Flow through Porous Media

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Lecture - 59
Characterization

I welcome you to this lecture of Flow Through Porous Media. We are almost near the end of this course. And, in this particular lecture, I am going to talk about Characterization of a porous media. In particular, how to measure for example, porosity, how to measure the internal surface area of a porous matrix because these are all very important if one wants to use porous media as a catalyst, then surface area is extremely important basically because of this advantage of high surface area of porous medium is chosen for as a catalyst.

I mean catalyst material is deposited on a porous media just for this reason so that you can utilize the high surface area. And, similarly what is how to calculate the pore volume if it is oil and water trapped in an reservoir in sub surface then how much is; how much is trapped so, that depends on what is a pore volume. Similarly, what is the transport I mean how well this fluid can be transported to this through this to this porous media, what kind of pore size distribution it has.

So, these are very important parameters and one is to characterize the porous media with respect to this parameters. So, this is something which we going to discuss in this lecture.

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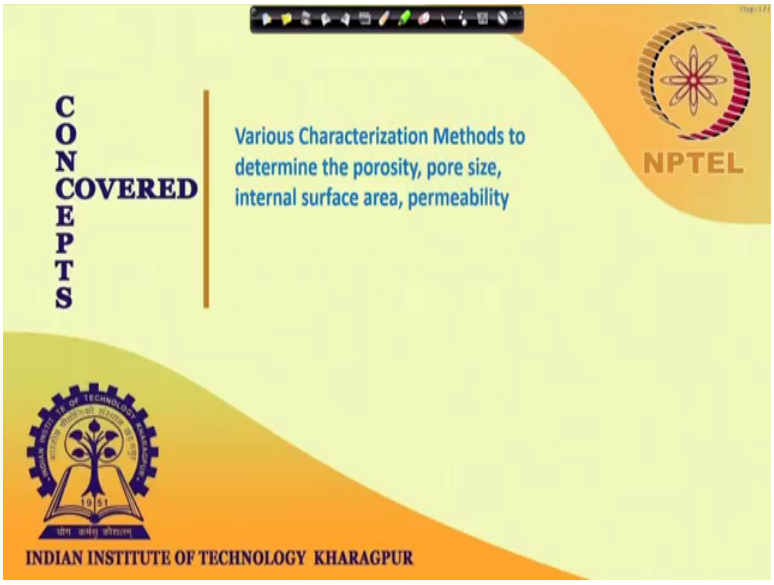

So, we are going to talk about various characterization methods to determine the porosity, pore size, internal surface area, permeability.

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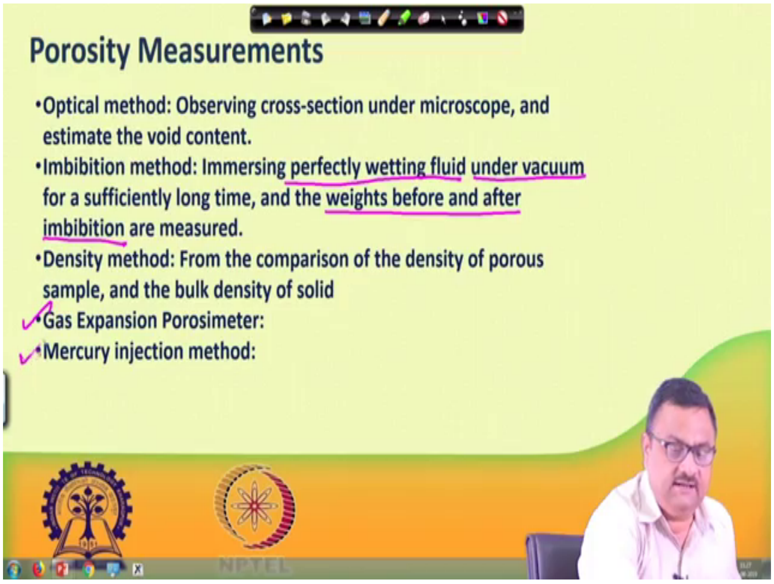

First thing is porosity measurements. See porosity measurements, porosity is all we started with by definition of porosity it is basically the void volume divided by the total volume. In 1 meter cube of total volume of this porous media if out of one out of 1 meter cube if we see 0.2 meter cube is the void area and 0.8 meter cube is the solid area, then 0.2 divided by 1, so, porosity would be 0.2.

