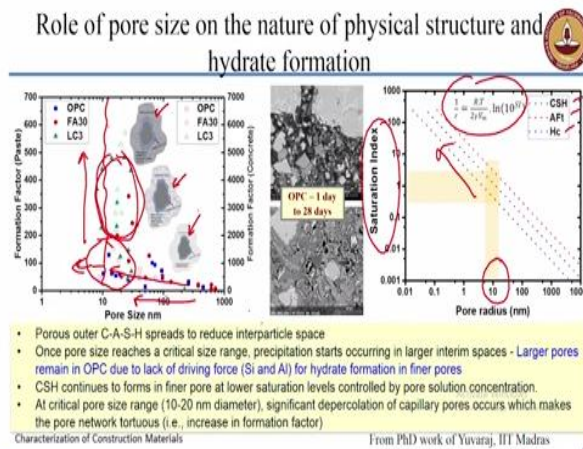


Characterization of Construction Materials
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Lecture -61

Porosity and Pore structure - Working of mercury Intrusion Porosimeter - Part 2

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Talking about structural development, there is a possibility that your system however refined it may be does not get below a certain level of refinement. Now why does that happen? You know that there are crystalline and semi-crystalline species that are getting formed because of the hydration of the cement. As the hydration continues to happen, you make your pores smaller and smaller. So what is presented is some sort of a schematic model here. So this is a grain of, let's say tricalcium silicate (C_3S), and around this grain of C_3S you have a largely porous system in the beginning because you have cement in water. With time what happens is this porosity starts getting filled up, the pore sizes becomes smaller and smaller. So you are moving towards this side in your axis (towards decreasing pore size). As you reach the critical level of hydration, your pore sizes have sort of stabilized in this 10 nm size range. Now irrespective of what you do, you are not being able to push the pore sizes finer and finer.

Now, please remember when the pore size comes to a very small diameter, you need a very high level of saturation index to start depositing hydration products inside the pore sizes of that size. This is not part of our course here, but in general, there is a concept of what is called as a critical degree of saturation being obtained for a system. So as the pores become smaller and smaller, it becomes more difficult for solid species to precipitate inside the pore, because the space available is simply not enough to cause that precipitation to happen. This is akin to the concept of the fact that in extremely cold regions when you use high performance concrete, the pore sizes are so small that the water inside the pores cannot freeze to form ice because of the pore pressures that are exerted, the water inside cannot freeze to form ice. Similarly even if you have the required ingredients inside to precipitate solid products like C-S-H, ettringite or hemihydrate inside these pores, the required degree of saturation will keep on going up as the pore size becomes smaller and smaller.

What does this mean? What is the connotation of this? This means that when you reach a critical pore size of around 10 μm , you simply do not have the conditions that are favorable for deposition of more products inside the pore. That is the reason why we see that despite increased curing, despite lowering water-binder ratio, irrespective of the type of binder, whether it is OPC or fly ash or LC3 binder, you are not able to reduce your pore size to less than around 10 nm. It is not exactly 10 nm but around 10 nm.

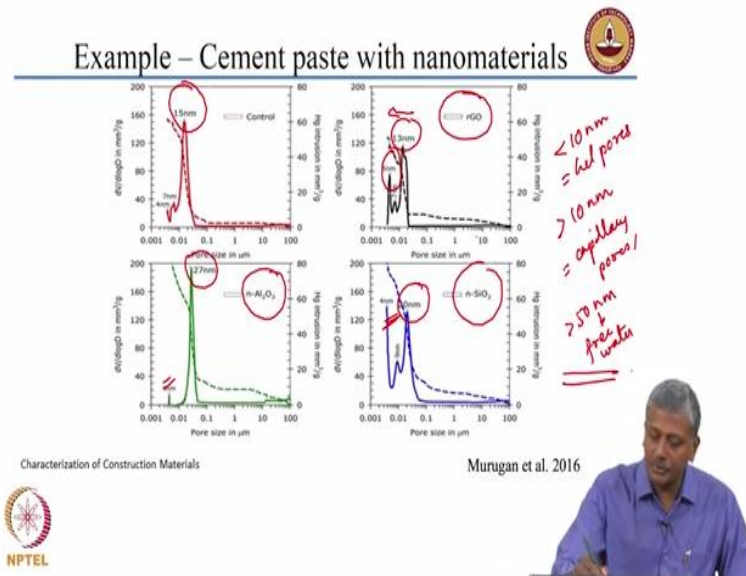
But what you see after this is that, even though you have reached that critical pore size, some systems like especially here the LC3 systems are showing an increased formation factor. Now without getting into the depths of what formation factor is, formation factor is indicative of the interconnectivity of the porosity. The greater the formation factor, the lesser the interconnectivity of the porosity. So what does this indicate? Your system now has continuously hydrated and reduced to a critical pore size, but because of the high degree of saturation index required to precipitate the solids inside the pore, you do not have any more precipitation taking place to reduce the size of the pore further, but what you do have is the continuous filling of the interim spaces that is happening to further increase the impenetrability of your system.

