Characterization of Construction Materials
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Lecture -65
Deliverables and Interpretation - Part 2

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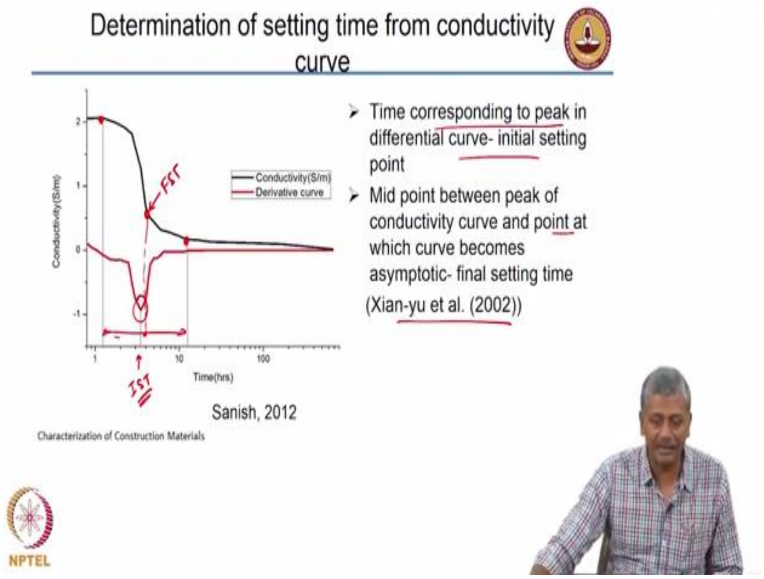

Determination of setting time from conductivity curve

- Time corresponding to peak in differential curve- initial setting point
- Mid point between peak of conductivity curve and point at which curve becomes asymptotic- final setting time

(Xian-yu et al. (2002))

Sanish, 2012

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Now can we use this conductivity information to actually pick out the points of setting? So here what is shown here is that empirically this was set as measurements of the setting point. So time corresponding to peak in differential curve was defined as the initial setting point. So initial setting time was marked here and the midpoint between peak of conductivity curve and the point at which the curve becomes asymptotic, which was based on a previous reference, was taken as final setting time. So, between those two points select the midpoint, project it up and that was taken to be the final setting time. Now you will ask me why? It is an empirical adjustment that we are doing here to find out whether this would have a significant bearing on the actual setting time that you measure using another empirical test, that is the Vicat test which we are quite familiar with. And indeed these values that we set as guides from the conductivity curves matched quite well with the setting time of Vicat apparatus.

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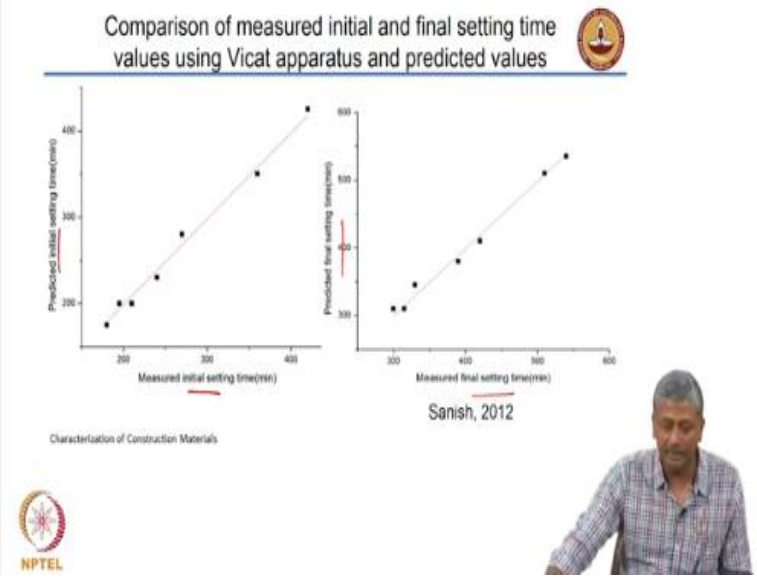

Comparison of measured initial and final setting time values using Vicat apparatus and predicted values

Sanish, 2012

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What is shown here is the initial setting time (IST) measured vs. predicted IST, final setting time (FST) measured vs. predicted FST and you can see that the data are quite well comparable. Now of course, you are predicting an empirical result with an empirical understanding. So, it is not truly correct, you need to relate this obviously to more fundamental development of the structure which is where we wanted to move in the future. So, this is around 2012 that this work was done and that time we were just getting our hands on this understanding and now we have a fundamental understanding developed based on electrical measurements which I will explain in further slides.