So, now, this porosity can be measured by different methods as pointed out here. The first one described here is optical method where one can observe the porous medium under a microscope observe the cross section under the microscope and estimate the void content. That means, if you take a cross section if you take a slice of the porous media and then put it under a microscope then you will see some parts are occupied by the solid and then some part as void space.

So, now one can calculate one can find out which part; which part of the area that we are looking at which part is solid and which part is void and from there one can do this calculation to find out what is the porosity right. So, that would be probably applicable per unit depth perpendicular to the image that is taken. So, that porosity can vary I mean one can take different slices at different actual at different actual positions and can find out what is the porosity variation. So, one way to look at it is obviously, the direct method which is optical method observe which part is void and which part is solid ok.

The second method is known as imbibitions method; imbibitions method is immersing perfectly wetting fluid under vacuum for a sufficiently long time and the weights before and after imbibitions are measured. That means, when you first of all there are you must note couple of things here one is that this has to be there has to be vacuum. So, this is under vacuum and then it has to be a perfectly wetting fluid. So, under vacuum means inside whatever suppose inside the porous medium there is some air in it, there is some volatile matter in it. So, all those things under vacuum they will come out.

So, it there is nothing inside the void and now you are dipping it immersing it in a perfectly wetting fluid. Wetting fluid means wetting fluid can penetrate every nook and cranny of this porous media everywhere ok. Had it been a non-wetting fluid then there comes this issue of capillary pressure and what pressure you are imposing, some pores will be penetrated some not, but wetting fluid it does not there is no such problem. So, wetting fluid will penetrate.

Now, you note the weight before and after imbibitions. So, that means, before putting water in this it has certain weight and after water fills all the pore you measure the weight. So, difference in these two difference between these two weights that gives the amount of water that has gone into this porous media. So, you know initial weight that is the weight of the solid matrix you know how much is from the difference; you know how much of weight of water has gone into this porous matrix and if the final weight is the sum of these two weights.

So, now, how much water is gone into this porous matrix divided by the sum or divided by the final weight which is water plus the original solid weight, so, that gives you the porosity. So, this is one very simple way one can get the porosity. Of course, the first one the optical method gives you a local porosity were as these imbibition method that gives you the porosity over porosity for this entire porous matrix that you are looking at. Suppose, you are looking at a core that then entire core that you will get one average porosity of the core. It is not a local porosity of any position.

Or one can do something call a density method where density method says that it is from the comparison of the density of porous sample and the bulk density of solid; that means, you measure the density of the porous matrix density means density is kg per meter cube unit; that means, what is the weight of that porous matrix divided by what is the volume of this porous matrix. So, one can find out what is the volume of the porous matrix taking measurements and then one can find out what is the weight of that porous matrix.

So, then you find out what is the density of this porous matrix and at the same time you know this porous matrix is made of some material and we already if you crush it to the finest of this finest of the size you will get to a something called the bulk density or this generally this bulk density of various known materials are already listed. So, you have a priori knowledge of what is the bulk density. So, from by comparison of these two densities one can get the get this density one can get the porosity of that sample.

And, the last two points that we have here one is gas expansion porosimeter and another is mercury injection method, these two we are going to discuss in detail.