What does this mean in terms of durability? It means that systems with mineral admixtures like LC3 or fly ash, may reach the same level of critical porosity as OPC, under the best circumstances. However a system like OPC will never reach the kind of resistance to fluid flow that can be obtained with LC3 or fly ash systems. So while all the binders seem to reach the same pore sizes, only certain binders which have the late reactions like the pozzolanic reactions that are taking place that start filling up the interim spaces, only those can cause an increase in the durability beyond that point. So this is actually a very critical result that we have recently analyzed and there is a paper that is about to come out on this very soon.

Well it is not an empirical equation; it is a fundamentally proposed equation that relates the fluid flow to the connectivity of the porosity in the system. So the formation factor includes the porosity of the system and a factor known as the pore-connectivity factor. So essentially the pore-connectivity factor is defined by the tortuosity of the pores, so how easy is it to go from one point to another in the pore system - is it a straight line or is it a zigzag line which makes it difficult? So the formation factor captures both those effects - the porosity and the pore connectivity.

With MIP we can say that the porosity in the system is getting refined to a certain extent. But we cannot indicate that just the critical pore size alone will give us an indication of the durability performance. If you are comparing the same binder system like only OPC, then very clearly what you can see is as the pore size reduces the formation factor also sees some sort of an increase and that corresponds to exactly an improved durability performance. So if you are making concrete only with OPC, the way to increase durability is to reduce the water-cement ratio. That is why in all your durability specifications in your IS 456, all it says is when you want higher durability choose concretes with lesser water-cement ratio. But when you start using mineral admixtures, you get other effects: the pozzolanic reactions, the delayed reactions, the kind of products that are forming - the calcium aluminosilicate hydrate; only that has the potential to refine your microstructure overall rather than just taking the pore sizes to a critically small range.

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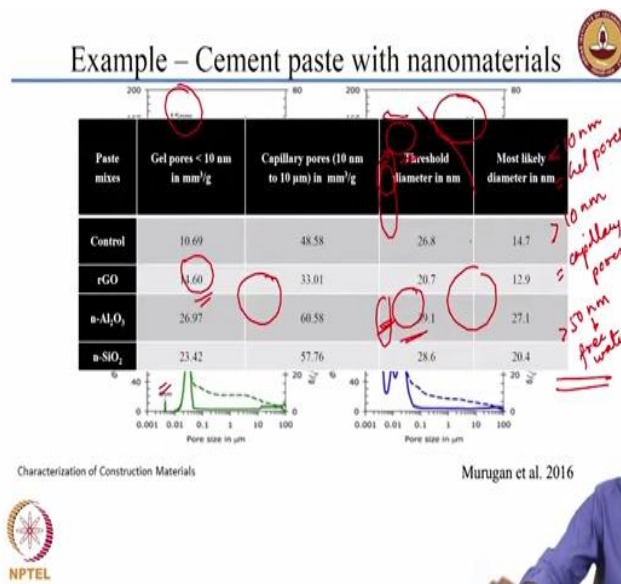


Now this is another example of how MIP was applied to understand how cement paste evolves with nanomaterials which are inside the system. Now there is recently a major interest in using nanomaterials for various technologies - water purification, medical processing and so on and so forth. Nano materials are also very useful as ingredients in cementitious paste or concrete, except that of course, you need to understand that when you are working with particles at a nano level, dispersing them inside concrete may become a big challenge. But once you achieve that dispersion, you can then try and understand what impact it may have on the structural properties.

