution as well. So, these are the different kinds of cement particles and this is analogous or this is in line with our discussion that cement paste is a suspension of cement particles in water. So basically, this part here is all water. Now, once water and cement are in contact with each other, just as the stars, just as water comes in contact with the cement hydration starts.

And, these hydration products or hydrates start to form. Now, you can see that these hydration products or hydrates overlap at this point, leave or catch some amount of water inside the different hydration products and so on. So, it is a very complicated, complex thing happening within the concrete matrix.

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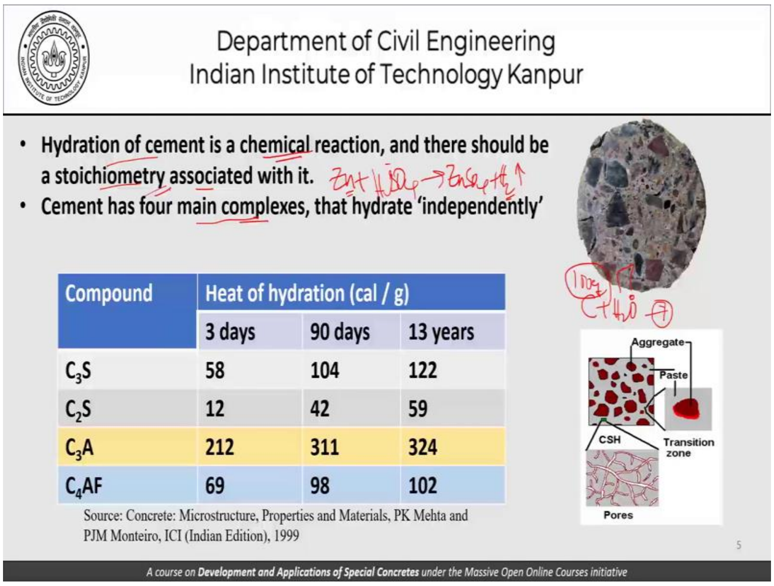

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- Hydration of cement is a chemical reaction, and there should be a stoichiometry associated with it. $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$
- Cement has four main complexes, that hydrate 'independently'

$100g$ $C + H_2O$?

Compound	Heat of hydration (cal / g)		
	3 days	90 days	13 years
C_3S	58	104	122
C_2S	12	42	59
C_3A	212	311	324
C_4AF	69	98	102

Source: Concrete: Microstructure, Properties and Materials, PK Mehta and PJM Monteiro, ICI (Indian Edition), 1999

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Having said that, we should also try to understand or remember that after all, the hydration of cement is a chemical reaction and therefore there should be stoichiometry associated with it. What is the stoichiometry part of it? i.e., we talk of any chemical reaction zinc + sulphuric acid giving you using sulphate and hydrogen gas. Now, we know that how much of zinc will give you how much of hydrogen, how much of zinc will react with how much of sulfuric acid.

Now, if that is the kind of chemical reaction that we know about then hydration of cement which means the reaction of cement and water that also should have a certain fixed stoichiometry that okay. For hydrating 100 grams of cement how much water is required? Now to answer that question, let us understand what cement is made up of? Cement is made up of four main complexes and they hydrate almost independently.

Now, this picture here tells you these four hydrates the tricalcium silicate, the dicalcium silicate, tricalcium aluminate and the C_4Af i.e., the tetra element of ferrites. Now these fellows, all of them hydrate more or less independently. So, if we go back to the previous model, we can say that ok here is a cement particle, part of it is C_2A, part of it is C_3S, part of it is C_2S, part of it is C_4AF, part of it is C_3A and so on.

Now, all these guys they start reacting with water independently and each of them has its own heat of hydration. Now this heat of vibration, if we look at this table closely at 3 days, 90 days or 13 years, what it shows is that in the initial period C_3A gives out a lot of heat. And, this heat can be looked upon as a proportion of what the total heat of hydration liberated from C_3A in 13 years.

Now, you can see that 66% of that is liberated here and more or less 90% of it gets liberated in just 90 days, this is not really true for something like C_2S, where this 12 is just about 20% of this 59 or 60 and this 42 is just about two thirds of this. So basically, cement hydration continues for a very long period of time. And, all our discussion of the 28-day strength and so on is just a model. It is an engineering approximation that a lot of hydration has taken place and whatever strength development happens beyond that point is a bonus.

Of course, in this discussion we are taking the heat of hydration liberated as a surrogate parameter to estimate the amount of hydration.

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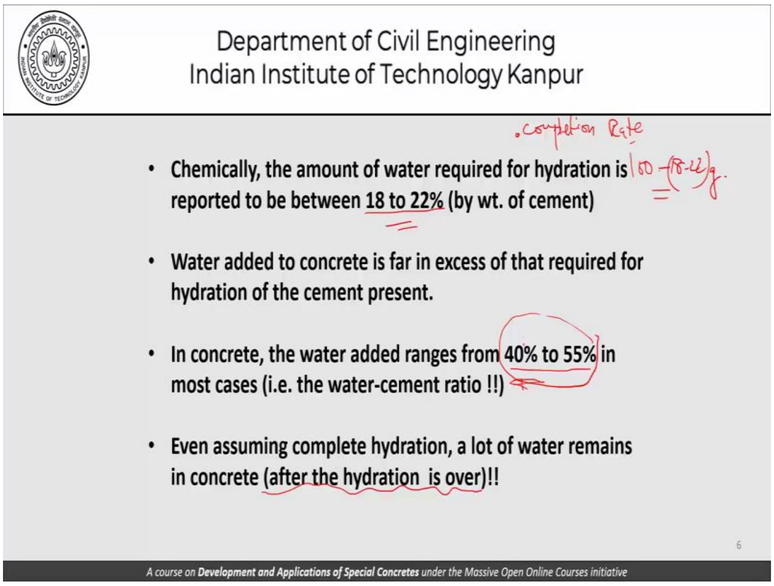

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- Chemically, the amount of water required for hydration is reported to be between 18 to 22% (by wt. of cement)
- Water added to concrete is far in excess of that required for hydration of the cement present.
- In concrete, the water added ranges from 40% to 55% in most cases (i.e. the water-cement ratio !!)
- Even assuming complete hydration, a lot of water remains in concrete (after the hydration is over)!!

• Completion Rate

100 — (18-22)g.

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So now, if that is what we kind of agree upon then let me also share with you that chemically the amount of water required for hydration is reported to be between 18 to 22% by weight of cement i.e., for hydrating 100 grams of cement we need 18 to 22 grams of water. Now of course, any reaction has two dimensions to it completion and rate. When I say that it requires 22 grams of water per 100 grams of cement for hydration, I am not talking about the rate.

How soon it will be consumed, how much later it will be consumed and so on? But let us take that with a pinch of salt and leave it at that and say that, okay the amount of water required for hydration of cement is between 18 and 22. So having said that, the water added to concrete is far in excess of that required for hydration. Those of you who are coming from the field or we have some experience with concrete know that in concrete the water added ranges from about 40 to 55% in most cases and that is what we call the normal water-cement ratio.

Now, sometimes we use something below this, sometimes we use something higher than this but this I think would be something like the normal range. Now, even in this normal range we can see that these values are much higher than these values. Now, what happens to this excess water that we add. It all remains in concrete after the hydration is over. Even, if we assume that all these 20 grams of water which is required or 20% of water which is required is actually consumed and all the cement is also and all the cement actually gets hydrated.

Because at the end of it, there is half a possibility that some part of cement does not get hydrated at all, so in that case even that amount of water which would normally have been consumed in hydration that also remains. In addition to that we have added so much more water and that is in any case going to be around in the cement matrix.

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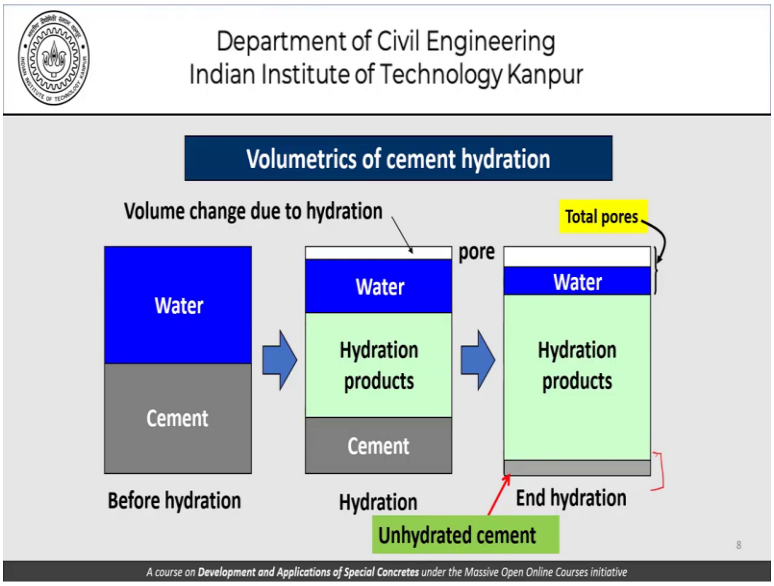

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Volumetrics of cement hydration

Looking at this picture graphically, if we start with cement particles here the amount of cement that is given here, we add a certain amount of water to it, at an intermediate stage of hydration this is what will have, some part of cement would have been hydrated. What this picture shows is that this amount of cement has been hydrated. This amount of cement is still remaining some hydration products have been formed and there is some water still remaining.

There is some volume changes that may occur due to hydration, we are not particularly looking at this right now. Let us keep it aside and let us keep moving forward. At the end of the hydration process, we can see that there is no cement left. And, all the cement has been converted to hydration products and this is the water which is remaining this is the pore space. Now, this total thing is what is giving you the total pore space because this water also can evaporate out can be moved out over a long period of time.

So, we will try to see just now in a little while, what is the nature of this water sitting inside the concrete? I just said sitting inside the concrete, but please remember go back to that picture which I showed you, this water is sitting not with the aggregates but within the hydration product, somewhere as we shall see in some of our model and schematic representations just now. Now this is the un-hydrated cement, there is another possibility that if the entire cement does not get consumed.

Then, we have some unhydrated cement as well and this unhydrated cement there will be some remaining water that is excess water, there will be some total pores hydration products. So, this is what is going to happen.

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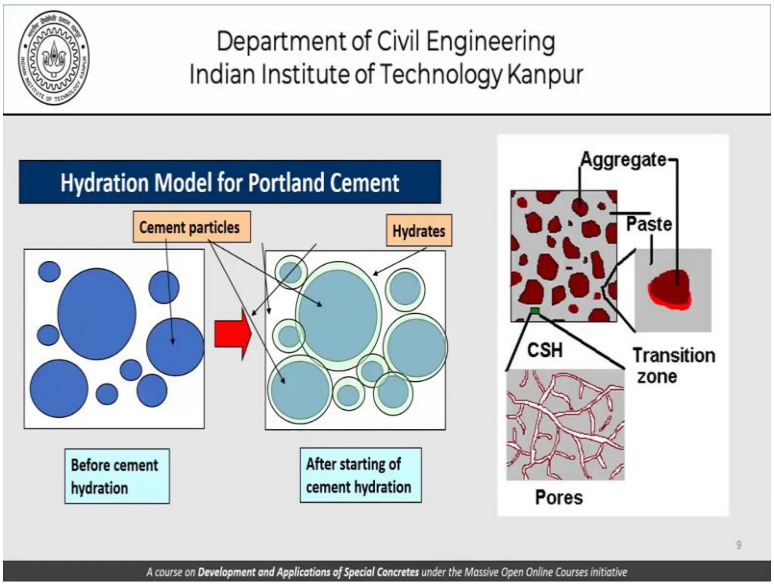

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Hydration Model for Portland Cement

Having said that, let us look at this picture once again that this is what we started with, this is what we have as an intermediate position and what is this picture trying to tell you? This picture is trying to tell us the evolution of this part of our discussion. That is what is happening in this part that is the mortar part of the paste part where water started to react with cement, formed hydration products which are shown here and led to some pore spaces which are shown here. Also, keep a close watch on this picture and we will come back to this picture in a while.

