Characterization of Construction Materials
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Lecture -59
Porosity and Pore structure - Introduction, Significance of Pore Distribution

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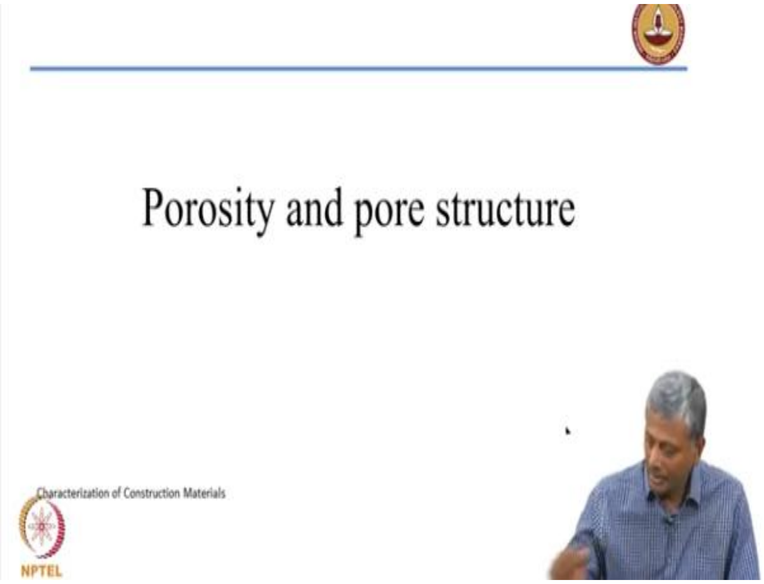

Porosity and pore structure

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So this chapter deals with the study of porosity and pore structure. Now you know that we have been dealing with cementitious materials and in general any construction material is a porous solid. The pore sizes and the distribution of the pores in the volume of the material have a lot of significance with respect to the kind of performance exhibited by these materials. So we need to look at techniques where we can actually assess the extent of porosity that is available in the system and the distribution of different pore sizes that govern the behavior of such materials in different environments.

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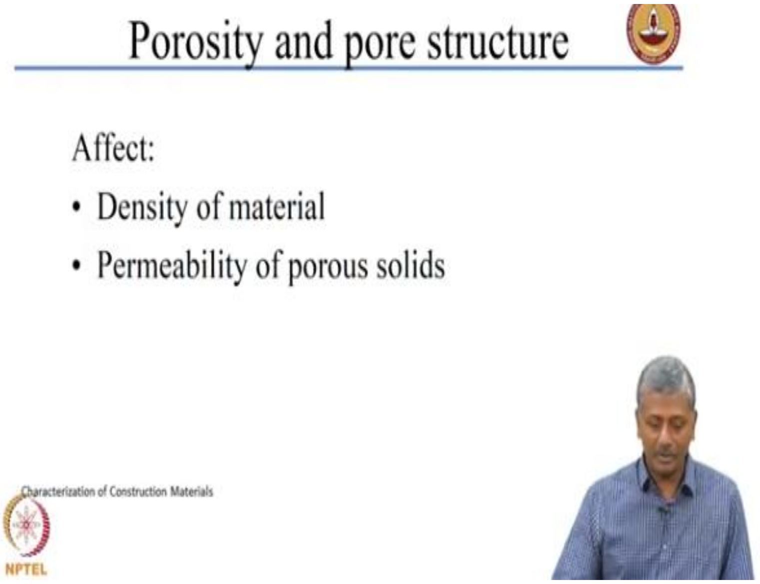

Porosity and pore structure

Affect:

- Density of material
- Permeability of porous solids

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So, porosity and pore structure, both obviously affect the density of the material and in terms of construction materials, we are interested in understanding the permeability because permeability is the driving factor which leads to the ingress of aggressive species and water from the external environment into the concrete that leads to other types of deterioration. So porosity and permeability are two very important characteristics with respect to construction materials. And we need to characterize the materials to assess their pore structure which controls both these parameters.