So here what we see is compared to the control cement paste, which had a critical pore size of 15 nm, when we used graphene oxides, you started to actually push the pores to smaller sizes. You still get this 13 nm or 15 nm porosity, but you shift some of the porosity to a finer pore size. Interestingly the nanoalumina and nanosilica in the study had pore sizes also in the higher ranges, which is quite surprising; we expect that when we start filling up with nano materials, our pore sizes should start getting filled up more and more. Now, this is exactly the problem of dispersion. What we found later was that the nanosilica and nanoalumina had a large tendency to agglomerate. And this agglomeration basically kills all the possibilities of reduction in pore sizes, you do get this finer pore sizes, but again at that level, we do not really know what is happening at less than 5 μm , we cannot really understand the system well enough in MIP.

Now if you read literature of cement paste and concrete, generally what they say is less than 10 nm are your gel pores, that means the pores that exist within the C-S-H. Greater than 10 nm are the capillary pores. And if you have learnt concrete technology, you would also know that when your pores are greater than 50 nm, the water present inside this pore is called the free water, what does that mean? The removal of that water will not cause sufficient shrinkage you will just remove or dry off that water without really causing significant shrinkage. So a general system of assessment of a cement paste microstructure says that you have <10 nm which are essentially gel pores, >10 nm are capillary pores and out of these capillary pores, the ones which are beyond 50 nm is where the free water is there, you do not really have substantially high capillary pressures holding that water that means that shrinkage will not be very high at extremely high capillary pores.

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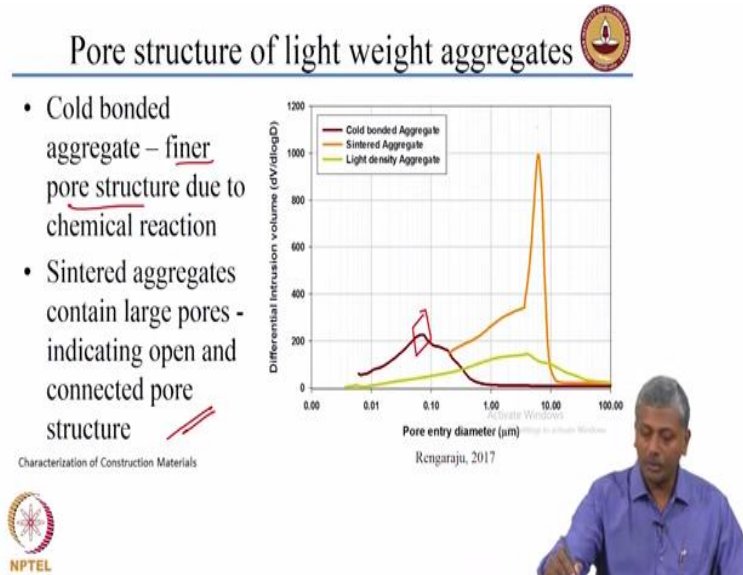


I am sorry that I am not able to rub off the red annotations; those have nothing to do with the numbers that have been shown there.

So what was attempted in this case was for the 4 different pastes, the characterization of two different pore types was done: <10 nm and >10 nm and also the threshold diameter and most likely diameter were also indicated from the cumulative intrusion curve and the differential intrusion curve. And you can see that with the reduced graphene oxide as a nanomaterial, you do have an improved tendency for lowering the most likely diameter as opposed to the control paste.

But you can see that the effects are not that significantly different. It is because they are again reaching this potential smallest pore size of around 10 nm in the case of control and rGO systems. You have to take the result with a pinch of salt; you cannot really think that the result is indicative of all the useful properties that you can think of in concrete.

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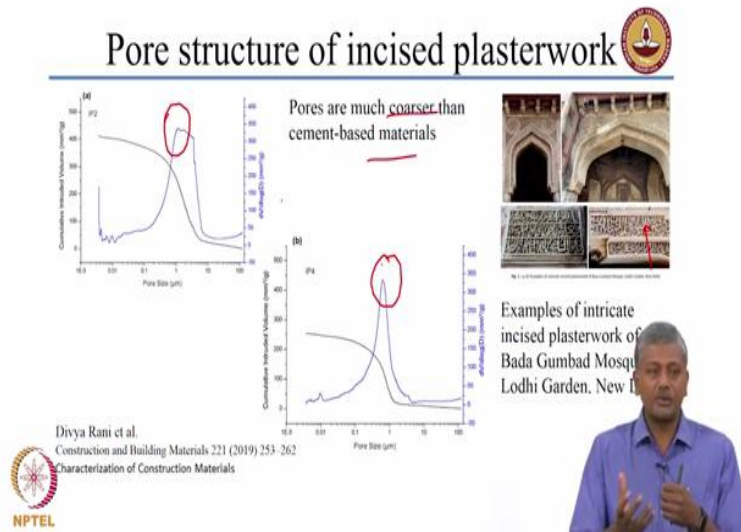