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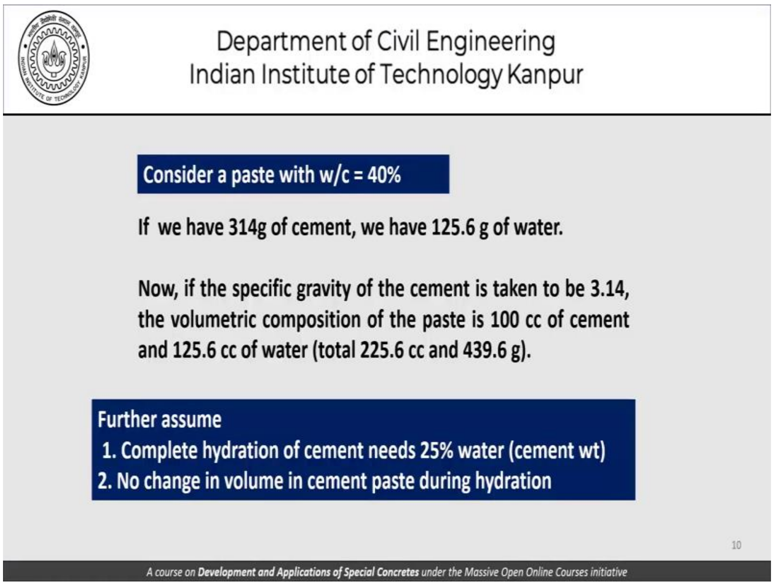

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Consider a paste with w/c = 40%

If we have 314g of cement, we have 125.6 g of water.

Now, if the specific gravity of the cement is taken to be 3.14, the volumetric composition of the paste is 100 cc of cement and 125.6 cc of water (total 225.6 cc and 439.6 g).

Further assume
1. Complete hydration of cement needs 25% water (cement wt)
2. No change in volume in cement paste during hydration

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Now, let us take a numerical example the numerical example says that if we have a water-cement ratio of 40% what does that tell us, that we have let us say 314 grams of cement and for that if we use 40 water-cement ratio, we have how much of water 125.6 grams of water. Now, assuming that this specific gravity of cement is taken to be 3.14 this 314 grams turns out to be 100 cc of cement and that 100 cc of cement and 125.6 cc of water gives us a total volume of the paste to begin with as 225.6 and 439.6 grams i.e., my mass it is 314 + 125.6.

So, this is the mass, this is the volume and the game begins the game in the sense, the hydration of the cement begins. If we assume and let us do that, I mean we will have to make some assumptions 25% of water by cement weight is needed for hydration. So, instead of that 18 to 22%, I am using 25% as the number. And, we also assume that there is no change in the volume of cement paste during hydration that is why I said that I am not going to particularly consider or follow the small changes in volume in the cement paste as hydration proceeds.

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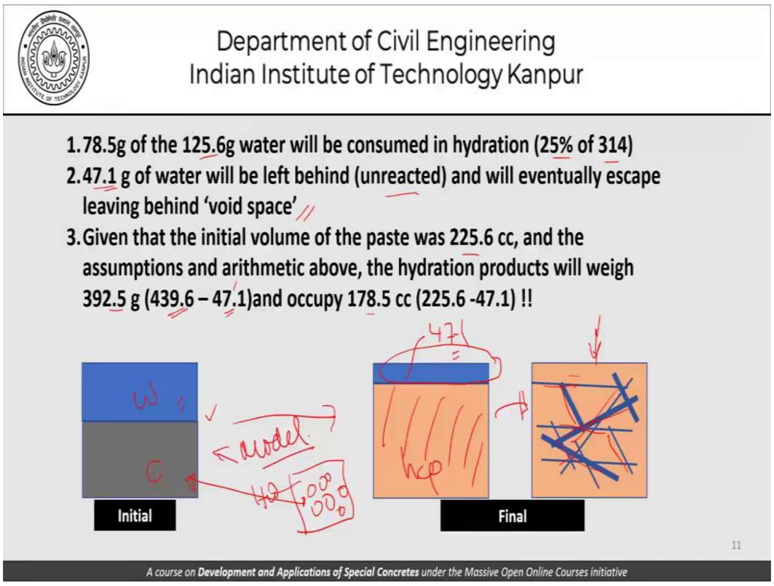

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1. 78.5g of the 125.6g water will be consumed in hydration (25% of 314)
2. 47.1 g of water will be left behind (unreacted) and will eventually escape leaving behind 'void space'
3. Given that the initial volume of the paste was 225.6 cc, and the assumptions and arithmetic above, the hydration products will weigh 392.5 g (439.6 – 47.1)and occupy 178.5 cc (225.6 -47.1) !!

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So, if you are making this assumption and if we do that then this is what we will begin with, cement here, water here and what is going to happen finally is that 78.5 grams of 125.6 will be consumed in the hydration of cement. We had 314 grams of cement 25% of that will get consumed, which means that 47.1 grams of water will be left behind this - this and that is the unreacted water and will eventually escape leaving void space.

Now, given the initial volume of the paste to be 225.6, the assumptions in the arithmetic the hydration products will weigh 392.5 grams i.e., the total mass that we started with - the water that is going to escape or we allow to escape. These fellows will occupy 178.5 cc of space. Now if we understand this discussion, what it really shows is something like this we have this as our hcp and this is my 47.1 is what I am talking about.

Now, this amount of water is not necessarily sitting here and all of it will evaporate. No for that matter even this is just a model representation of cement particles surrounded by a certain amount of water. So, what we did was, we lumped all the cement particles into solids here and then allowed all the water to be coming here. So, this is what exactly the model which we have used as far as proportioning of concrete mixes is concerned, we said OKAY.

All those particles, the solid volumes together will be put at one place giving rise to that volume of coarse aggregate, volume of sand, volume of cement here also in the paste phase i.e., exactly the model we are using. In real practice this is what the situation is that is we have cement paste all over the place and within this paste we have some kind of water, which is available in different channels, if you want to use the word i.e., the exactly the picture that I showed you from that small part of paste.

This is the water which is available all over the paste and the total of this water is equal to the volume of unreacted water.

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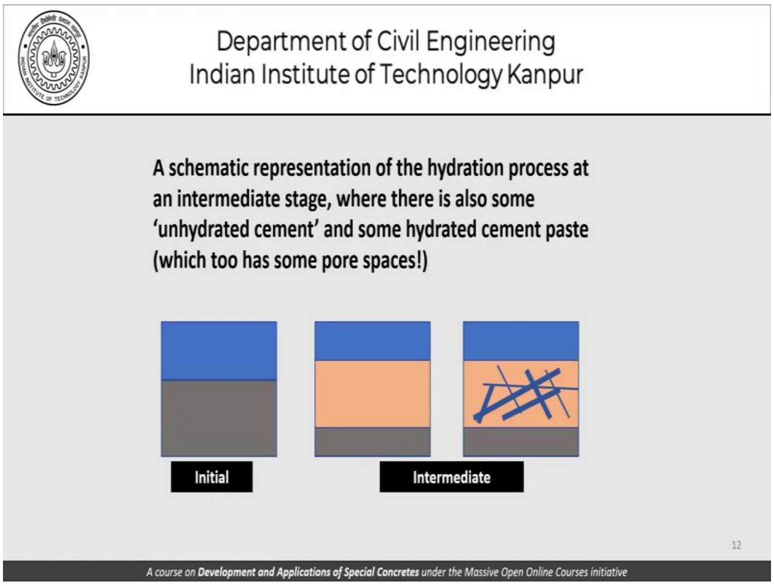

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A schematic representation of the hydration process at an intermediate stage, where there is also some 'unhydrated cement' and some hydrated cement paste (which too has some pore spaces!)

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And therefore, what I said about the hydration products and the water present within the hydration products at the final stage is also true at the intermediate stage i.e., the hcp here in the intermediate stage also has a certain amount of water sitting within the hcp.

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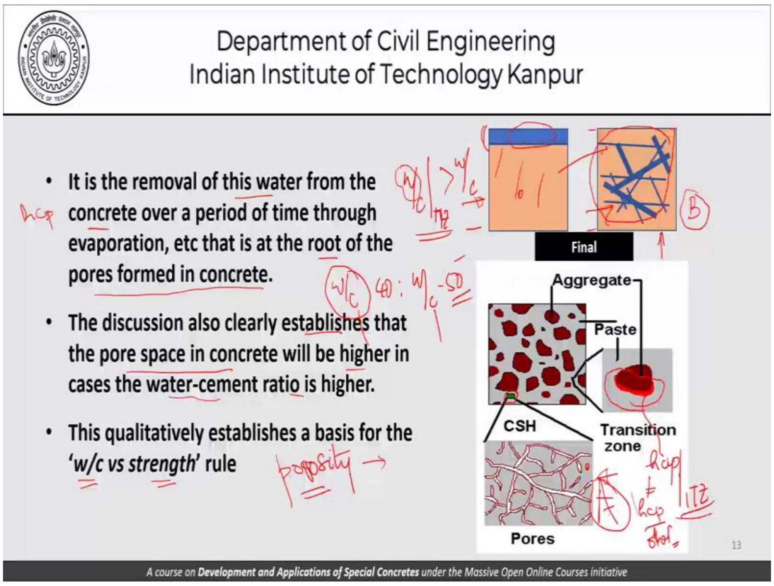

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- It is the removal of this water from the concrete over a period of time through evaporation, etc that is at the root of the pores formed in concrete.
- The discussion also clearly establishes that the pore space in concrete will be higher in cases the water-cement ratio is higher.
- This qualitatively establishes a basis for the '*w/c vs strength*' rule

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And, it is the removal of this water from the concrete again, I am using the word concrete strictly speaking, it is hcp over a period of time through evaporation and so on is at the root of the pose formed in concrete. So once again look at this picture here, this picture here shows the model that we talked about that this is my hcp which is over here but the volume of this hcp is actually the whole thing here.

And this water, which I have depicted as free water available here is distributed all over the hcp here. Now, all this business here is happening within this small element of cement paste which is expanded into this form. So, this part this picture here A is nothing but this picture B which is shown here with the four spaces being shown what it is. Therefore, now let us try to take a closer look at this part in the beginning of the lecture, I had talked about it that.