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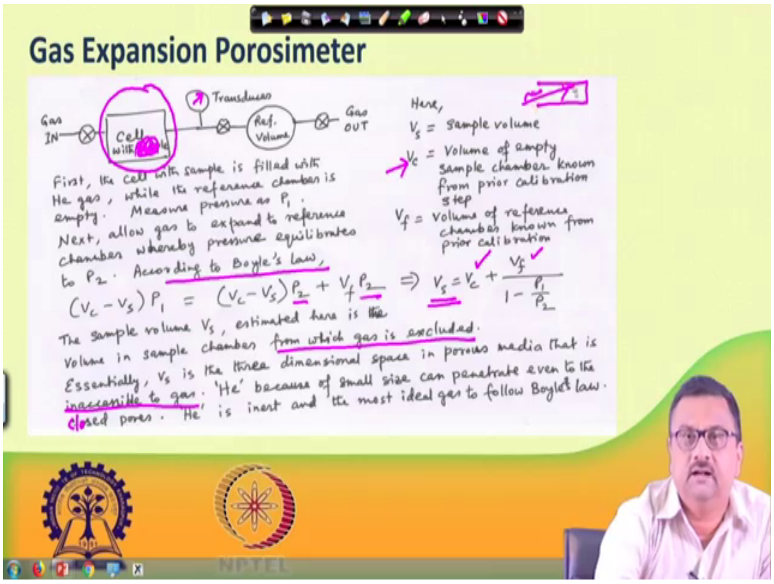

So, this is the description of a gas expansion porosimeter. So, what we see here is there is a cell sample there is the cell sample; there is a cell with samples. So, there is one cell here and this cell is containing the porous solid for which we want to measure the porosity. There is the sample and then we know the; we know the volume of these cell we know the volume of the cell and first what you do it is you create vacuum and clear this there is one reference cell.

So, you clear this reference cell, you take out all the gas out from this. So, there is there exist vacuum the close this valve you close this valve and then you close there was vacuum and there is this sample and then you open this valve so that the gas goes in here. So, gas goes in here after some gas goes in here you will see this valve is closed, this valve was closed.

So, there is a in this transducer there is a pressure reading. So, you note down what is this pressure because and then you close this valve, you note down what is this pressure and the pressure is P 1 let us say. So, at this time I have solid sample present so, let us say this is the solid sample and there is this gas present and the gas is at a pressure P 1.

Then, what you do is after the these entire thing equilibrates then you open the this valve is closed now you open this valve, so that some gas can flow from this one to the reference volume. So, as soon as the because this one was originally vacuum.

So, there is there will be flow of flow from this pressure P 1 to vacuum, so, there will be flow of gas to this reference volume and then there would be an equilibration. So, after equilibration let us say the pressure noted by this transducer is P 2.

So in that case we can do some quick calculation here. We can make use of something called Boyle's law. So, initially let us say we have V c as the sample of as the volume of empty sample chamber. So, the volume of this sample chamber this is called sample chamber or cell sample cell, here let us say the volume is V c and V s is the solid volume that you are given which is called sample volume whose porosity want to measure. So, you this is called V s.

So, V c minus V s V c is the volume of the sample cell and V s is the volume of the sample. So, V c minus V s gives you the volume of the gas that is occupying here and that multiplied by P 1. So, P 1, V 1 V is the volume of the gas occupied in this sample cell. So, that P 1 we are the same gas now after equilibration after allowing the flow from this cell to the reference cell so, at that time the pressure became P 2. So, the same gas earlier it was in P 1 V 1, now it has to be P 2 V 2. So, what is that?

So, that would be P 2 into now we have this volume remains same V c minus V s. So, some gas will be in these and some gas would be in this chamber which was earlier in vacuum. So, if the volume of these reference cell is V f. So, P 1 V 1 would be P 2 into V f some is here some of the gas is here and the rest of the gas is remaining there, but both of them I will equilibrated to a pressure P 2. So, this is the relation Boyle's according to Boyle's law P 1 V 1 has to be equal to P 2 V 2; that means, after expansion P 1 V 1 will remain same.

So, you if you now use this equation if you now use this equation this will take you to if you simplify it then V s the sample volume will be given by V c plus this quantity. So, now, V c is already you known to you that is your creation you have created the sample sell. So, you know the volume of the sample cell, V f is the volume of the reference cell. So, that also your creation you know that and you have made this measurement of P 1 and P 2. So, you know what is P 1, what is P 2. So, with this you can find out what is the V s, volume of the sample.