Now again, this is a pore structure of lightweight aggregate, which is being shown here. When you use fly ash to make lightweight aggregates, there are different ways of doing it: you can actually sinter it, like if you have Type F fly ash or calcined clay you can sinter it and make lightweight aggregate; or with Type C fly ash which has its own reaction with water, you can do what is known as cold bonding - that means you make pellets and allow them to cure just like your cement paste would cure.

But interestingly what is seen is the pore structure that forms in the lightweight aggregate differs depending upon the type of aggregate. So in the cold bonded aggregate you get finer pore structure due to chemical reactions. The hydration reactions that are taking place of the Type C fly ash are resulting in a smaller critical pore entry diameter.

In the case of sintered aggregates from Type F fly ash, you get porosity in a much larger scale. So again, it helps you to identify differences between different types of lightweight aggregates.

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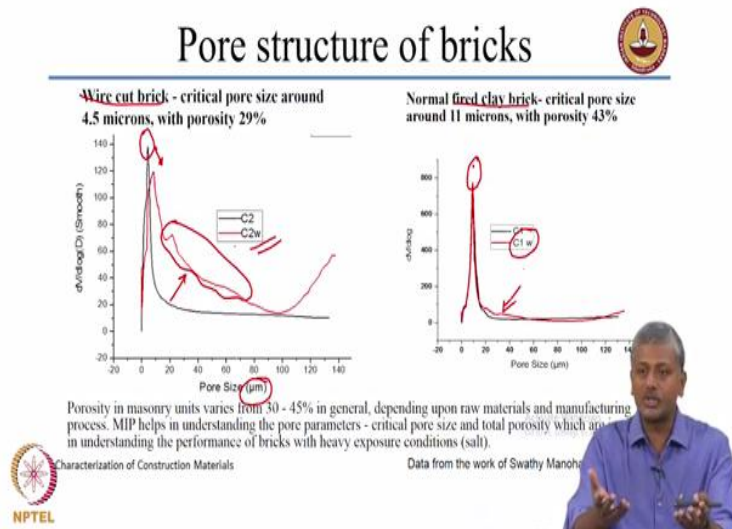
This is something which we had done for a historical monument and we evaluated the plaster that was available in this historical monument. You can see that this plaster is of a decorative type, you can actually see the Islamic calligraphy on the structure and this is an incised plaster work example carried out by Persian workman for the Lodhi dynasty monuments in Delhi.

And what is interesting is the pore structure that is exhibited by these plasters are generally, of course, in any case lime mortars are much coarser as compared to cement based materials. But what is interesting is within the lime mortars, these incised plasters actually gave cumulative intrusion patterns as well as your pore sizes which were much finer than what you find in typical mortars that are used for historical monuments. That means that this incised plaster had a very fine texture and microstructure, so here you can see that the critical pore diameters around close to about 1 μm size, whereas we saw in cement paste you can actually go up to 10 or 20 nm - that small size in cement paste, but here we are talking about in lime mortar we get only pore sizes of 1 μm.

Any idea why that happens? What is the cause for this critical size being so large in the case of lime mortar; I am saying it's large, but for incised plaster, the pore sizes are much finer than what you get for typical bedding mortars. So there the pores are even shifted to the right. But why are pores in lime mortars expected to be coarser as opposed to cement mortars? What

does lime form upon reaction finally? You ultimately end up forming calcium carbonate. Now calcium carbonate is a well-defined crystalline species, so it can saturate and precipitate in a given size in a given shape, whereas C-S-H on the other hand, you know that there is a silica network that is forming, you have sheet-like structures, so it starts filling up the space in a much better fashion as opposed to calcium carbonate. So when you have a semi-colloidal structure like C-S-H, it has better pore filling characteristics than crystalline materials like calcium carbonate. Because of that you see a much better effect of refinement of pore size in cement mortars than lime mortars.