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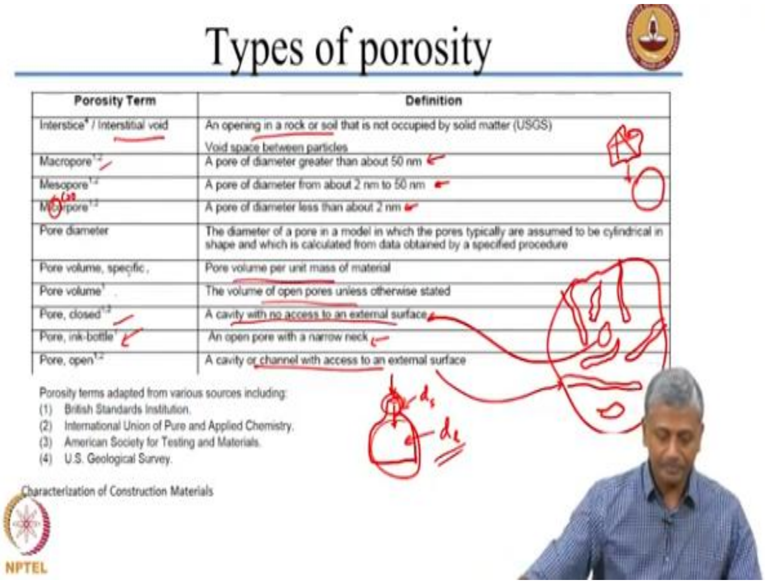

Types of porosity

Porosity Term	Definition
Interstice[4] / Interstitial void	An opening in a rock or soil that is not occupied by solid matter (USGS) Void space between particles
Macropore[1,2]	A pore of diameter greater than about 50 nm
Mesopore[1,2]	A pore of diameter from about 2 nm to 50 nm
Micropore[1,2]	A pore of diameter less than about 2 nm
Pore diameter	The diameter of a pore in a model in which the pores typically are assumed to be cylindrical in shape and which is calculated from data obtained by a specified procedure
Pore volume, specific,	Pore volume per unit mass of material
Pore volume[1]	The volume of open pores unless otherwise stated
Pore, closed[1,2]	A cavity with no access to an external surface
Pore, ink-bottle[1]	An open pore with a narrow neck
Pore, open[1,2]	A cavity or channel with access to an external surface

Porosity terms adapted from various sources including:

(1) British Standards Institution.
(2) International Union of Pure and Applied Chemistry.
(3) American Society for Testing and Materials.
(4) U.S. Geological Survey.

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So what are the different types of pores that you can find in your system? First of all, what is the distinction between a pore and a void? Generally when we refer to the term void, we refer to a 3-dimensional entity in the system. Of course that does not mean pore is 2 dimensional; but by 3-dimensional we mean that there is a finite size to a void. Whereas a pore can be of a length scale that is much larger as opposed to a void which is of a very small finite length scale. Now while I say that, I should also tell you that a discrete entity in the system is generally termed as a void whereas an entity which is more or less continuous in the system is a pore. So generally the definition most commonly accepted for an interstitial void or an interstice is an opening in a rock or a soil or other solids that is not occupied by solid matter.

So truly speaking, a pore also falls in the category of a void; but for purposes of distinction we generally refer to voids as the 3 dimensional spaces that are created in the system which have a finite size in all 3 directions. A pore on the other hand can have an almost infinite size in 1 direction, whereas in the other direction it is either circular or square or rectangular whatever the shape of the pore may be or even irregular. But in the third direction, it is almost an indefinite connection of different small spaces, which leads to a channel being formed in your solid.

So those pores based on the diameters or size of the openings, can be characterized as macro-pore where the diameter is greater than 50 nm. We are talking about still macropore but greater than 50 nm. Mesopore - which is between 2 and 50 nm. And micropore - which is of pore diameter less than 2 nm. Now again, we say micro, but actually it is in nano scale the pore diameter is in the nano-scale ranges.