So, now what is the volume of the sample? The sample volume V s estimated here is volume in sample chamber from which gas is excluded. So, that means, think of it this is a porous material whose volume you are trying to measure. So, what is this volume? This volume. So, gas had gone into when you did the equilibration gas has gone into this cell a gas has gone into this porous matrix and then when the pressure is reduced because there is flow from gas from this side to this side automatically some of the gas came out from the pores.

So, what is V s? V s is basically the volume from which the gas is excluded; that means volume of the solid true solid volume, not the porous medium volume the true solid volume where the gas could not penetrate because the rest the void space within the porous medium that is anyway accessible by the gas. So, that is; so, that is basically the gas volume included. So, now you get the volume of the solid.

Now, if you have the information of what is the total volume of the matrix and now you have the information of what is the solid volume then total minus the solid volume is the void volume. So, by this way you can find out what is the; what is the porosity. Now, here the type of gas that is used see essentially V s is the 3-dimensional space in porous media that is in accessible to gas we understood that. Helium because of small size can penetrate even to the closed pores. So, it is very important that you use gas whose size is very small ok.

So, that is I mean it is not should not be large molecules because you want it is to be you wanted to have the high, mean free path, you want to have the good diffusivities so, all this thing. So, helium is the choice here. So, helium is inert and most ideal gas to follow Boyle’s law. So, helium is a good choice here and you want even if it is a closed pore; closed pore in the sense it starts with the pore starts it is like this. So, helium can enter I mean, but helium cannot leave.

So, still since it has a high mean free path it and helium can enter and gradually occupy the space. So, this is more or less a structure by which this gas porous symmetry is conducted.

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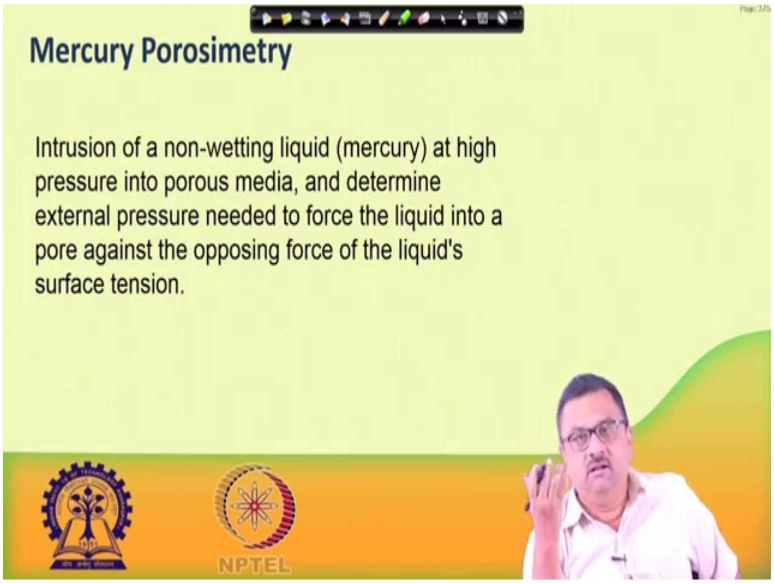

The next one is mercury porosimetry. Here intrusion of a non-wetting liquid or mercury at high pressure into porous media and determine external pressure needed to force the liquid into a pore against the opposing force of liquid's surface tension. You must recall one thing here is that this mercury would be considered here as a non-wetting liquid and you know when you want to push a non-wetting liquid inside a porous medium one has to overcome one has to provide some extra pressure because it does not get a favorable contact angle.

So, as you increase the pressure you will see some pores penetrating. This is unlike the case of imbibition method we discussed. You put it in a perfectly wetting fluid and wetting fluid will penetrate every nook and cranny of that porous medium, but when it comes to mercury which is considered here as a non-wetting liquid it will not enter into the porous medium that easily. I mean, it has that problem of contact angle adverse contact angle.