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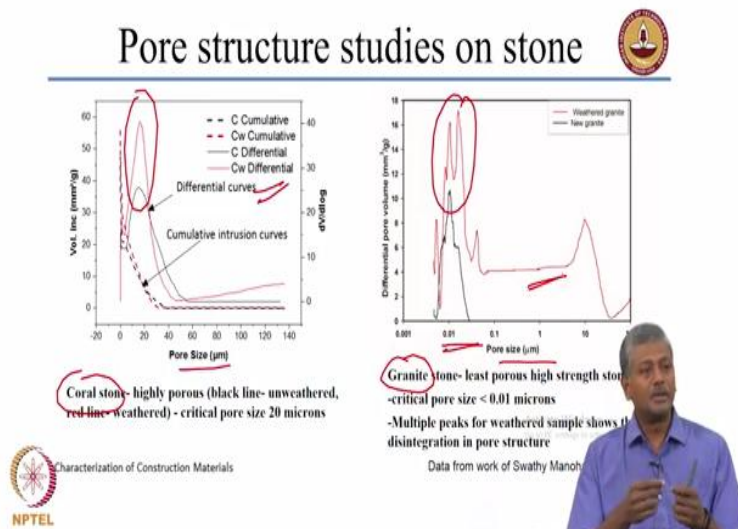
Here, pore structure of bricks is being compared. There are two types of bricks that are being captured here: one is a wire cut brick which you can imagine has a very nicely defined shape and size and generally a much better mixture composition and this is a normal fired clay brick that you commonly find in most of your construction processes.

So what you see here is, of course you cannot discern this very clearly, is the critical pore size in the wire cut bricks as well as in the normal fired clay bricks, which is probably occurring between 5 and 10 μm . Again the pores are much coarser even compared to lime mortar and much, much coarser compared to cement mortar because you know that bricks are highly absorptive - they take up lot of moisture.

But what is interesting is when you subject the bricks to weathering cycles - salt crystallization and weathering - it seems to indicate that there is a coarsening of pores in the wire cut brick which is of higher quality to begin with, whereas in the poorer quality bricks, the weathering does not shift the pore sizes. What does that indicate? Look at what is happening to this curve here - much coarser after weathering but here (normal fired clay brick) there is practically no difference. This seems to indicate that the system with larger porosity or even larger size pores does not suffer from large crystallization pressures, which lead to this cracking and coarsening of the structure after weathering.

Now this is interesting, in concrete we always talk about reducing the pore size but here we are operating at a slightly different size range where the dominant mechanism of failure of the material is salt crystallization. And that salt crystallization creates more disturbance in the finer pore systems as opposed to a coarser pore system. Again why? Please recall our discussion earlier about the saturation index; there is a crystallization pressure that relates to the pore diameter. The smaller the diameter, the higher will be the pressure of crystallization. So that is what the interesting characteristic here is you do not always choose a higher quality brick to improve your salt crystallization resistance. You need to have your microstructure with the right size of pores and not just a higher strength or higher quality brick.

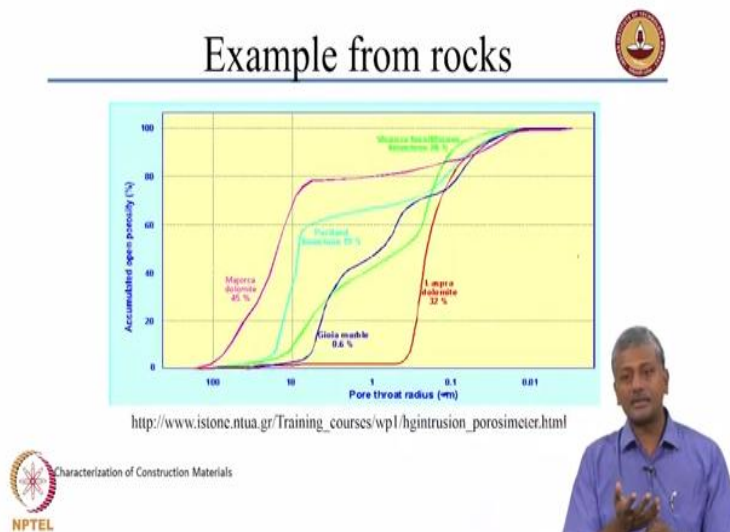
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Again on stone also you can actually do similar sort of studies. Here two different stones are given: you have the granite stone which is known to be a very dense packed stone, very high strength stone. On the other hand, you have highly porous coral stone that means the stone that is formed by coral depositions. Coral deposition again will be mostly calcium carbonate from shelled organisms you deposit this