Please look at this picture carefully, we are going to come back to this. Now what this shows is exactly this. Now, what is the nature of hcp here in this area, which is shown in the red part that is my hcp in the itz what is the nature of the hcp here? This hcp in the itz is different is not the same as the hcp other places. What is the difference? The difference will be this kind of water which is present in the hcp in this neighbourhood that is in the itz and this kind of water which is available or present in other places as far as the mortar of the hcp is concerned.

So, if we keep this in mind the discussion or the understanding is much better what when we said when we said that the water-cement ratio in the itz is higher than the water-cement ratio in the paste. Otherwise, what it means is there is more water here in the cement paste finally in the hydrated cement paste at the end of it also. Moving forward, this discussion that we just had clearly establishes that the pore space in concrete or hcp will be higher in case the water-cement ratio is higher.

Obviously, when we have water cement ratio 40% compared to a water cement ratio of 50% for the same amount of cement, we are adding more water here. But the amount of water which will be consumed during hydration will be the same. And therefore, this excess water will be greater, if the water cement-ratio is higher, the initial water-cement ratio is higher and that really is the root of the issue that higher water-cement ratios lead to lower strengths.

Because there is a porosity involved in between, higher water-cement ratios gives you greater porosity, which has lower strength. And this lower strength, part of it is something which is pertaining to the mortar. Remember that the aggregates themselves their strength is not coming into play. I have possibly said that in one of the lectures before that the strength of the aggregates as far as normal concrete is concerned is much higher than that of the cement paste that we use or the mortar that we use.

This may or may not be true, it starts becoming a little difficult to defend this kind of an assumption as we go higher in strength but most of the time it is true. And that is why, the general rule that the strength of concrete is governed by water-cement ratio is coming from this kind of discussion here.

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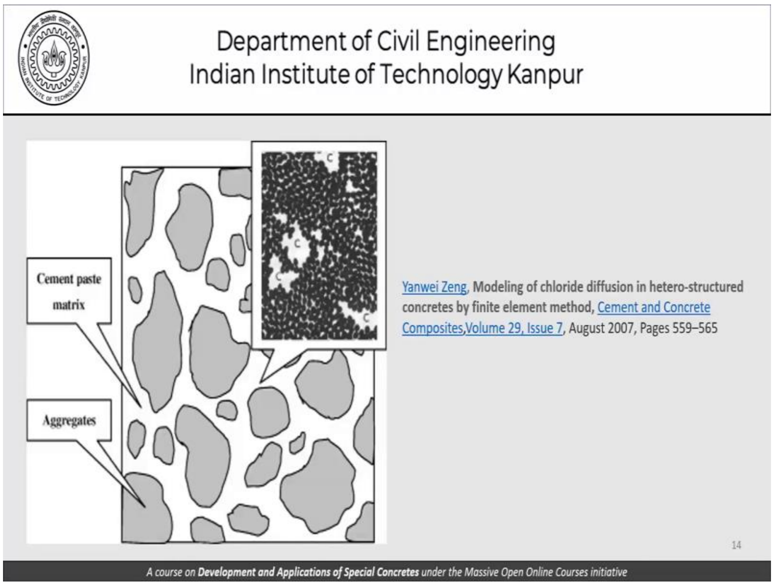

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Yanwei Zeng, Modeling of chloride diffusion in hetero-structured concretes by finite element method, Cement and Concrete Composites, Volume 29, Issue 7, August 2007, Pages 559–565

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This is a picture which is taken from one of the research publications, where the authors were trying to model chloride diffusion and hetero-structured concrete by finite element method. Now, what they were trying to do was study the diffusion of chloride ions into concrete and that was possibly being done by studying the diffusion of chlorides through the cement paste and therefore through the pores in the cement paste.

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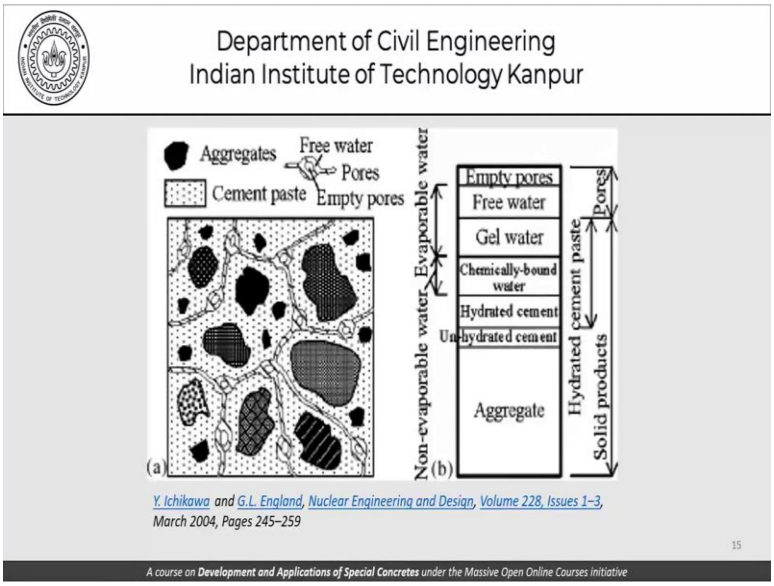
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Y. Ichikawa and G.L. England, Nuclear Engineering and Design, Volume 228, Issues 1–3, March 2004, Pages 245–259

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Similarly, this picture here talks about the pore structure that we expect in concrete and we have several types of structures associated. We have solid products, which is aggregates, un-hydrated cement and a bit of hydrated cement. There is chemically bound water there is gel water, free water and empty pores associated with the concrete structure. I hope you can see that this picture here is something very similar to the kind of model that we have tried to draw possibly much simpler.

And if you look at water alone, which is sitting inside the concrete we have evaporable water and we have non-evaporable water. This non-evaporable water is the chemically bound water which is sitting with the hydration products. The remaining water which was shown in blue colour in those slides was gel water and free water and i.e., possibly evaporable and we can get rid of it.

So therefore, this + this gives me the clear pores gel water is a little more difficult to expel but it is not chemically bound. So, this is basically the entire cement paste part unhydrated. This part here is the cement paste hydrated cement chemically bound water and gel water within the hydrated cement paste i.e., how we can model or we can understand what is going on in this entire body of concrete.

So, we have not only the aggregates which are solid but some other things have also solidified the hydration products are solids except that they have some layers of water sitting in them.

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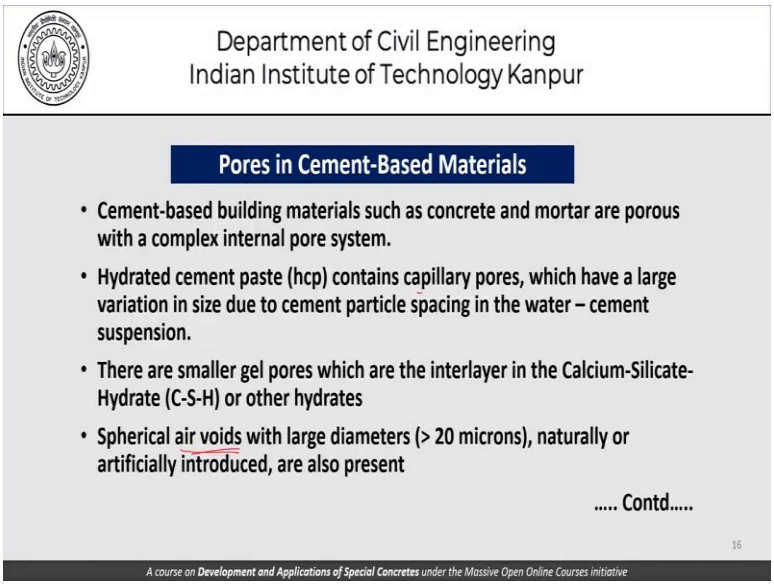

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Pores in Cement-Based Materials

- 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

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As far as some comments on the pores in the cement-based materials, let us try to summarize our understanding. Cement based building materials such as concrete and mortars are porous with a complex internal pore system. Hydrated cement paste hcp contains capillary pores, which have a large variation in size due to particle spacing of cement the cement particle spacing in water and cement suspension.

There are smaller gel pores, which are the inter layer in the CSH or other hydrates spherical air-voids in large diameter which is greater than 20 microns naturally or artificially introduced are also present. So, we are here talking about entrained air.

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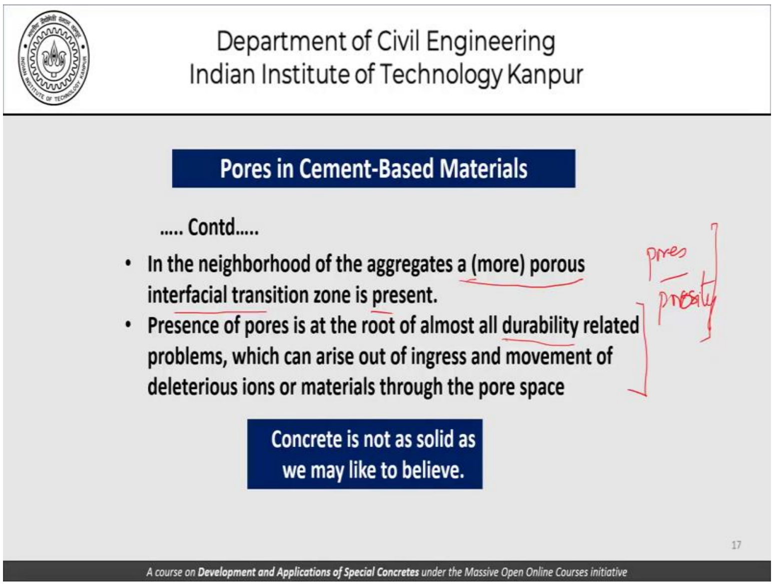

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Pores in Cement-Based Materials

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- 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

pores
porosity

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

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Continuing further in the neighbourhood of the aggregates a more porous itz is present and that is what we talked about just now. Presence of pores is at the root of almost all durability related problems, which can arise out of the ingress and movement of deleterious ions and materials through the pore space. So that is why, we really need to have a very good understanding of pores and porosity in concrete.

And that is why, I thought that among the things that we need to review as part of our discussion here as an introduction to special concretes is a closer look, a relook at the pores and porosity and porous nature of the concrete. Concrete is not as solid as we may like to believe. With this understanding let us try to move forward.

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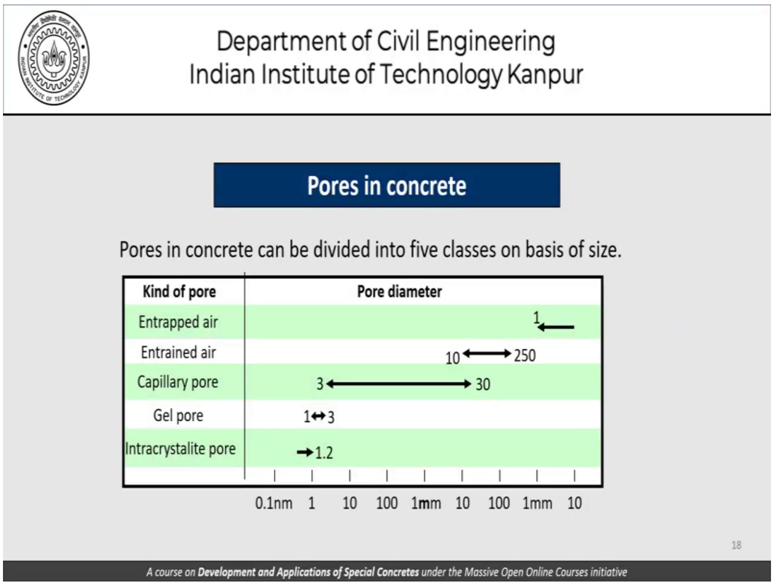

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Pores in concrete

Pores in concrete can be divided into five classes on basis of size.