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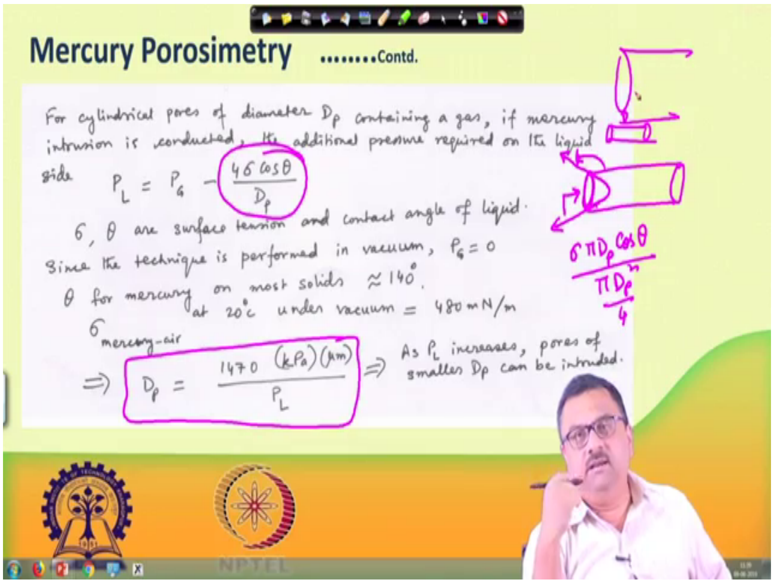

So, the way you must look at these is that it has to overcome something called the capillary pressure you must recall why now that we had we had a discussion that if there is a cylindrical pore, if there is a cylindrical pore and if the if non-wetting fluid is pushed into this. So, originally let us say you have a vacuum and you want to push this non-wetting fluid. So, let us say you have air at very low pressure on the other side and then you want mercury to go in there.

So, in this case we will see that the liquid pressure; liquid pressure is equal to the gas pressure which is if you considered this to be vacuum this will be closed to 0 minus 4 sigma cos theta divided by the diameter of the pore. This you must recall that we have you remember if there is a surface tension force then this is this you must recall that there is there would be a meniscus like this and then this meniscus will have this meniscus will have this is this would be the contact angle.

So, contact angle will be this much greater than 90 degree and as the fluid penetrates and you have you know the surface tension force acting is sigma into pi into D P that is basically 2 pi r, the perimeter multiplied by cos theta. So, that is the force which is acting over the area of pi D P square by 4. So, these gives me; these gives me the pressure the additional pressure that has to be provided to the liquid phase here ok.

So, now, this is so, this is basically here this cos theta would be in this case negative. So, this will become positive. So, P L would be higher than P G. So, you have to provide these additional pressure then only the mercury will penetrate. So, you can see here that sigma theta etcetera these are defined here, the numbers are given. So, if you put these numbers you can see the pore diameter you will be given as 1470 kilo Pascal into micrometer divided by P L where P L is the; P L is the liquid side pressure.

So, what it says is that as you increase the pressure suppose I want mercury to penetrate into the pore and I have pores of different dimensions some are small, some large. So, then so, mercury will penetrate moment I increase the pressure in the mercury phase I will see mercury will penetrate in the largest pore because this as the pressure increases. So, here you can see as P L increases pores of smaller D P can be included. So, for the lowest pressure the largest D P would be included and then as P L increases you will see that small and smaller D P will be penetrated ok.

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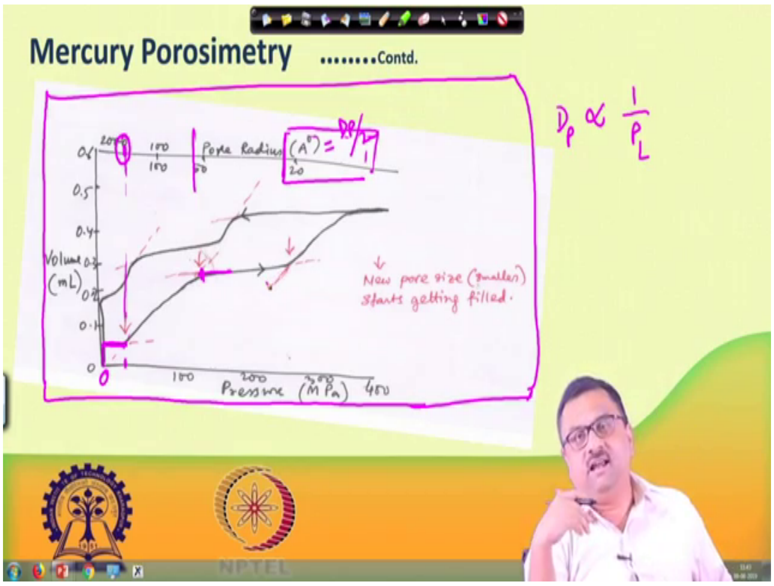