The pore diameter is the diameter in a model in which pores are assumed to be cylindrical. Now, you may have irregular shaped pores also. What you need to do is convert this irregular shape pore by taking measurements to an equivalent diameter. So if you convert this to an equivalent circle, what would be the diameter of the circle, basically that represents the pore diameter.

Specific pore volume is pore volume per unit mass of the material. Overall pore volume is the volume of open pores unless otherwise stated. Now what is an open pore and a closed pore? An open pore is a cavity or a channel which has access to the external surface. So in terms of porous solids like aggregate or concrete, these are the pores that are open to ingress of moisture from the outside. Whereas, a closed pore is a cavity with no access to the external surface. So you may have a solid, in which you have lot of porosity, which has connection to the external surface, but there may be also smaller voids and pores which are inside the volume of the solid which do not have any access to the external surface. So an open pore is here, and that is basically your close pore (as shown in figure drawn)

In some cases, you have pores which are called ink-bottle pores. So, what is the shape of an ink-bottle? Many of you probably are not even aware of ink-bottles because you may not have used ink-bottles in your student life, but in our student life the ink bottle was an inseparable entity we used to carry our ink pens and ink bottle for any examination and whenever the ink gets over we need to actually draw the ink from the bottle. So ink-bottle looks like this, you have a diameter which is small at the top and a diameter which is larger at the bottom. So now what will happen if you consider this to be a pore, supposing a fluid has to actually penetrate this pore, it has to penetrate with a pressure that is equivalent to the smaller diameter. But once it crosses that it will suddenly fill up a very large volume because the pressure to cross this diameter is much greater than the pressure required to fill up the smaller diameter. You know, very well that the pressure is inversely proportional to the diameter. That is basically the basis of your mercury intrusion porosimetry experiment. So again, that is called an ink-bottle pore - when you have a large pore, that is having a smaller pore at its opening. So it’s an open pore with a narrow neck - that is an ink bottle pore.

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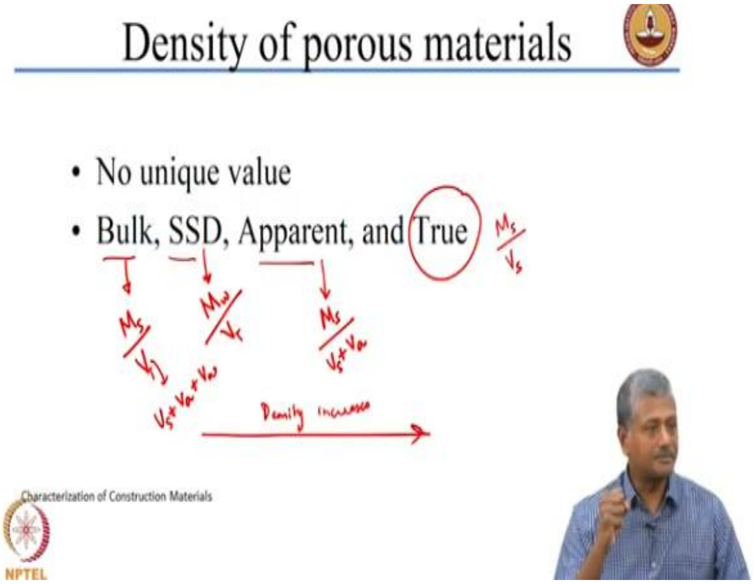

Density of porous materials

- No unique value
- Bulk, SSD, Apparent, and True

$\frac{M_s}{V_s}$

$\frac{M_s}{V_T}$ $V_s+V_a+V_w$

$\frac{M_w}{V_t}$

$\frac{M_s}{V_s+V_a}$

Density increases

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So how do we determine density of porous materials? We know that there is no unique value because there is no way that we can actually completely remove the solid part and completely remove the pores and quantify both. So we go with different types of estimates we have the bulk specific gravity or density, we have the saturated surface dry value, we have the apparent density which is closest to the true density. And then we have the true density which is nothing but the mass of the solid in the material divided by volume of the solid (M_S/V_S). Because your porous solid is a mixture of pores and solids. The true density is nothing but mass of the solid by the true volume of the solid.