What you see here is very clear. The pore sizes are extremely different for different types of stones. Here you have pore sizes in the range of 10 to 20 μm and in granite, the pore sizes are less than a 10th of a micron. But again weathering creates very different effects in coral stone and granite; weathering does not seem to affect coral stone very much. The properties have not changed after weathering significantly, but granite has completely transformed after weathering. The porosity has just opened up in granite because of weathering. So you need to approach other building materials, masonry materials like brick and stone with a slightly different angle as opposed to cement concrete. In cement concrete, salt crystallization is very unlikely because the pore sizes are so small that the salts may actually not end up crystallizing there.

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Again, another example of different types of rocks is shown. For rocks and bricks, MIP is possibly the best technique to really capture the internal structure

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Issues



- At high pressure, sample will also get compressed; so will Hg
- Corrections need to be applied!
- Usually, these corrections are built in with the instrument



As I was saying earlier, there are some critical issues with MIP which you need to understand and understand its influence on the result. At high pressure you are compressing your sample and also compressing the mercury. So there has to be some corrections to be applied for the compression, and for most common samples, the instrument itself actually helps you apply those corrections directly. You do not need to physically do anything; the instrument has built-in corrections for the type of sample and obviously for mercury there will be a standard correction for compression.

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Advantages



- When Hg enters the pore, it doesn't just fill the pore, but also covers the inner surface area of the sample
- This involves an energy change (as the solid surface goes to a solid-liquid interface)
- The surface area can thus be measured



The other aspect that you can help study with mercury is the opposite of what we did with the adsorption. In adsorption I said that you can get the surface area, you can also possibly convert

the overall adsorbed surface to the pore sizes and pore diameters across which the adsorption is happening. Vice versa here, while you are measuring the pore diameters and sizes you can also determine the total area of the pore walls that are in contact with the mercury and convert that into a surface area measurement. But again, just like pore size measurement was indirect in adsorption techniques and not really useful, here also the surface area measurement may not give you very accurate results, because it will depend upon the characteristics of the mercury interaction with the specific surface which you are trying to measure.

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Limitations

- Major limitation is the 'ink bottle effect'

The diagram shows a solid with a pore structure. The pore has a narrow neck with diameter d_1 and a larger internal chamber with diameter d_2 . A handwritten note says "Experiment will only measure d_1 !!!". A graph shows a sharp increase in intrusion volume at a specific pressure, corresponding to the neck diameter d_1 .

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Another limitation of MIP is what we already discussed earlier – ink-bottle effect. So supposing on the surface of this solid, you have a small pore (of diameter d_1), but inside you have a very large pore (of diameter d_2). So what will happen now? Your system will have to be pressurized to an extent that it overcomes this d_1 .

So if you draw the intrusion curve, your system will have almost no intrusion until the pressure d_1 is obtained, and then as soon as you overcome this d_1 , there will be a sudden increase in your intrusion, because this pore d_2 is much larger than d_1 . Now, it will look like your porosity is all in this range. This will tend to indicate that your porosity is all in the range of d_1 . So this is called the ink-bottle effect. Now, this is the biggest criticism that people have of mercury intrusion porosimetry, people say that because of these kinds of effects you never know what you are really looking at.

Again just going back to the typical charts here (in slide – Example from rocks), when you have the sudden increase in the intrusion into the system, does it really mean that this is the breakthrough diameter or does it mean that there is a much larger porosity right next to it? So critics of MIP say that, because of this, MIP will never be a 100% accurate tool to determine pore sizes because you do not know what is actually going on beyond this. Are you filling up the same size pores and smaller pores or are you flooding into a chamber that has a very large size pore? So anyway you need to understand that is the limitation. So when you interpret the results, make sure that when you are actually doing the experiments the same sort of conditions apply to all the samples that you are trying to compare and make your judgment wisely. Of course, making a judgement wisely goes with any characterization technique and not just with MIP.

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References



- Micromeritics and Malvern brochures
- Wikipedia
- Douglas Winslow – Lecture notes from Purdue University



We have several references that you can actually refer to. The references deal also with the brochures from the companies that actually manufacture these instruments. And of course in Wikipedia also you can find significant cross-references that you can actually look at, to understand the technique better.