So, essentially if you try to plot this here; if you try to plot this here it is the volume penetrated volume penetrated as a function of the volume penetrated as a function of the pressure here we see that the pressure as the pressure increases we will see that the more and more fluid will be penetrated. So, more and more mercury would be penetrating into the porous medium. And, every pressure here in mega Pascal corresponds to some pressure of corresponding to corresponds to some D P.

So, some D P this pore radius is basically what? Pore radius is basically D P by 2 and we have already seen that D P is proportional to some proportional to 1 by P L. So, as the pressure increases you can see that D P by 2 decrease. So, it is basically these two these two axis they are synonymous. In this case, you have the pressure is increasing from 0 to 100 to 200 to 300 mega Pascal 400 mega Pascal corresponding pore radius ok. Just in the last slide we had a discussion; in the last slide we show that corresponding to this your this is changing 2000 angstrom, 100 angstrom, 50 angstrom like this. So, pore radius is degree decreasing.

So, now, as the pressure increases smaller pores are getting penetrated. Now, you can see here there is a trend first of all this is going like this and then it is reaching a constant value; so, that means, constant means you are increasing the pressure, but no change in volume. So, nothing is being penetrated, whatever was there status quo is maintained, then beyond this threshold pressure I see again the volume started changing. So, from this point some invasion starts.

So, some so, I can see now I tally this and I can see that there is some number of pores of this particular dimension. This particular pore radius of so many angstrom, this particular dimension there are few pores, because I can see now in the porous medium the volume of mercury included is they start increasing. Again, here it starts flattening; that means. So, from this side to this side there was continuously some pores were invaded, but from this size to this size there was no invasion because volume does not change, but pressure continuously is increased, but then again this from this point again I see increase.

So, again from this point onwards there would be there would be some pores in that matrix which are of this dimension. So, there is no pore present there of this pore dimension. There are some pores present in this dimension, again no pore in this dimension. So, from this you can get a picture what are the pore pores in the present in is porous media they belong to which what size rangers I mean this to this these. So, these are the; these are the pores that are present in the system by looking at this curve from mercury that this curve is generated from mercury intrusion porosimetry.

Of course, when you come back on the rivers there would be a huge hysteresis and these hysteresis we are familiar with because you remember oil-water case then when oil entered it entered in one way, but when you are retracting, when you are taking out oil so, from the other side then air is entering so, then that means, from the other side it would happen from other side. The mercury which is a non-wetting fluid it will enter to the largest.

So, if you have a; if you have a varying cross section it will mercury will enter through the larger end of the pore, whereas the pore where the cross sectional area is larger whereas it will enter the gas it will when it leaves that time the gas will enter from the other end where the cross-sectional area is smaller because this is non-wetting fluid is. So, this we have study in case of oil and water and this hysteresis, we talked about drainage and imbibition and we had this capillary stressed.

So, the same thing will happen on the, but we are not bothered with the I mean we are let us focus only on the on this part and one can find out what all pore sizes are present in the porous matrix and what all sizes are not present.