Now if you take an aggregate piece, how to determine the true volume of the solid. You cannot, even when it is dry you have porosity inside, you have the volume of the air and water that is present in the system. So that is why we come close to it by calculating the apparent density, which is the mass of the solid divided by the volume of solid plus volume of air that is in the system. But then for the most part - we use the bulk density, which is the mass of the solid by total volume (Total volume is obviously $V_{solid} + V_{air} + V_{water}$) where V_{water} is volume of water is the volume that fills up from the accessible porosity of the surface of the voids.

What about SSD? It is basically wet mass divided by total volume. So as you go from bulk to true, your density increases. Now this you have already done in your basic construction materials courses, so I will not really touch upon how you measure the density - that is something you all know very well, we can measure the density using a pycnometer or we can measure density using the suspended mass method applying Archimedes principle.

So we will not go through that. What we will try to do now is try to see how we assess beyond the accessible porosity, can we actually determine what the network of this porosity is which causes the absorption of the moisture or other aggressive chemicals into the material.

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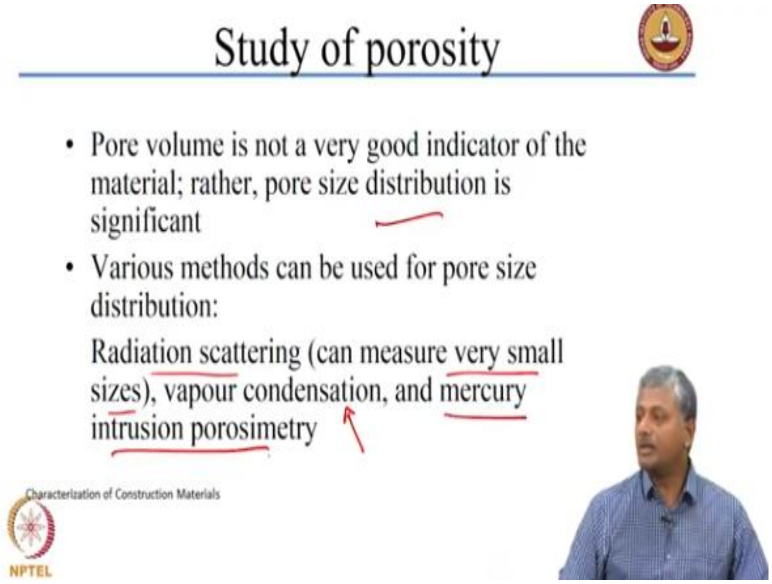

Study of porosity

- Pore volume is not a very good indicator of the material; rather, pore size distribution is significant
- Various methods can be used for pore size distribution:

  Radiation scattering (can measure very small sizes), vapour condensation, and mercury intrusion porosimetry

So we are worried more about the pore size distribution. So pore volume is not a very good indicator of the material, but the pore size distribution is the parameter that we want to look at for its significance in relating to the other characteristics or performance of the construction material. So there are different methods which can be used to assess pore size distribution. One is radiation scattering - what is radiation scattering is if you have radiation like X-ray, which is interacting with your material, we know that part of this X-ray gets rebounded and part of it gets absorbed, some of it may get transmitted, when it gets transmitted it will get scattered. So by looking at the extent of scattering that happens in a porous system, we can try to understand the pore size distribution of the material, of course, but what happens is although we can resolve very small sizes using radiation scattering it is a very difficult experiment to perform.

