Environmental Geomechanics
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Lecture No. 56
Pore-structure characterization - II

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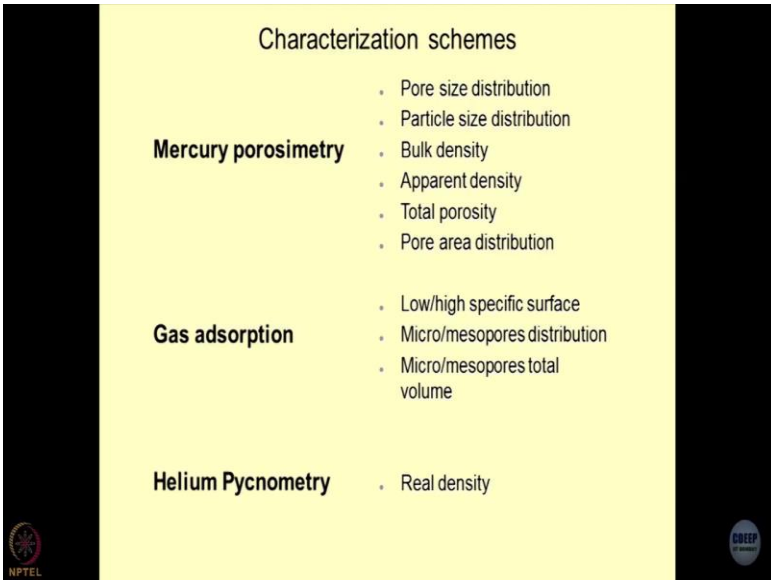

These are the guidelines which are normally used, which equipment should be used for what type of characterization of the geomaterials, so we have three techniques. That is the mercury porosimetry, gas absorption and the helium pycnometry. And these instruments are becoming very common in the environmental geomechanics laboratory. Helium pycnometry gives you the real density. Real density, the specific gravity which is skeletal.

Which is the gas absorption technique which we had talked about when we were discussing the specific surface area and cation exchange capacity? Gas absorption gives you the surface area micro and mesopore distribution and total volume of the pores. And when we do mercury porosimetry, we can obtain pore size distribution, particle size distribution, bulk density, apparent density, real density, total density and pore area distribution.

So, these are the guidelines which researchers have come out with and depending upon your requirements, you can adopt these techniques either in isolation or in combination with each other.

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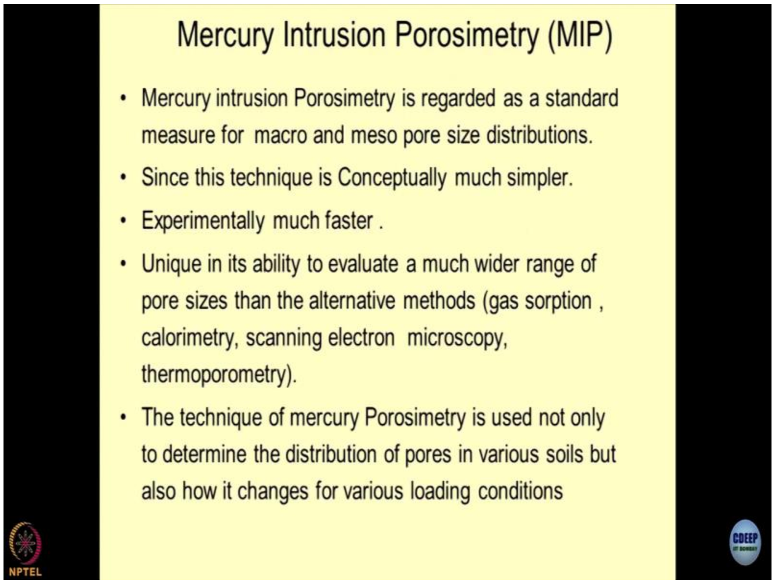

Rather than discussing this, okay let me give you a quick idea about what MIP is so, this is a standard method for determination of macro and mesopore size distributions. And it is a very simple technique where you are intruding Mercury into the sample under some pressure so conceptually do the simple thing. Mathematical modelling is quite easy, easy to conduct the experiments.

And this is a unique test to evaluate a much wider range of pore sizes than the alternative methods like gas sorption. People have used colourimetry also scanning electron microscopy and thermoporometry this is as I said earlier, the MIP is not only used to determine the distribution of the pores in the soils, but it also gives you an idea about how the pores are getting changed because of different loading conditions. So, it appears to be a very versatile tool.