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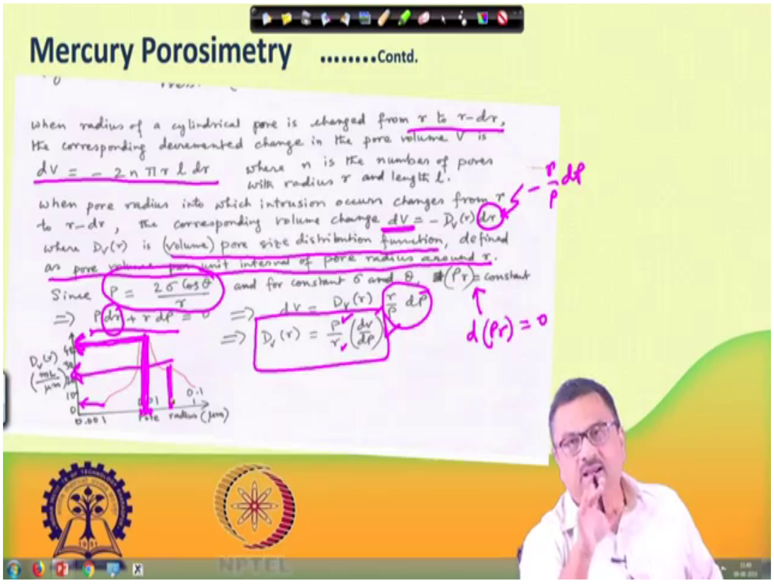

So, with this understanding let us now look at when the radius I mean suppose if I want to generate a pore size distribution how it looks I can give it here. When the radius of a cylindrical pore is changed from r to r minus dr the corresponding decremental change in a pore volume V is given by dV which is this quantity minus 2 n pi r l dr because this change in volume it would be and it is the corresponding decremental change in the pore volume would be given by this quantity where n is the number of pores with radius r and length l.

So, there are n number of pores of radius r and length l. So, corresponding change from r to r minus dr is this quantity. So, now, when the pore radius in to which intrusion occurs changes from r to r minus dr the corresponding volume change dV that would be equal to minus D capital D subscribe V as a function of r dr where this D subscript v as a function of r is pore size distribution in terms of volume. Pore size distribution function defined as pore volume per unit interval of pore radius around r ok.

So, this is defined as pore volume per unit interval of pore radius around r. So, now, we already know that the pressure we have already defined these expression. So, if that is so, we know that the P into r if sigma and theta these are all system properties, so, P into r is equal to constant. So, one can write d of V is equal d of V is; so, since P into r is equal to constant.

So, one can write d of Pr would be equal to 0 and d of Pr equal to 0 means P dr plus r dP equal to 0. So, P dr plus r dP equal to 0, what that means, is that one can write the this dV is equal to minus D v r dr instead of this dr we can use this dr. So, this dr would be here this dr would be minus r by P dP. So, this is minus r by P dP. So, that is brought here. So, dV is equal to dV into r and this minus and minus became plus r by P dP.

So, then this dV can be written as P by r dV dP ok. So, now, one can plot these dV as a function of r dV as a function of r and one can generate a curve like this. It is this P for a particular r you know what is P and what is corresponding dV dP. So, one can generate this curve based on the mercury porosimetry information. So, what essentially this gives?

This gives let us say I am talking about the pore radius of let us say 0.01. Micrometer. So, 0.01 micrometer this is this corresponds to this value of dV, whereas if I am looking at 0.001 micrometer that is giving dV as this. So, dV is once again the dV is the volume pore size distribution function which is basically the pore volume per unit interval of pore radius around r. So, what that means, is for this particular r these dV gives me pore volume per unit interval of pore radius around r.

So, this is basically so, this gives me. So, if this is highest here; that means, at this particular pore radius you have the maximum number of pores and the pore volume that is having a pore radius of this around this you have unit interval. So, these basically this particular this particular interval here that is having this much of pore volume. Similarly, you can have this interval is having this much of pore volume.

So, here essentially by looking at this plot you can say I can see 0.01 micrometer size pore is mostly present and from that you can find out I would say 75 percent of the pores are of 0.01 micrometer and probably 5 percent of the pores are of this. So, one can get this kind of understanding of the porous medium by performing this analysis. So, you can.

So, this is as far as a mercury porosimetry is concerned and I want to stop this session here stop this particular lecture here and I will talk briefly about other characterizations methods which are not that I mean other characterizations methods we will touch upon this those are not exactly for the porosity or pore size distribution, but for other purposes we can use those characterization method that I am going to talk about in my next lecture. That is all.

Thank you very much.