So we want to actually look at easier methods - one of those is vapour condensation. You have learnt earlier about the use of the BET technique to determine the surface area of powders. Now please remember in that same technique you can also determine the surface area of the open porosity that is present inside the system because the vapor will start condensing on all surfaces that are available in your system. So if you want to determine the porosity or pore size distribution in a solid chunk of concrete, which has lot of these interconnected pores, you will actually start depositing the vapor or condensing the vapour in those locations also, there will be adsorption happening on the surfaces of your pores also. So the amount of adsorption will be related to the overall surface area that is available inside the system. That is how we calculate the fineness of very fine powders for instance using the BET method but the same technique can be modified to actually obtain the surface area of the porosity that is present in the system and lead you to determine the pore size distribution also.

But again that is an indirect method of determining your pore size distribution. That is a good method to detect the amount of reactive surface that is available for instance. But for determining pore size distribution, may be it is a very indirect measurement. The direct measurement for pore size distribution is Mercury Intrusion Porosimetry.

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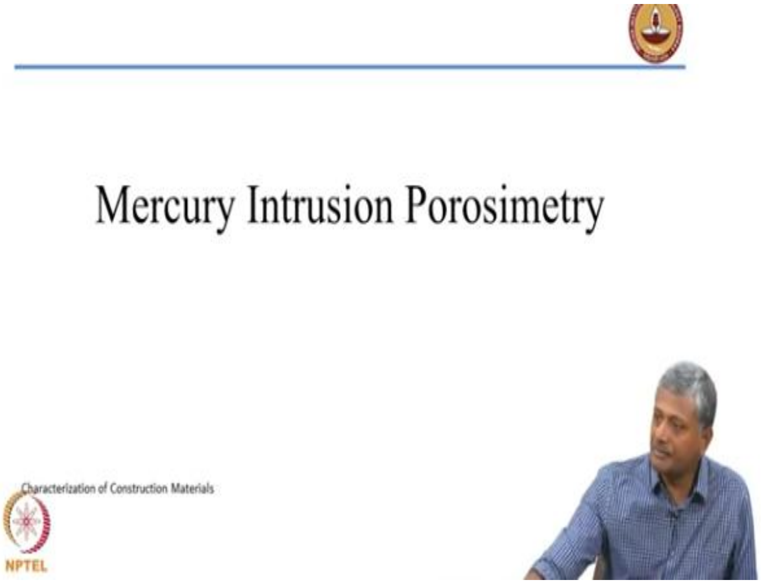

Mercury Intrusion Porosimetry

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Of course, the term mercury intrusion porosimetry deals with the penetration of mercury into porous solids, which determines the pore structure of these pores solids. But the first question is why do we use mercury? (Atomic size of mercury is much larger as compared to other commonly known species like water for instance mercury has a much larger size particle) But there is a characteristic of mercury which makes it very suitable for such measurements:

- It does not react definitely in porous systems like concrete or rock or brick, mercury will not react definitely.
- The mercury has a non-wetting characteristic, so this way we are able to fill the pores without any adherence to the pore surface. So it directly simply fills the pore without getting adhered to the pore surface. So that is a very positive thing for us because all we need to do is keep on applying more and more pressure with which the mercury will penetrate smaller and smaller pores in your system.

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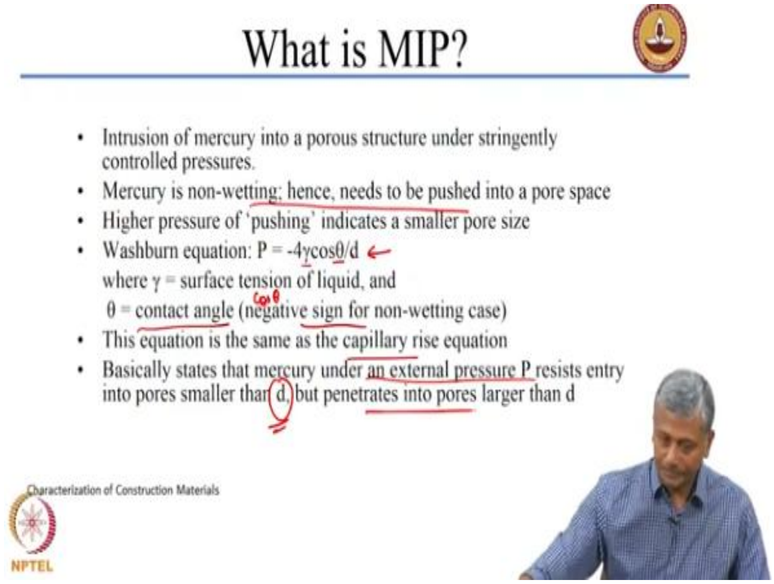