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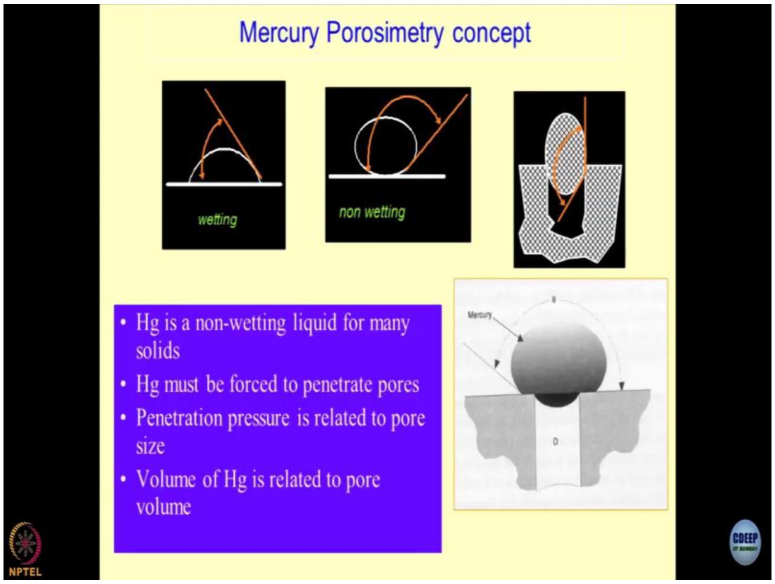

This is the basic concept; we were discussing the wetting and non-wetting fluid. So, if this is a surface on which you have a drop of fluid, the wetting fluid will always give you an acute angle, our non-wetting fluid will always give you an obtuse angle. So, imagine that this is the pore in the geomaterial and there is a mercury drop. So, when you pressurize it, Mercury being a non-wetting liquid, theta angle is going to be higher.

So, at what pressure, the size of the mercury drop which is going to enter the pore. If I can measure this, I will know the size of the pore. This is a simple as this. So mercury intrusion porosimetry utilizes the concept that Mercury is a non-wetting fluid, and this can be forced into the pores up to the smallest size. And what we assume is that the size of the pore is the same as the size of the mercury drop which is entering into it.

And if I can measure the amount of volume of the Mercury which has been displaced into the pores that is nothing but the volume of the pores. So, prima facie all these assumptions appear to be valid, how do you ensure that the size of the pore is not changing due to pressurization? Very good. So, you have found out the biggest loophole in the mercury intrusion porosimetry.

So, she is saying that how will you make sure that the size of the pore is not changing when you force Mercury to pass through it, and that is the biggest limitation of the methodology. So, in the process are forcing mercury to drop into the pores you can destroy the pore structure because the pore structure is very delicate and you are applying very high pressure. So, yes, the chances of destroying the pore structure are possible. But then there is no other method.

So, every technique has its own limitation. Another question you can ask is supposed the soil has minerals which are swelling and shrinking type. Alright. So you are adding on to the complications. And this is where a researchers metal is tested to come out with something which people can believe in. So, these are the issues which are still to be addressed. But my simple Answer to your question would be if you do not have any other gadget which gives me something lets say with 50% accuracy also.

I will go back to the device, which is reliable at least and scientific. So, this technique seems to be quite scientific and reliable. Of course, the limitation which you have talked about is valid. Is it okay?.

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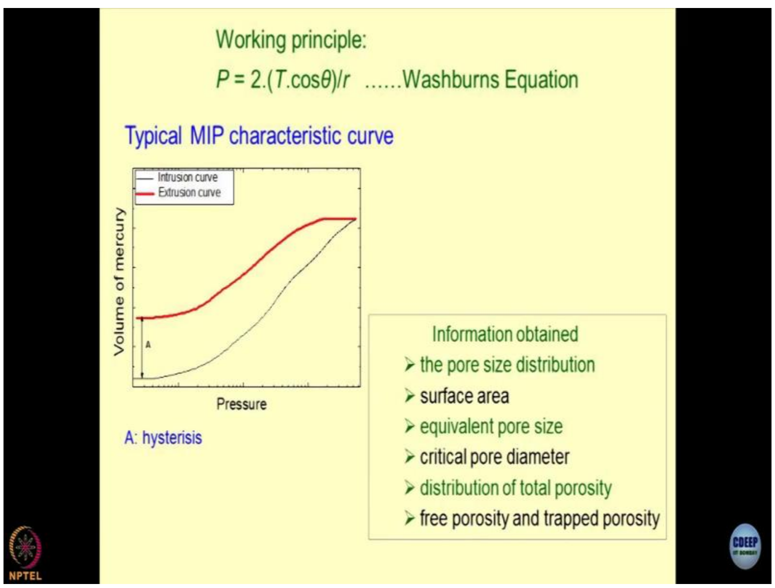