Kind of pore	Pore diameter
Entrapped air	1 ←
Entrained air	10 ↔ 250
Capillary pore	3 ↔ 30
Gel pore	1 ↔ 3
Intracrystalite pore	→ 1.2

Here is a distribution of pores in concrete. As far as size is concerned, these are the 5-6 different types of pores that we have, we have entrapped air, entrained air, capillary pores, gel pores and intra-crystallite pores. Now, entrapped air as far as size is concerned, this is the diameter or this is the size, it could be anywhere between one millimetre to anyway, I mean it is a void basically.

Entrained air is in this range, capillary pores in this range, gel pores is here, inter-crystalline pores here and waters can be sitting all over the place except of course in entrapped air except of course, in the entrained air kind of particles or phases. So, this water is easiest to move out, this water is impossible to move out under normal conditions this is possibly somewhere in between.

So, once we talk of how much water can be moved out, we have to go back to some kind of a diagram like this. Remember that, water sitting in larger spaces is easier to move out. Water sitting in smaller spaces is more difficult to move out keep that in mind when we study other characteristics of concrete as well.

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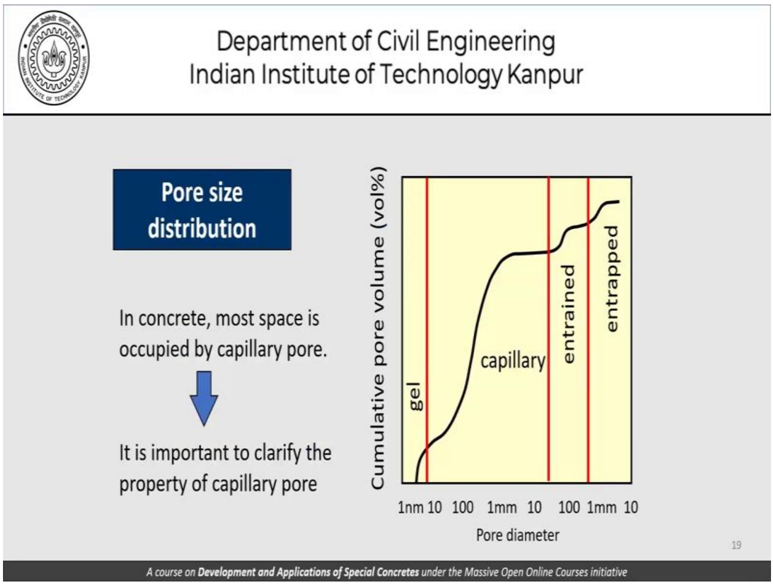
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Pore size distribution

In concrete, most space is occupied by capillary pore.

It is important to clarify the property of capillary pore

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This is another representation of the pore size distribution and the pore spaces within concrete the gel pores, the capillary pores, entrained air and entrapped air. As far as concrete is concerned, most of the space is occupied by capillary pores. In fact, this cumulative pore volume exactly shows that from here to here, this amount of volume is occupied by the capillary pores which may range from here to here as far as diameters are concerned.

And, it is important therefore to understand the properties of the capillary pores and that something which is beyond the scope of our discussion here. Suffice to understand for you that yes, there is a region of pores which is more important than the other regions and the pores in concrete are not necessarily all of the same size. They may be saturated with water not saturated with water, the water present in them may move out more easily, less easily, may never move out at all and so on.

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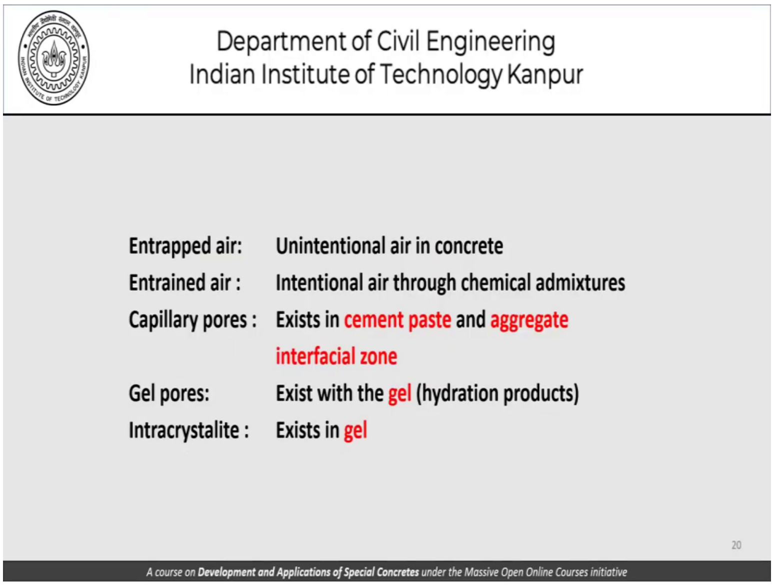

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Entrapped air: Unintentional air in concrete
Entrained air : Intentional air through chemical admixtures
Capillary pores : Exists in cement paste and aggregate interfacial zone
Gel pores: Exist with the gel (hydration products)
Intracrystalite : Exists in gel

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This again is just a recap entrapped air, is unintentional air in concrete, entrained air is intentional air through chemical admixtures. Capillary pores exists in the cement paste and at the aggregate itz, gel pore exist within the gels of the hydration products and inter-crystallite water or pores exist within the gel itself.

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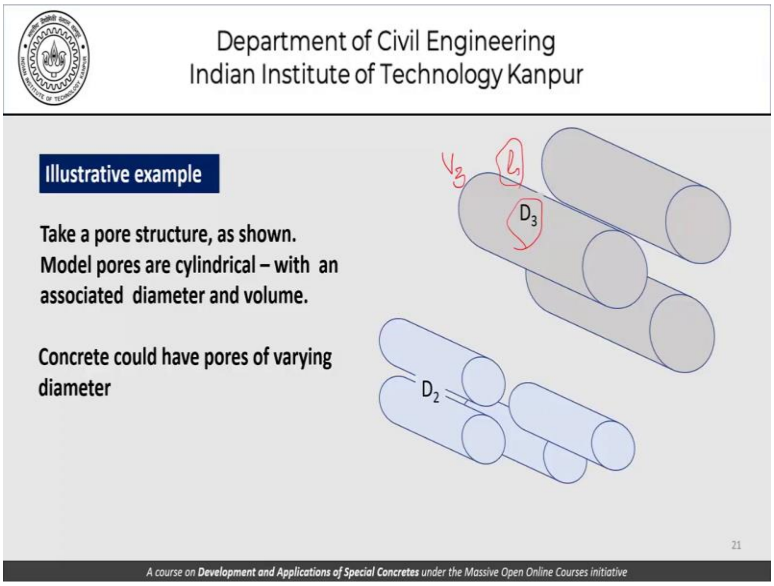

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Illustrative example

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

Concrete could have pores of varying diameter

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Let us try to understand some of the concepts that we have covered today through an illustrative example with a pore structure pores being taken as cylindrical associated with a diameter and a volume. Let us take cylindrical pose having a diameter of D_3 and they have a volume associated with them let us say V_3 which means that we need to have a certain amount of length associated with it we can take it as L_3 and we get a volume V_3.

Similarly, for D_2 length L_2 and we will get a volume V_2, for a diameter D_1 we have a length L_1 and we have volume associated with them as V_1.

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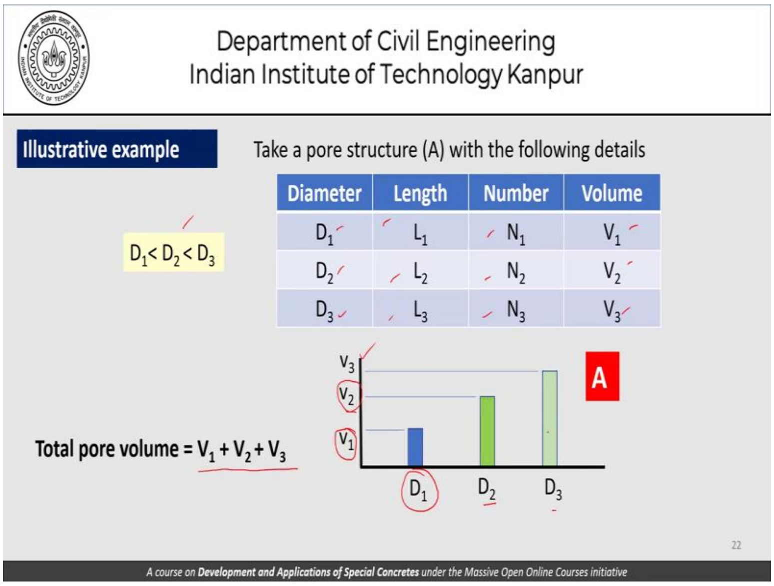

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Illustrative example

Take a pore structure (A) with the following details

Diameter	Length	Number	Volume
D_1	L_1	N_1	V_1
D_2	L_2	N_2	V_2
D_3	L_3	N_3	V_3

$D_1 < D_2 < D_3$

Total pore volume = $V_1 + V_2 + V_3$

We try to take a pore structure with the following details. We are conceptually extending what we did in the previous slide now. There is a D_1, D_2, D_3, D_1 less than D_2 less than D_3 lengths associated such and such. The numbers associated with them so much and we will have certain volumes associated with them. Now, it is always possible that we try to draw this diagram that is the volume associated with the pores having an equivalent diameter of D_1 volume associated with pores having a diameter d_2 and a volume associated with pores having a volume d_3.

The way, I have drawn it, d_3 has the maximum volume V_3 is larger than V_2 which is larger than V_1 that is not necessarily true as we will just see in a discussion subsequently. The total pore volume in this situation is $V_1 + V_2 + V_3$. So, there is no denying that if we have a pore structure the way we just saw it in terms of the diameter and the total lengths we can calculate the equivalent volumes or the volumes for different diameters and draw this kind of a diagram.