What is MIP?

- Intrusion of mercury into a porous structure under stringently controlled pressures.
- Mercury is non-wetting; hence, needs to be pushed into a pore space
- Higher pressure of 'pushing' indicates a smaller pore size
- Washburn equation: $P = -4\gamma\cos\theta/d$ ←
  where γ = surface tension of liquid, and
  cos θ
  θ = contact angle (negative sign for non-wetting case)
- This equation is the same as the capillary rise equation
- Basically states that mercury under an external pressure P resists entry into pores smaller than d, but penetrates into pores larger than d

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So intrusion of mercury into a porous structure under stringently controlled pressures is basically your mercury intrusion porosimetry. So all you need to do is simply push mercury into a pore space. If you use water there will be absorption of water directly by the pores, but mercury even if you put a block of concrete and mercury it is not going to go in. It needs some pushing it needs to be pushed under pressure. Will mercury open the pores? Yes and no; we will come back to that question later. So higher pressure of 'pushing' obviously indicates a smaller pore size, we know that the pore pressure is related inversely to the diameter of the pore, you have done the capillary rise experiment before, you know, that the lower the diameter, the higher the capillary rise, obviously high capillary rise means higher pore pressure.

$$P = \frac{-4\gamma\cos\theta}{d}$$

Where γ is the surface tension of the liquid

θ is the contact angle (negative sign for non-wetting case).

So pore pressure is related to these factors one is γ which is surface tension of the liquid and θ which is the contact angle that the liquid makes with the surface. Now Cos θ has a negative sign for a non-wetting case. Angle made with the surface is obtuse not acute. So equation for MIP is quite similar to your capillary rise equation - the Laplace equation that we typically use the capillary rise. The Washburn equation is actually quite similar to that. So Laplace equation is again using radius (r) instead of diameter and because of that this becomes $P = \frac{-2\gamma \cos\theta}{r}$. So you get the same sort of an equation. So in general what is happening in this experiment is you have mercury which is pushed into the porous system under pressure and mercury under an external pressure 'P' will resist any entry into the pores which are smaller than the particular size 'd' governed by this equation. So if your diameter that you need to intrude is 1µm, the pressure that you need to apply will be directly determined from this equation. But if you have pores larger than 'd', the mercury will easily enter the pores at that pressure. So if you keep changing the pressure you will be penetrating pores that are smaller and smaller; keep increasing the pressure you penetrate pores that are smaller and smaller and by assessing the pressure or conversely the diameter of penetration you can now get a pore size distribution of your system.

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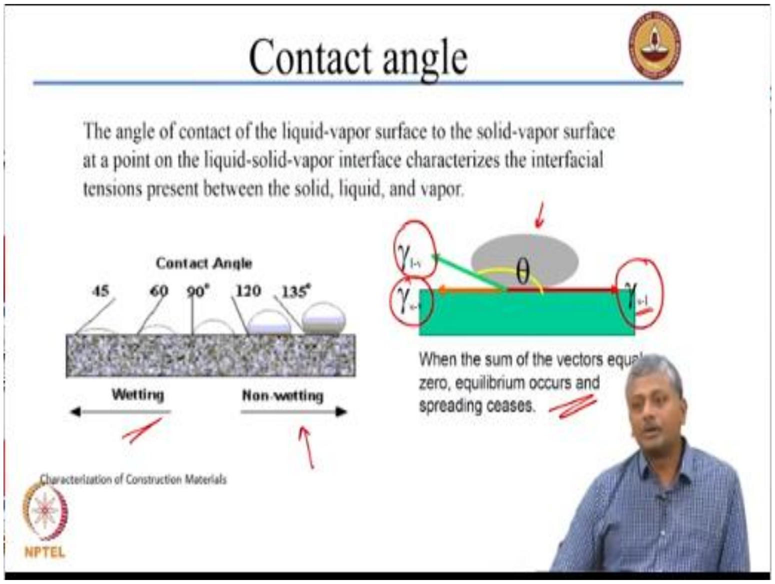