The working principle is based on the Washburn's equation, that is you must have studied $(2T. \cos\theta)/r=P$. So, this is the pressure which is being applied on to the sample, and r is the radius of the pore. And T is the surface tension. And θ is the contact angle; this is how a typical curve looks like. And I think it becomes very important for all the scientists and the researchers who are working in the field of mercury intrusion porosimetry to understand how to analyze the MIP curve.

We have two types of tests which have to be analyzed, under the head of MIT, the first one is the intrusion curve. So, if I plot pressure on the x-axis, and from 0 the pressure is increasing on y axis if I plot the volume of Mercury, which is intruding into the system that can be measured by using some electronic device or by using some device, which is going to tell you how much is the drop of Mercury in the control volume.

So, the way you will read this graph is as the pressure is applied on to the sample, Mercury being incompressible will enter into the pores try to fill up the pore, and it will attain the maximum possible volume of Mercury which can enter into pores. Now, this is where you have to understand a few things, this pressure is mechanically applied, and r is the radius of the pore which are inversely proportional.

So, the higher the pressure the r is going to be minimum understood. So, that means for capturing the finest possible pores in the sample you require extremely high pressure. So, when extremely high pressure is applied on the soil sample, as you said rightly, not only the pore structure, the volume of the soil sample itself might get changed, that correction also has to be applied. So, anyway, this is what is known as the intrusion curve.

This tells you how much pores are available for Mercury to be intruded. Having done this, what people try to do is they try to extrude Mercury out of the pores by suction. So, this curve shows how much amount of Mercury can be retrieved from the pores. And what you are observing is the two points do not match with each other at a given pressure. Why? That answers your point, that in the process of forcing the fluid inside Mercury inside and extracting it.

I have damaged the pore system, clear. The second thing there would be the finest possible pores through which the Mercury cannot be taken out because of extremely high pressure which are required, or you never know there could be some dead-end pores, with mercury goes and gets trapped inside. In most of the advanced countries, MIP is banned. Yes. The reason is simple. The question is ultimately having done this analysis.

And what this curve tells you that some amount of Mercury is going to remain inside the pores of the sample. Where are you going to throw the samples because these are mercury-contaminated samples? So for researchers, this is a big challenge, and then there is a good answer. What they do is they take out the sample, and they retrieve 100% mercury out of it by using a simple chemical process.

So, you can take out a sample, you can crush it, and you can make sure that the entire Mercury comes out. So, conducting these experiments in the laboratory itself is a violation of environmental law. By the way, you have to take permission from the agencies that you are conducting these type of experiments. And the big question is, what are you going to do with these samples which have been tested, so I have given you the full Answer.

Now, once this hysteresis graph or the MIP characteristic curve is ready, our job is done. I can get all these parameters from here, that is the pore size distribution, surface area, equivalent pore size, critical pore diameter, distribution of the total porosity, free porosity, and the trap porosity. You will be surprised to know the industry which is still going for this type of analysis starting from the Coal to steel to the resins to different types of catalysts to rocks, petroleum industry, I have done consulting for all of them.

I mean, you will be wondering why the steel company would be doing such a test. The answer is simple they want to study the properties of the ore similarly with Coal also. So, unless the Coal has a proper porosity, you cannot really incinerate it in the furnaces. The cost of smelting is going to be extremely high unless the ores exhibit a proper, pore size characteristics. So, less than that and more than that, the plant operations will suffer.

So, this has a lot of commercial value for this type of testing. Another interesting example would be most of the pharmaceutical companies I think, which have been citing since long where the basic structure is of the clay minerals. So, unless you create a porosity of a certain known value, you cannot dose it with the desired chemical or the pharmaceutical or the enzyme or whatever. So, this is a very interesting area to work on. Hope you have got a feel of it.