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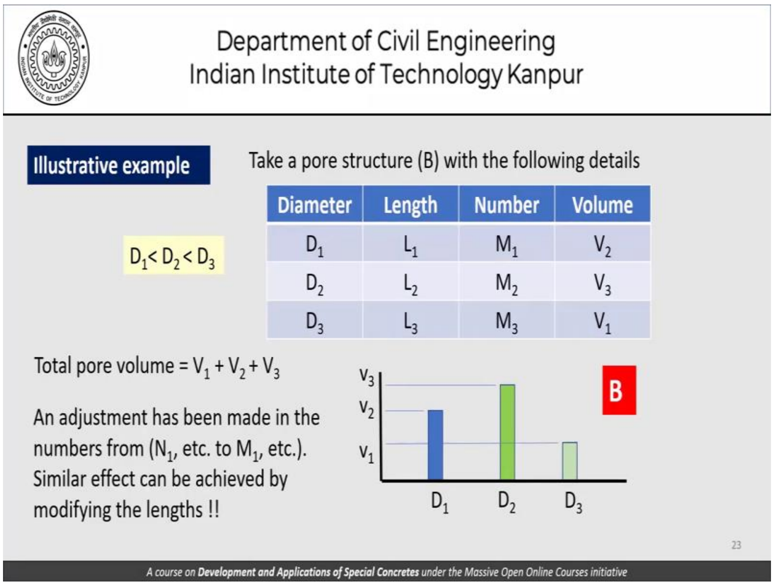

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Illustrative example

Take a pore structure (B) with the following details

$D_1 < D_2 < D_3$

Diameter	Length	Number	Volume
D_1	L_1	M_1	V_2
D_2	L_2	M_2	V_3
D_3	L_3	M_3	V_1

Total pore volume = $V_1 + V_2 + V_3$

An adjustment has been made in the numbers from (N_1, etc. to M_1, etc.). Similar effect can be achieved by modifying the lengths !!

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Now, we can draw for another material B, we can do the same kind of discussion here, where the volume corresponding to d $_3$ is the smallest the volume, corresponding to d $_2$ is the largest and the volume corresponding to d1 is somewhere in the middle taking there by or maintaining there in the total pore volume still being V $_1$ + V $_2$ + V $_3$ so it is all the same.

So, the total pore volume as far as materials A and B are concerned that is the same except that the volume is distributed differently. As far as the pore sizes are concerned, this adjustment can always be done by doing something with the numbers of pores and the lengths and so on. So that is not so difficult for you to understand, and I will leave it at that now.

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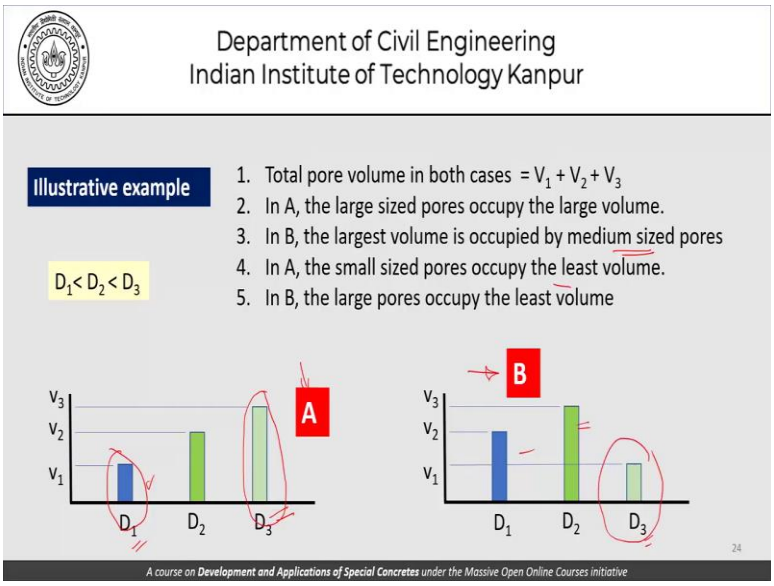

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Illustrative example

$D_1 < D_2 < D_3$

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

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Having said that, this is what we have done so we have pore structure A and a pore structure B with d_1 less than d_2 less than d_3, what are the kind of conclusions that we can draw from here? The total pore volume in both cases is $V_1 + V_2 + V_3$ except that here V_1 corresponded to pores having diameter d_1, here V_1 corresponds to the pores having diameter d_3 and here V_3 corresponded to the volume of pores with diameter d_3, here V_3 corresponds to the volume of force having diameter d_2.

So, the total pore volume in both cases is $V_1 + V_2 + V_3$. In A, the large size pores occupy the largest volume that is very clear V_3 is the largest. So, here the larger pores are contributing greater or more to the total pore volume. In B the largest pore volume or the largest volume is occupied by medium-sized pores. In A, the small size pores occupy the least volume which is here compared to B.

As of course clear in B, the large size pore occupies the least volume. Now, I am leaving it to you to think as to what will be the implications of these comments that we have made in terms of the properties of these two materials. Properties in terms of strength, let us say and permeability. The ease with which water will move in these two materials this is something which we need to ponder about.

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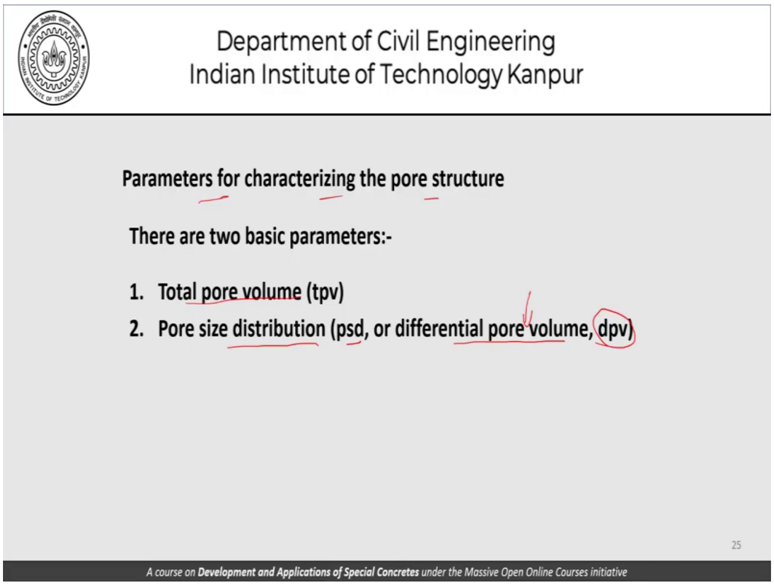

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Parameters for characterizing the pore structure

There are two basic parameters:-

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

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Basically, what we have discussed so far, is that parameters that can characterize the pore structure in a material like the hcp or the concrete there are two. One is the total pore volume and the other is the pore size distribution which is given as psd or the differential pore volume that is dpv. So, the differential pore volume is nothing but how much is the pore volume corresponding to each diameter.

The sum of that gives you the cumulative pore volume and the total finally gives you the total pore volume.

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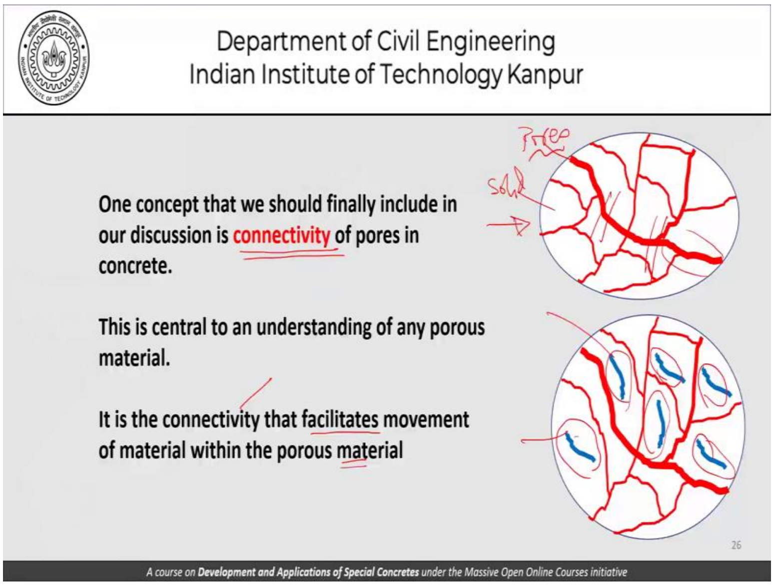

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One concept that we should finally include in our discussion is connectivity of pores in concrete.

This is central to an understanding of any porous material.

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

Having said that let us try to look at a slightly different aspect. A concept which you have not touched is the issue of connectivity of pores. This picture here shows some kind of pore structure in a solid so this is the solids that I have and these are the pores. So, these are all interconnected pores but there is always a possibility, we will have these kinds of pore spaces. Because at the end of it, we are talking about hydration products so it is not that we have created.

The material will get naturally created and these kind of pore spaces, if they are formed these are not connected to the main pore structure. And, it is very difficult to measure the porosity or account for these non-connected pores when we are trying to do any studies relating to porosity and the porous structure of a solid like hcp. This is central to our understanding of any porous material. This is something which we must understand that there could be or there are continuous pores of different diameters.

And then within that solid, we could also have discontinuous pores. The connectivity is the one property which facilitates movement of material within the porous material or that solid. So, hcp is a solid but there are pores through which deleterious material water chloride ions carbon dioxide all of it moves. As far as concrete is concerned and the connectivity facilitates it. So, if the pores were in not connected.

So, if the pores were not connected there were discontinuities. Then the material movement within the concrete would be much lower. So that something which we need to keep at the back of our mind when we try to understand porosity and try to study properties related to porosity such as permeability or movement of material through the solid.

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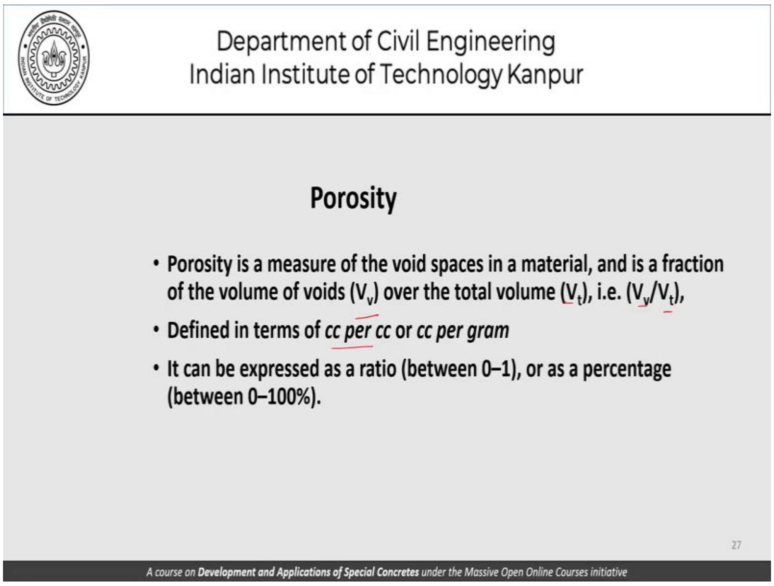

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Porosity

- **Porosity is a measure of the void spaces in a material, and is a fraction of the volume of voids (V_v) over the total volume (V_t), i.e. (V_v/V_t),**
- **Defined in terms of *cc per cc* or *cc per gram***
- **It can be expressed as a ratio (between 0–1), or as a percentage (between 0–100%).**

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So, porosity basically is a measure of the void space in the material, it is a fraction of the volumes of voids to the total volume that is V v by V t and this could be defined obviously therefore in terms of cc per cc or cc per gram. And, it can be expressed as a ratio between 0 and 1 or as a %age.