Contact angle

The angle of contact of the liquid-vapor surface to the solid-vapor surface at a point on the liquid-solid-vapor interface characterizes the interfacial tensions present between the solid, liquid, and vapor.

When the sum of the vectors equa zero, equilibrium occurs and spreading ceases.

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Now again just to refresh your memory on contact angle - this is the angle of contact with the liquid-vapour surface to the solid-vapour surface at a point. So again here, for example, when you have this droplet of liquid sitting on a solid surface, there are different forces that are acting. You have the surface tension of the solid-liquid interface, you have the surface tension of the solid-vapour interface and surface tension of the liquid-vapour interface. Now depending upon the relative surface tension values, you can actually get a characteristic of the droplet to be wetting or non-wetting.

In the case of water, what will happen? The surface tension of the solid-liquid interface will govern much more and the droplet will simply spread across. So when the sum of the vectors equals to 0, you have equilibrium that is occurring and the spreading ceases. So in such cases, for example, if you drop mercury on a solid surface, what happens? It does not spread. So it has a state which is non-wetting. So, how do you make this table surface non-wetting even to water? We coat it with a varnish. We put varnish on tables and then it becomes non-wetting. Of course non-wetting of a wood also implies that you increase the lifetime of the wood because only by wetting you decrease the properties of wood. So again the contact angles for wetting liquids are acute and for non-wetting liquids the contact angles are obtuse.

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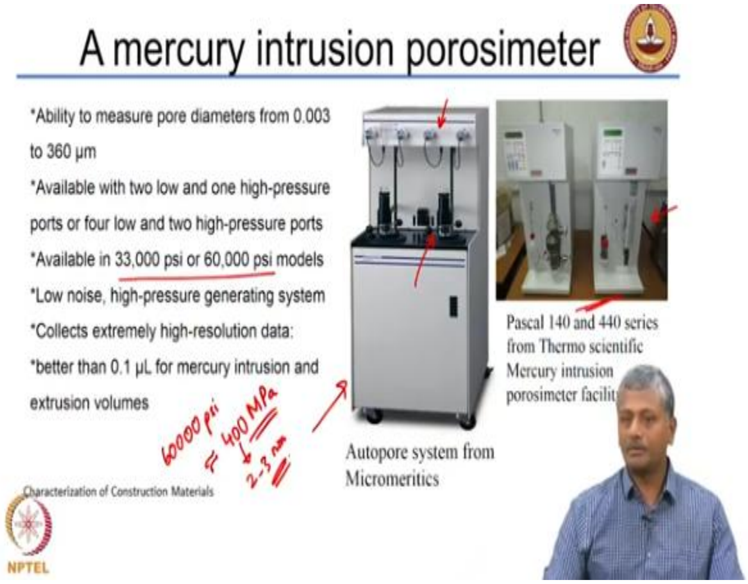

A mercury intrusion porosimeter

- Ability to measure pore diameters from 0.003 to 360 μm
- Available with two low and one high-pressure ports or four low and two high-pressure ports
- Available in 33,000 psi or 60,000 psi models
- Low noise, high-pressure generating system
- Collects extremely high-resolution data:
- better than 0.1 μL for mercury intrusion and extrusion volumes

Autopore system from Micromeritics

Pascal 140 and 440 series from Thermo scientific Mercury intrusion porosimeter facilit

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So this is a typical mercury intrusion porosimeter. So this is a system from Micromeritics, which is a very popular instrument across the world and this is something that we have our lab, it’s from Thermo scientific - it is called the Pascal 140 and 440 series.