And of course, the concrete technologists who are the ones who utilize mercury intrusion porosimetry maximum, because these are the guys who are talking about the porosity and the strength relationships, you must have come across in your strength of material and concrete technology course. And ultimately this gets related to the what do you call it as the durability of the concrete. So, what type of microstructure should be created, so that the durability is maximum? So, everything boils down to the pore size characteristics.

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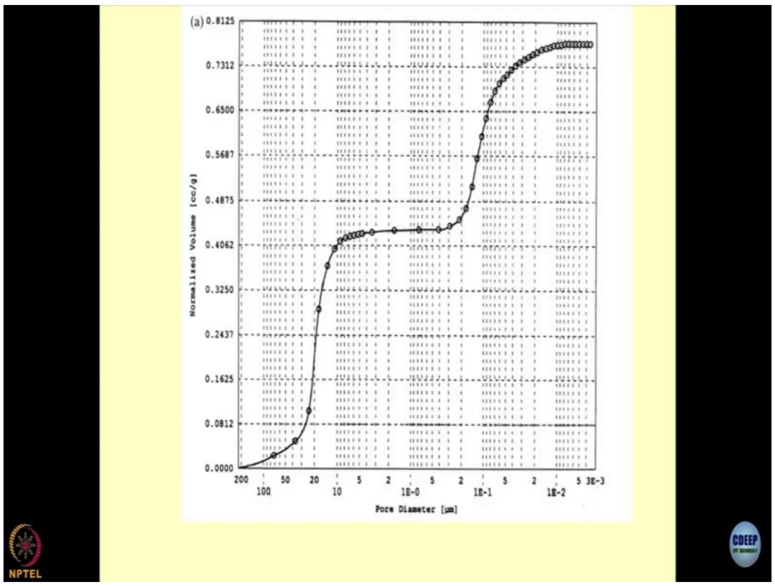

So, let us interpret one of the typical graphs that you will be getting from MIP. So this is an intrusion curve, that means the Mercury is being intruded into the pores. So, as the pressure here I have plotted pore diameter, which is inverse of the pressure. So, these are the coarser pores, and these are the finer pores. And this is the normalized volume that means the volume of the Mercury which enters divided by the volume of the sample.

So, what we will observe is, as the pressure increases, the first pores to get filled up is the biggest pore. And then Mercury goes into the finer pores. So, I am sure one of the philosophies you will appreciate is that the distribution of this graph, which is the mercury intrusion graph is similar to the particle size distribution curve. So, many times people utilize this concept to decipher the type of soil on which you are working and what composition of the particles and their morphology is present in the soil.

So, the first part of the graph shows pressure increases, volume increases fine, and then there is a situation where the graph becomes constant, the graph becomes constant to indicate that the volume of the Mercury which is going into the pores is becoming constant. The simplest possible analogy would be, if you consider the particle size in this range of the pressure which you have applied, they are all filled of this certain volume of Mercury, is it not?. Beyond which if you want to further pack the pores with the Mercury, you have to apply very high pressures.

And that is that the chances are that you might be distorting the pore structure. Still, there is a hope what you were talking about. Looking at this graph, I can make out whether the sample has undergone a sort of distortion in it or not. So, a scientist what he or she does, he or she basically tries to justify whatever he or she is doing by obtaining the results and analyzing them in a very very meticulous manner.

So, you need not worry. Now, I am negating of what I said sometime back. So still, if I have this graph, I know what I have done, and where the sample is yielding. Now, 2-3 ways are there to negotiate this type of situation. First of all, I will never expose the sample to very high pressures fully knowing the fact that this might crumble, or this might, the capillaries or the pores might collapse.

But if you reanalyze this graph, you will realize that the constant volume indicates that what could be the reason this could be the inertia of the fluid also or the Mercury also clear, because the pore diameter is still changing from 10 to 2. Now, this is where you have to go for the microscopic examination of the types of pores which are present in the system. And you never know that this could be dead-end pores, this could surface pores.

Because even if you are applying pressure, the volume is not increasing. So, the interpretation could be different. Is this okay? So, these type of analysis as I said are being used by the people who are into the industrial processes of minerals ores, different types of metals, tissues, we get lots of samples in our laboratory from biosciences, they would like to analyze the tissues, thin films, which are being done by the physicist for various purposes, a different type of surfaces that you want to create for adsorption to occur or for coatings.