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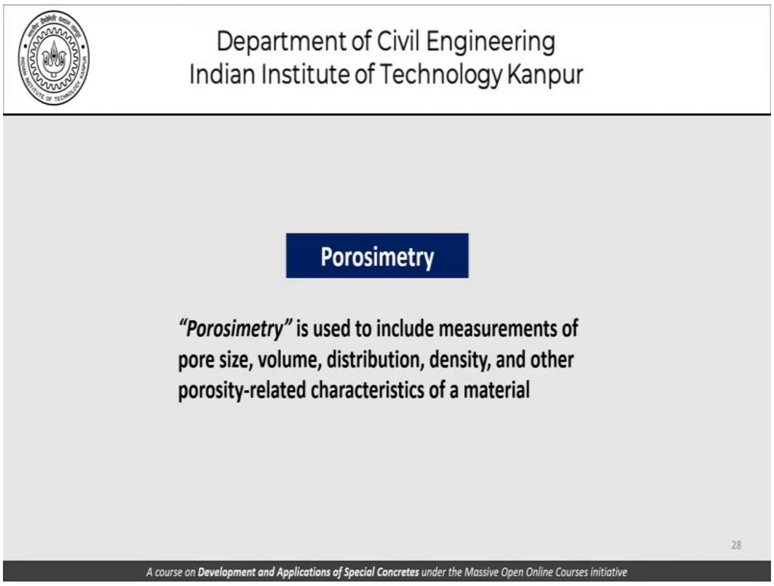

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Porosimetry

"Porosimetry" is used to include measurements of pore size, volume, distribution, density, and other porosity-related characteristics of a material

And, we use a technique called porosimeter to measure pores, study the pore sizes, the volume the pore, size distribution, the density and the other porosity related characteristics in the material. So, porosity is the science and I think we will take an example. Now, of how this porosity is actually carried out.

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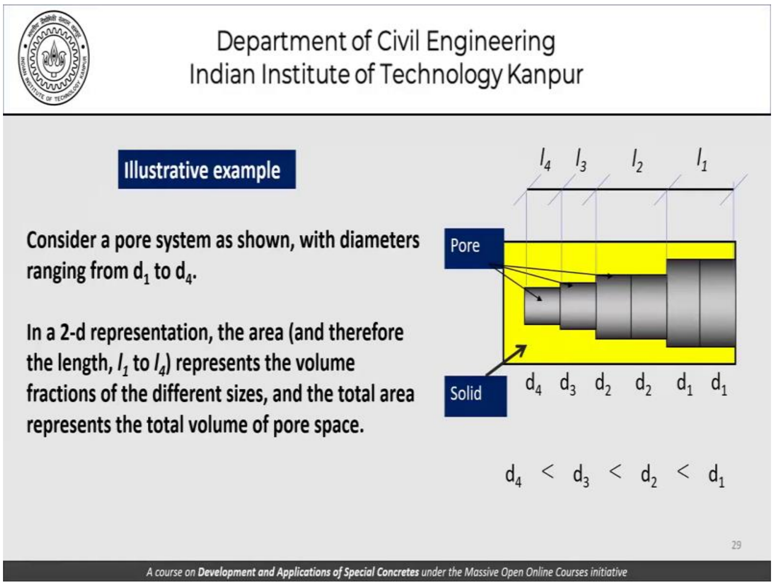

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Illustrative example

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.

$d_4 < d_3 < d_2 < d_1$

This is an illustrative example again consider a pore system as shown with diameters ranging from d_1 to d_4. Of course, being a 2D representation the areas here represent the volume so this is the solid space that we have the diameter d_1 is greater than the diameter d_2 greater than diameter d_3 and d_4, these lengths will give us the areas in this case and can be used to translate this area into the volume.

So, we can again talk in terms of how much volume is associated with pores of diameterd $_1$ the volume associated with pores of diameter d $_2$, d $_3$ and d $_4$.

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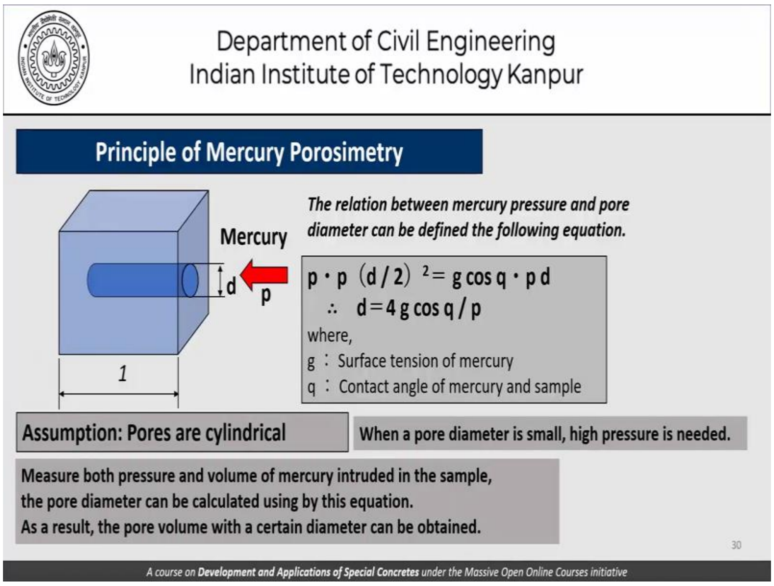

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Principle of Mercury Porosimetry

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

$p \cdot p \ (d/2)^{2} = g \cos q \cdot p d$

$\therefore \ d = 4 g \cos q / p$

where,
g : Surface tension of mercury
q : Contact angle of mercury and sample

Assumption: Pores are cylindrical

When a pore diameter is small, high pressure is needed.

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.

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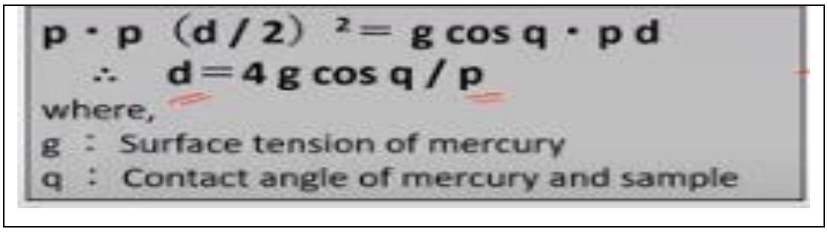
So, once we are able to do that then what we try to do is to try to push mercury into this pore and that is the principle of mercury porosimeter i.e., one of the methods that is used to study the porosity in hcp and concrete. Now, the ease with which the mercury goes in is inversely related to the diameter of the pore. So, if we increase the pressure or we have to increase the pressure in order to ensure that the mercury penetrates into smaller pores.

And, this is the equation that governs or tells us about the diameter of the pore, which will be filled for the pressure that we apply. Of course, the assumption is that the pores are cylindrical and when the pore diameter is small high pressure is needed. Measure both the pressure and volume of mercury intruded in the sample. We will quickly see, how it is done and the pore diameter can be calculated using this equation.



$p \cdot p \ (d/2)^{2} = g \cos q \cdot p d$

$\therefore \ d = 4 g \cos q / p$

where,
g : Surface tension of mercury
q : Contact angle of mercury and sample

As a result of that, the pore volume with a certain diameter can be obtained. So, we will try to study this part of the discussion here in the next couple of slides, with again illustrative examples.

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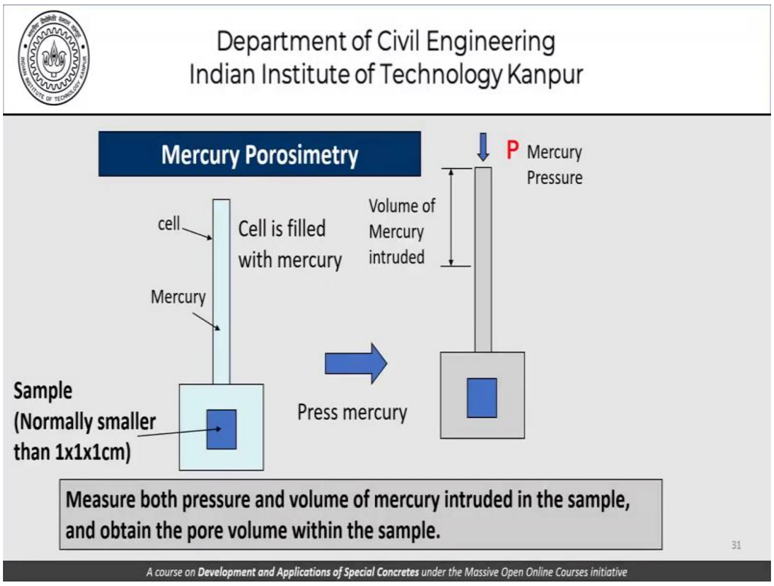

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Mercury Porosimetry

Measure both pressure and volume of mercury intruded in the sample, and obtain the pore volume within the sample.

This is the picture of a mercury porosimeter cell. We use our hcp here, which is a very small sample, 1 centimetre by 1 centimetre, maybe sometimes even smaller. Fill this cell with mercury and then as we apply the pressure. This mercury moves away that is this mercury which was here moves down to this place. Now, where did this mercury go it went into the sample that we have.

And, once we know what pressure we have applied, we know that equation, then we will say, that ok this is the amount of volume of pores which will get filled in this material at pressure P. We go to the next pressure step, again a certain amount of mercury will be intruded. Let us say, it is that much and this amount of mercury is now filling up the smaller pores. Next, amount of mercury is filling the even smaller pores and so on.

So long as we measure both the pressure applied and the volume of mercury intruded in the sample, we can obtain the pore volume and the pore size distribution within the sample.

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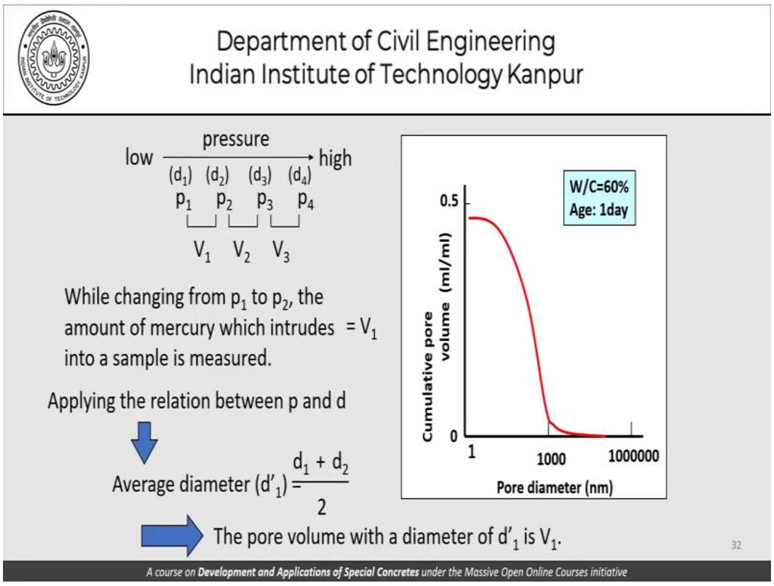

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low $\xrightarrow{\text{pressure}}$ high

(d_1) (d_2) (d_3) (d_4)

p_1 p_2 p_3 p_4

V_1 V_2 V_3

While changing from p_1 to p_2, the amount of mercury which intrudes $= V_1$ into a sample is measured.