Now, the concept is quite similar - you have two ports; you have a low pressure port and a high pressure port. So we know that our porous materials have a range of pore sizes. Some of those do not need a very high degree of pressure to be filled. But some pores which are extremely small need extremely high pressures for filling. So generally what happens is you have low pressure ports located separately and then the high pressure ports also located separately. So again, this Pascal system also has the low pressure and high pressure systems presented separately for the instrument.

So first you start off by using your sample inside the low pressure port. So where you evacuate and create a vacuum like condition so that you are starting off with very small pressures and then you are pushing mercury at those pressures. Once you come out to the atmospheric pressure, you then remove the sample from the low pressure port and put it inside the high pressure port, where you start applying pressure beyond the atmospheric to all the way up to about 60000 psi (which is almost equal to about 400 MPa), so the pressure applied in the high pressure port can go all the way up to about 400 MPa and this 400 MPa corresponds roughly to about 2-3 nm sized pores and in most of our porous systems that extent of determination is more than enough you do not really need to go much further down.

Now we saw earlier when we tried to use something like a scanning electron microscopy study for understanding pore systems, that we were severely restricted by the extent of resolution we can get at high magnifications. When you want to use the backscatter system, we discussed that the highest magnification you can get probably is about 5000, 6000x and not more than that. Now when you use a secondary electron imaging system, you can get 200,000, 300,000x but to understand the size and shape of a pore using secondary system will be very difficult. So you'd rather use a backscatter system with a polished surface so that the pores are directly cut across to determine the size and shape of the pores. But because of the resolution difficulties it becomes quite difficult to resolve pores that are anything smaller than may be tenths of a micron. You can probably get 1 µm resolution easily in SEM, but going to less than tenth of a micron that is about 100 nm, becomes very difficult with respect to scanning electron microscopy. But here with MIP, you are actually reaching a pore range that can be detected up to 2 - 3 nm, so you are actually in a completely different scale with respect to SEM.

You also have to be aware of when you need to do this experiment. As I have discussed several times before in this course, the more sophisticated the technique the more expensive it becomes and probably the less representative also it becomes. So for example, if you want to just determine the pore structure for the purposes of understanding relative differences in water absorption by different concrete systems, what type of technique would you use? You may just stop with some macro-level techniques like water absorption or sorptivity. And that could actually give you substantial differences in different types of concrete without having to go through a MIP study or an SEM study to determine the pore structure. So all those become very complicated and expensive - SEM and MIP, so you need to understand what is it that you are trying to resolve.

However, now you are trying to resolve something like what happens to the pore structure of the paste when you reduce the water-cement ratio, or when you use a new type of binder. Now the effect that you get on concrete with the help of sorptivity or absorption experiment is a bulk measurement and you may not be able to get the finer nuances of what happens at the paste level. For that it is reasonable to go for a higher level investigation using scanning electron microscopy or mercury intrusion porosimetry.

Now with MIP we can go down to very small pore sizes but you also have to understand that we are using a material that is highly toxic - mercury is highly toxic and because of this toxicity of the mercury and the fact that even at temperatures of more than 25 °C, the vapours of mercury itself can cause toxicity. The usage of mercury is banned in several countries for such purposes. So the mercury intrusion porosimeters are very powerful devices to understand cementitious material; but the usage of MIP is declining day by day because many countries are now banning mercury intrusion porosimetry technique because of the use of mercury. So, there may be a day when we cannot use this technique anymore but in the next segment I will show you as to what would be the significance of using MIP and how it actually helps us distinguish performance of different types of cementitious materials.