And so on. Interestingly, you can correlate the void ratios with the mean pore diameter of the sample. So, mean pore diameter would be the statistical distribution from there, you can compute what the mean pore diameter is, and you will realize that as the void ratio increases the mean pore diameter increases.

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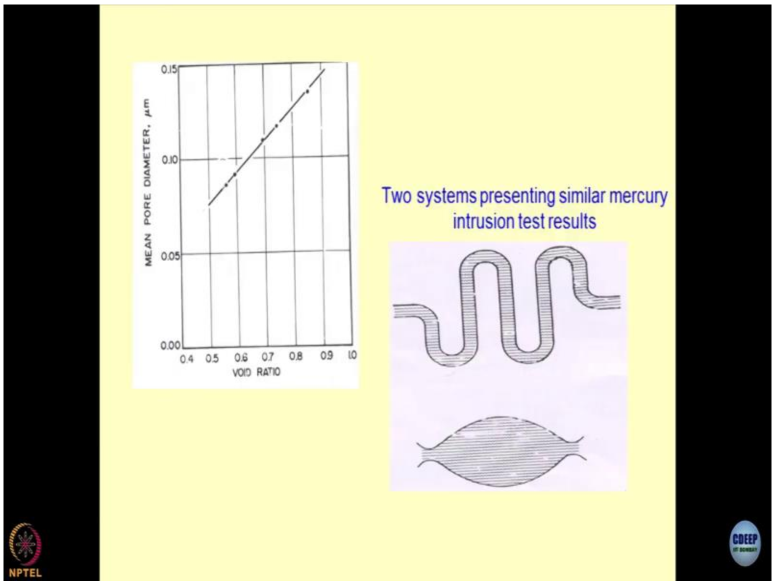

And this is where the small catch could be when we use this concept of mean pore diameter, we have to be careful that when I have different types of arrangement of the pores, particularly let's say zig-zag fashion like this, or there could be a pore which is sort of an ink bottle type. So, I hope you will realize that the total volume of these pores and these pores are going to be same. And hence, it becomes very difficult for the person who is doing MIP to differentiate between the geometry of the pores, because this is a volumetric analysis.

So, truly speaking, MIP is blind of the shapes of the pores. So, for that now, latest in the market is CT scanning or 4-dimensional X-ray scanning. We are trying to work on that but still a long way to go. And because we learned ourselves. And nobody wants to encourage us to use soil samples and rock samples and these sophisticated systems because of the dust element. So, you have to learn by conducting experiments yourself, and people do not have knowledge about it much yet. These are the recent trends in the geotechnical engineering, but I hope you must have got an idea that as a geotechnical engineer, how would I relate the pore diameters to the void ratios and this is good enough for me to go ahead with my research work.

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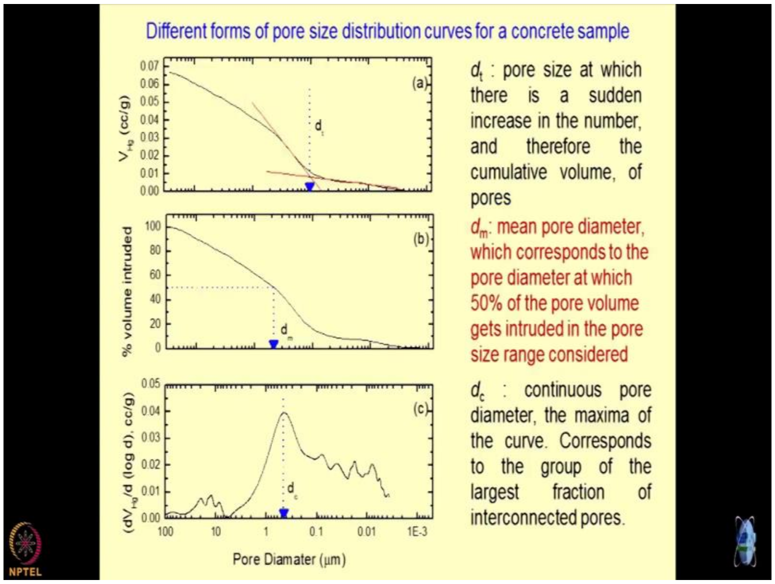

Just to give you an example of how different types of pore sizes are obtained. These are the test results of the concrete samples. And this study was done by my PhD scholar Dr Bibuthi Bhushan Das, a faculty member at NIT Suratkal. He was a concrete technologist, and out of curiosity, we wanted to see whether the porosity of the concrete is a standard material can be linked with heat migration through it or not.