Applying the relation between p and d

Average diameter $(d'_1) = \frac{d_1 + d_2}{2}$

The pore volume with a diameter of d'_1 is V_1.

Now, having said that this is what we really do, we keep applying pressure from the low end to the high end and we keep getting volumes of mercury intruded. The volumes of mercury intruded V_1, V_2 and V 3. The pressure is being changed from P 1 to P 2 to P 3 to P 4, at P 1 some d 1 is there that is one number. When we go from P 1 to P 2 in this range all the pores between diameters d_1 and d_2 will be filled.

And therefore, the average diameter for this would be taken as $d_1 + d_2$ by 2.
Average diameter = $(d_1 + d_2)/2$.
So, that is how we determine the cumulative pore volume using mercury porosimeter and this is one of the pictures that we have for a cement paste of what is cement ratio 60% at an age of one day. So, you can draw your own conclusions there is a lot of information that needs to be given to you in order to be able to make meaningful conclusions from here.

So, this is just an illustration of how this cumulative pore volume looks like with respect to the pore diameters.
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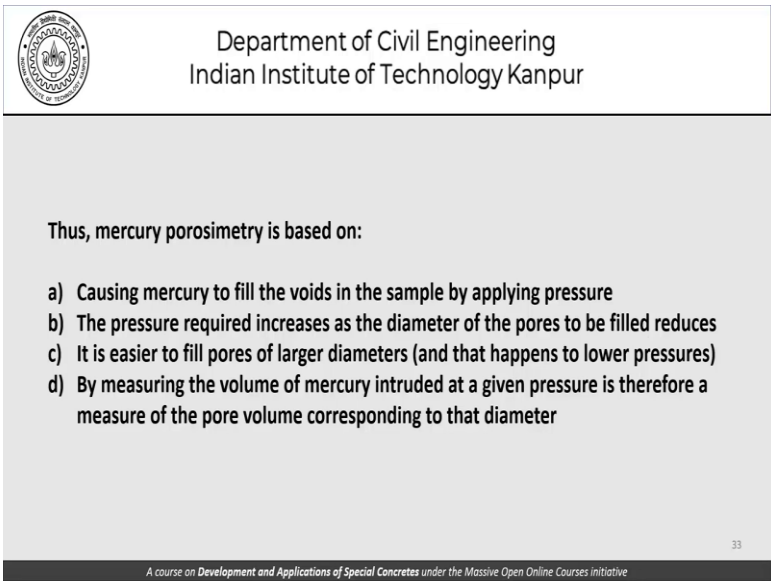

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Thus, mercury porosimetry is based on:

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

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Now, this mercury porosimeter or the summary 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 at lower pressures, lower pressures higher diameters, higher pressures lower diameters. By measuring the volume of mercury intruded at a given pressure is therefore a measure of the pore volume corresponding to that diameter.

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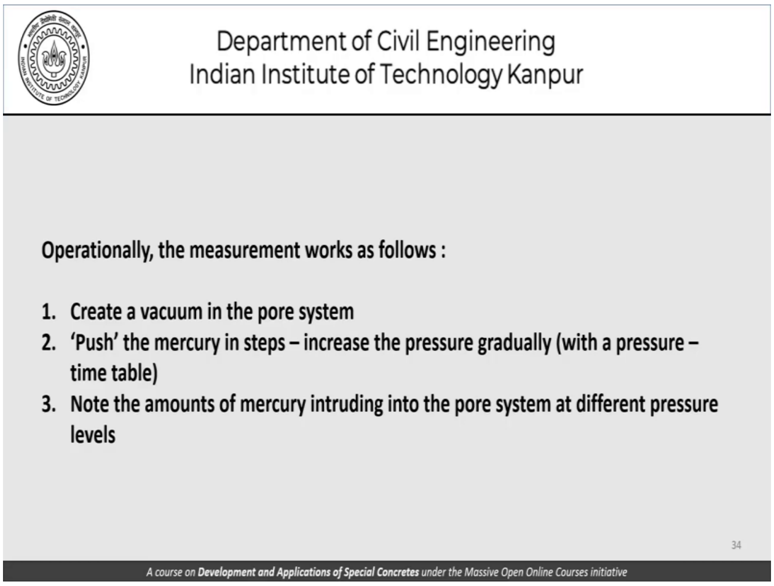

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Operationally, the measurement works as follows :

1. **Create a vacuum in the pore system**
2. **'Push' the mercury in steps – increase the pressure gradually (with a pressure – time table)**
3. **Note the amounts of mercury intruding into the pore system at different pressure levels**

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And, operationally the measurement works as follows. Create a vacuum in the pore system push the mercury in steps, increase the pressure gradually, use a pressure time-table and note the amounts of mercury or the volumes of mercury intruding into the pore system at different pressure levels.

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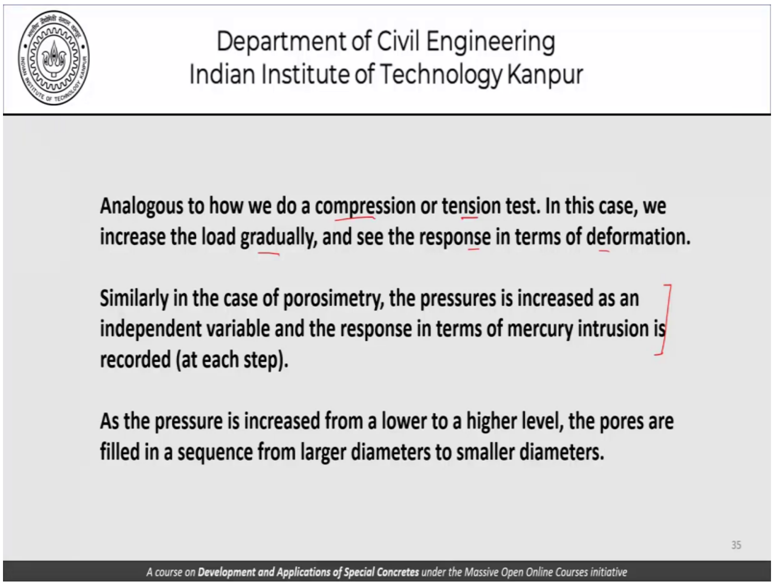

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Analogous to how we do a compression or tension test. In this case, we increase the load gradually, and see the response in terms of deformation.

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).

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.

This discussion of applying pressure in steps and measuring the amount of mercury intruded is analogous to how we do a compression or a tension test. In this case i.e., in the case of compression or tension tests. The load is applied gradually and we see the response in the specimen in terms of deformation. But here what we do is, increase the pressure gradually with the pressure time table and measure the volume of mercury intruded.

So, this is what is given here in words I just said that 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. And, as the pressure is increased from a lower to a higher level the pores are filled in sequence from larger diameters to smaller diameters. Now, this is all very nice.

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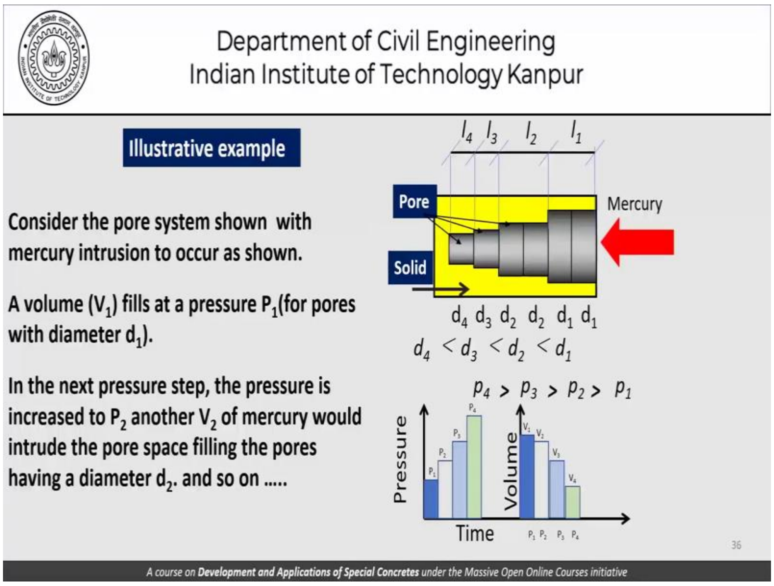

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Illustrative example

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 next pressure step, the pressure is increased to P_2 another V_2 of mercury would intrude the pore space filling the pores having a diameter d_2. and so on .....

What it says is, that so long as we start filling the pores from here the larger diameter, this smaller than that, smaller than that, smaller than that, we will keep getting differential pore volumes and we will get the total pore volume as far as this system is concerned. So, this is what we will get. We will get the pressure, we will get the volumes, we can get the differential pore volumes, how much volume was intruded in the diameter d_1, d_2, d_3 and d_4. The way we have shown it d_1 and the pores corresponding tod 1 are the largest. But this is schematic representation, so if we sum this up, we will get the cumulative volumes.

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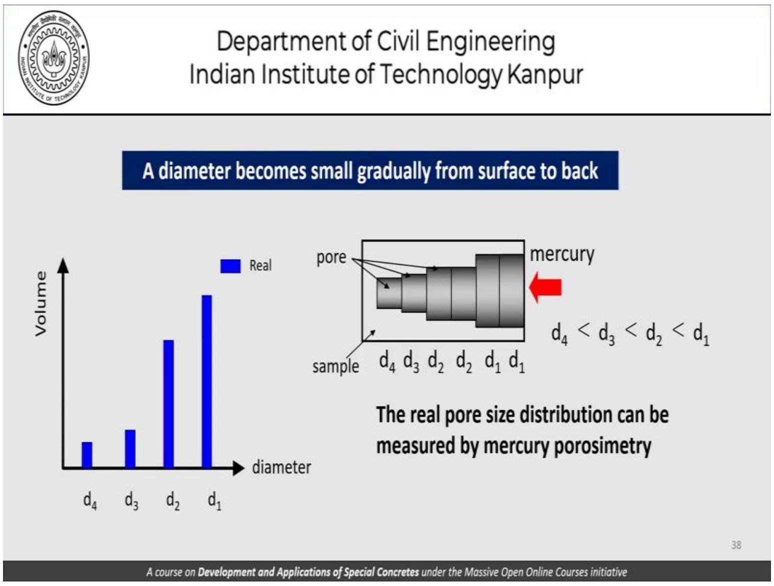

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A diameter becomes small gradually from surface to back

The real pore size distribution can be measured by mercury porosimetry

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As the diameter becomes small gradually from the surface to back, now this is something which we have assumed that as mercury is being intruded the smallest diameters are sitting conveniently hidden at the back. And, here we have a larger diameter than this, here we have a larger diameter than these, here we have a larger diameter than this. So, the diameters are very nicely arranged and that is what the beauty of a presentation. I can put my diameters or the pores any which way I like. And, we will get a pore size distribution the weight is shown.

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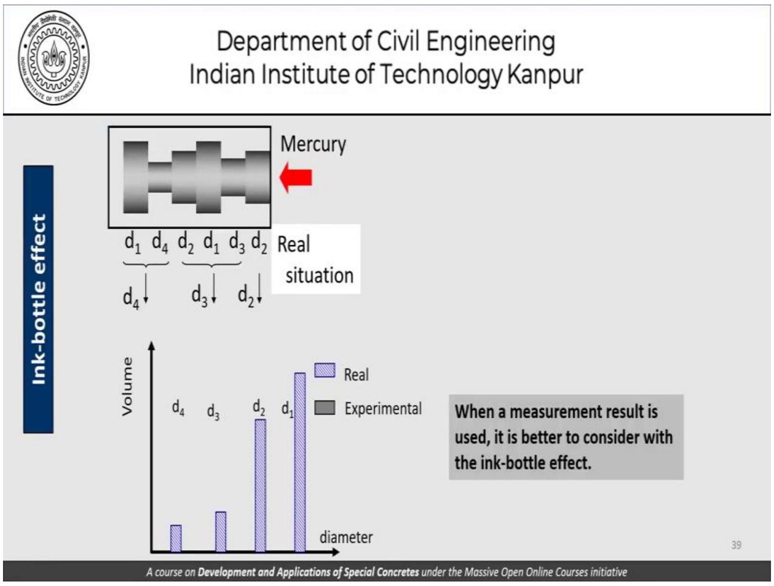

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Ink-bottle effect

When a measurement result is used, it is better to consider with the ink-bottle effect.

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In a real situation however, that may not happen we may have some diameters sitting here with d_2 or some pore sitting here with the diameter d_2, d $_3$, d_1, d_2 again d $_4$ here and d $_1$ here. Now, in this kind of a situation how will mercury porosity work? What is the kind of thing that will happen? What will happen is that when the pressure is p 1 which would have normally filled a diameter of d 1 mercury will not intrude in the sample because the first diameter that it encounters is not D 1 but D 2.

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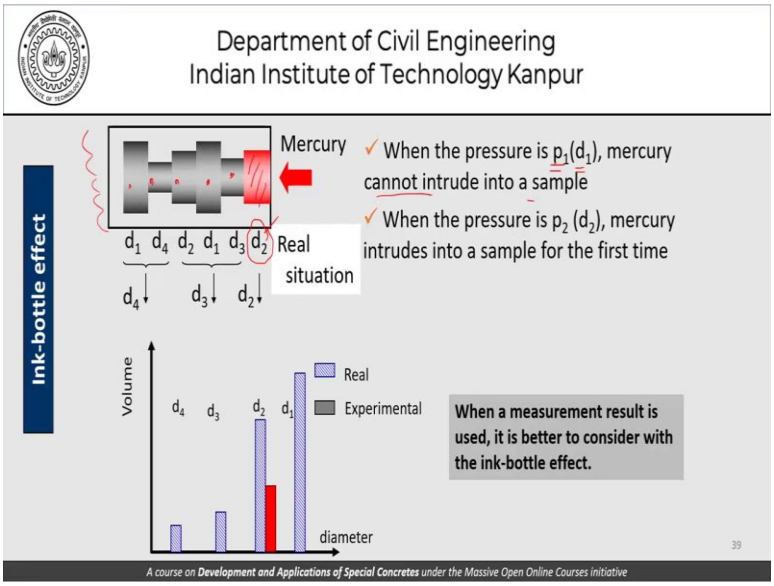

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Ink-bottle effect

✓ When the pressure is $p_1(d_1)$, mercury cannot intrude into a sample

✓ When the pressure is p_2 (d_2), mercury intrudes into a sample for the first time

When a measurement result is used, it is better to consider with the ink-bottle effect.

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Having said that, further when the pressure is increased to p 2 which corresponds to the filling of pores with diameter d 2 the mercury intrudes into the sample for the first time and this space gets occupied. In the next pressure step when we go to p 3 it is not only this diameter or this space which is getting filled but also this and this because these diameters are larger than this. The pressure being applied is for this diameter obviously it will fill these two diameter pores also and that is an error.

This is not the real pore size distribution this entire this volume here this entire volume here is getting counted as if it was d 3. Similarly in the next pressure step when it comes to d 4 corresponding to p 4 this volume will also get counted as if it was a d 4 pore. So, this is something which is a bottleneck here. Now, this is something which we should keep at the back of our mind try to understand this effect as far as mercury porosimetry is concerned, this kind of a limitation.

And, this limitation is called the ink bottle effect. I am not sure how many of you have used fountain pens and you are familiar with an ink bottle, it used to be something like it used to look something like this. And, there was a mouth here the diameter here was much smaller than the diameter of the bottle here that is precisely what is happening here. So, this small mouth here with the larger diameter here gives us erroneous results. But then that is the best, that we can do and therefore we live with it.

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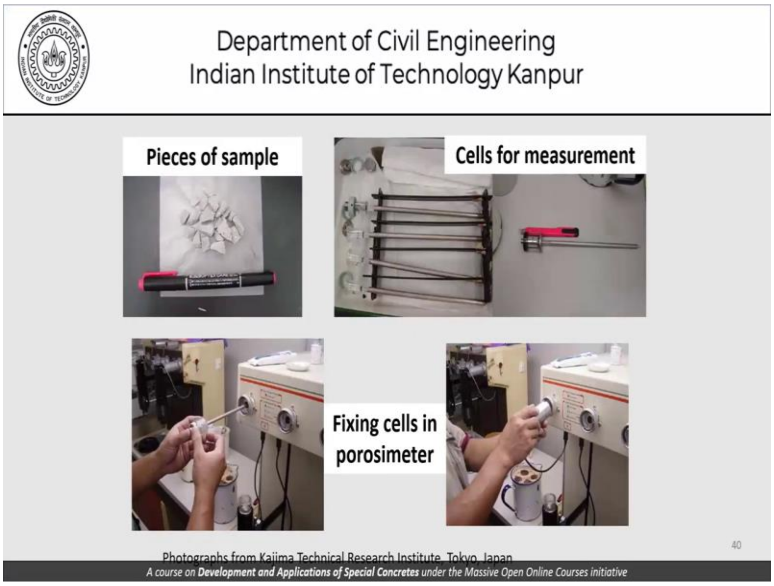

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Pieces of sample

Cells for measurement

Fixing cells in porosimeter

Photographs from Kajima Technical Research Institute, Tokyo, Japan

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This slide here shows pictures of the mercury porosimeter in actual practice, the actual experiment we can see here some samples which have been taken off from hardened cement paste. This is the cell that we talked about. These cells have these things here i.e., the cell this is the stem and the samples are placed inside this stem and these cells are placed inside this machine here locked up and then mercury is filled into these cells and finally the pressure is applied to make sure or measure how much mercury intrudes into the samples which have been placed inside this cell.

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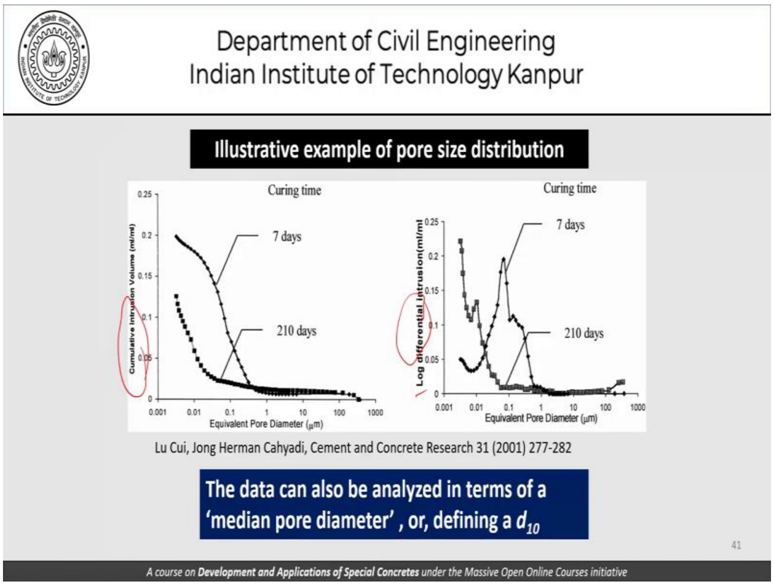

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Illustrative example of pore size distribution

Lu Cui, Jong Herman Cahyadi, Cement and Concrete Research 31 (2001) 277-282

The data can also be analyzed in terms of a 'median pore diameter' , or, defining a d_{10}

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Now, with this kind of a study we get this kind of distributions. This here is the cumulative distribution i.e., the cumulative pore volume and here is the differential pore volume. It is a matter of detail that sometimes we use the log scale to plot some of these numbers bear in mind. And if you read this kind of literature, please be careful how the authors talk in terms of the ink bottle effect and interpret the results from mercury porosimetry for hardened cement paste.

There are other terms that are used in this context. Sometimes we talk in terms of a median pore diameter or a d_{10} and I am leaving it to you to think about it to determine or find out the definitions of a median pore diameter or a d_{10} when it comes to the porosity and pore structure of hardened cement paste. And, obviously you will find that the hardened cement paste, the pore size distribution and the cumulative pore volume they are a function of the water-cement ratio, the kind of cement that we use and so on and so forth.

Let me conclude by saying that, hydration as a process leads to two things one is a reduction in the total pore volume and the other is a refinement of the pore structure. We probably spend some more time in some other class in explaining these two but I am sure a lot of you actually understand what these two things mean. And, with that I am coming to an end of the discussion today it has been a long discussion.

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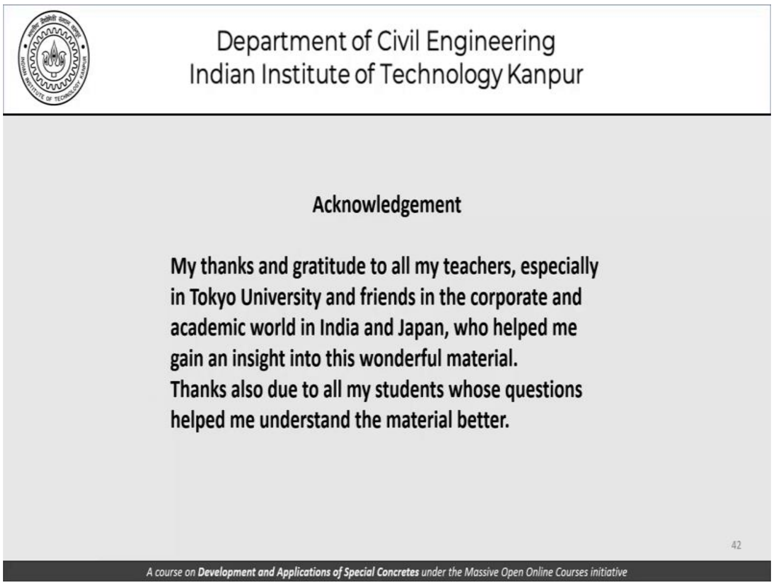

Acknowledgement

My thanks and gratitude to all my teachers, especially in Tokyo University and friends in the corporate and academic world in India and Japan, who helped me gain an insight into this wonderful material.
Thanks also due to all my students whose questions helped me understand the material better.

And, I must express my gratitude to all my teachers and students, friends. Thank you once again and I look forward to continuing this discussion with you on special concretes.