So, if you remember the heat migration is also a function of packing of particles and the porosity gamma d and so on. So, we wanted to use a standard manmade material like concrete to relate the processes; it is a typical intrusion curve which you will be getting when you do NIP that is the volume of Mercury which enters into the pores. The only thing here is that the diameters are plotted in the reverse fashion, decreasing fashion, point of inversion of the curves if I extend and find out the intersection.

Now, this gives the dt. Now, dt is basically a cumulative pore diameter. From the percentage of the volume intruded into the sample, when you go for 50% this becomes the mean diameter and then corresponding to the 50% intrusion of the Mercury into the sample. Whatever diameter is this becomes the mean pore diameter, and the third thing is which is slightly more which follow the pattern or which is statistical in nature is if I do some mathematical modelling with the data volume of the Mercury.

Which is entering into the pores with a function of the log of the diameter of the pores of the incremental change in the diameter of the pores, this is on the y-axis, and this is plotted with respect to the pore diameter. So, where you have the maximum value, this corresponds to dc, which is known as continuous pore diameter. So, these 3 parameters are utilized for defining any porous media dt dm and dc.

So, dt corresponds to the cumulative volume of the Mercury which has gone into the material dm is the mean pore diameter and dc is the continuous pore diameter. So, these parameters have been linked with several mechanical properties of geomaterials.

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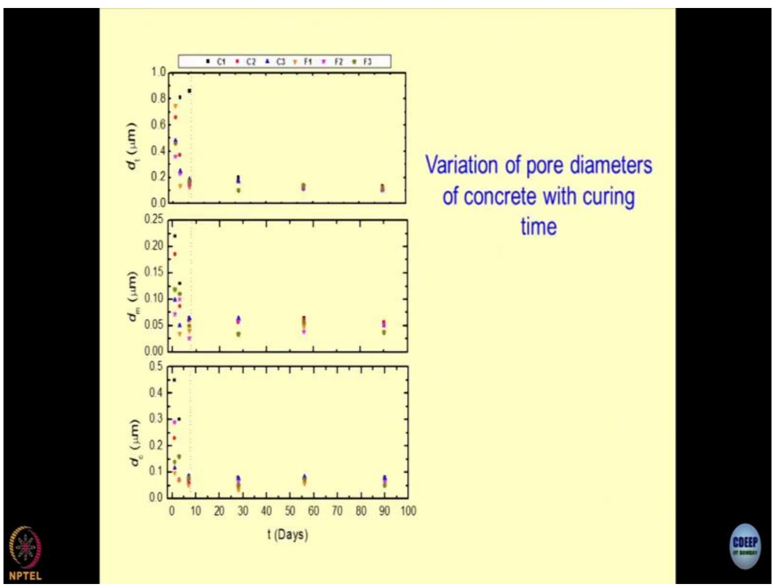

So, this is a good example of how it varies over a period of time in case of concrete which is getting cured. Why I am citing this example is concrete is still a very stable material as compared to the soils. But when I deal with the minerals which are active or the processes which are very active as a function of time inside the soil matrix, it becomes very difficult to capture the phenomena by using MIP.

So, in this case, if you see the dt, dm and dc they decrease as a function of time, and this is how we define the curing of the concrete. So, curing of concrete is itself is a very interesting research area where people have utilized MIP and impedance spectroscopy to observe what type of jelling which is taking place as the time progresses and the water phase disappears. Correct. So, here also, I can utilize the TP mixing model.

Which we were talking about the dielectric coefficient and the dielectric constant of the composite. So, this is the interesting area where people are still working, trying to see how the pore structure changes with time, what type of chemical processes are occurring and whether these mechanisms can be captured by using MIP and impedance spectroscopy. And nowadays, the most interesting and very latest thing which is in fashion is the nuclear magnetic resonance NMR which is being used for obtaining the amount of moisture which is present in the material at a given time. So, I thought I would share some of these ideas with you because those of you who are working in the field of environmental geomechanics would find this discussion very useful and quite contemporary.