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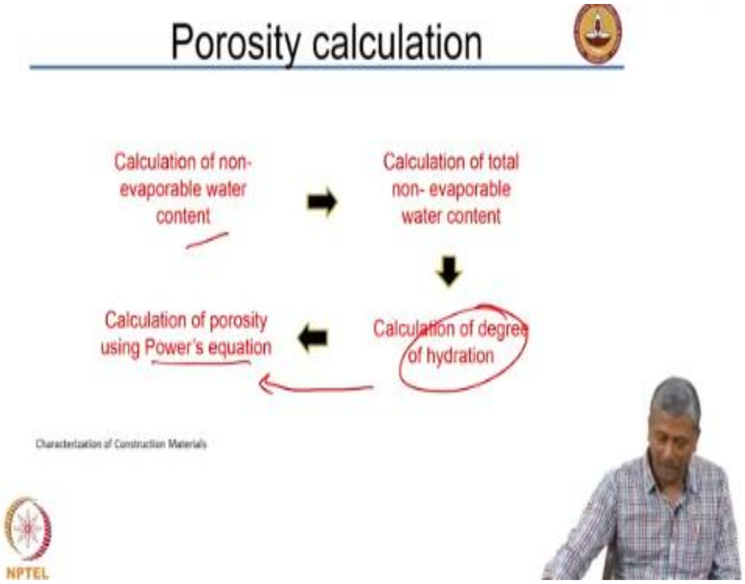

Porosity calculation

Calculation of non-evaporable water content

Calculation of total non- evaporable water content

Calculation of degree of hydration

Calculation of porosity using Power's equation

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So, in this same work of Sanish, we also tried to see how is the porosity developing during the same interval of time? So, porosity can be estimated using many ways. We saw earlier mercury intrution porosimitry is one of the best ways to get the level of porosity and pore size distribution but at this time when we did this work, there was no MIP available. There was no SEM available where we could easily do several images and collect, and there were SEMs but we did not have the time to work on the SEMs because we could not get slots to work on the SEM. So severe restrictions were there, and so we did an indirect approach.

We calculated the non-evaporable water content first. In cementitious materials, what is the non- evaporable water content? The water that cannot be removed by simply drying. That means it is the chemically bound water in the system. So is the water that is bound to the structure of the cement. So, this bound water has to be removed by heating cement between 100 and 1000 °C, typically 100 to 600 °C would do it but generally for the purpose of completion, we do the loss on ignition test: 100 to 1000 °C for the cement paste and that is expressed as bound water or non-evaporable water content. Now the greater the degree of hydration, the more will be the non-evaporable water content. So, from the non- evaporable water content we get the degree of hydration and that is converted to porosity using equation supplied by Powers.

And all of you who do cement chemistry have to be familiar with the name Powers, because he was one of the leading cement chemists of the past and a lot of his work is still being understood today He has written so many papers and whatever extra advancements have been there in concrete technology, we always come back to the basic equations that were suggested in the 50s and 60s by Powers.

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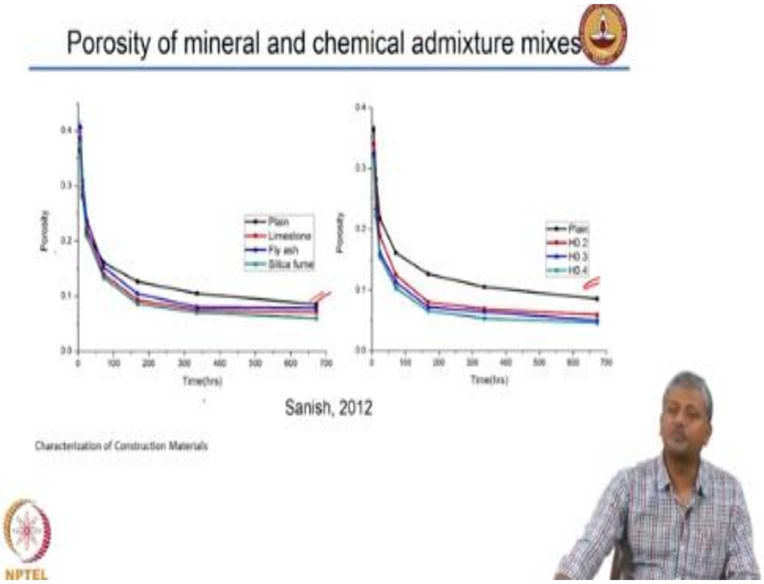

Porosity of mineral and chemical admixture mixes

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So porosity was calculated in this indirect fashion and what is shown here is that change in porosity with respect to time for the different systems involving mineral admixtures and chemical admixtures. But what is interesting is now - can we use the estimate of the conductivity to show the porosity and how do we do that?

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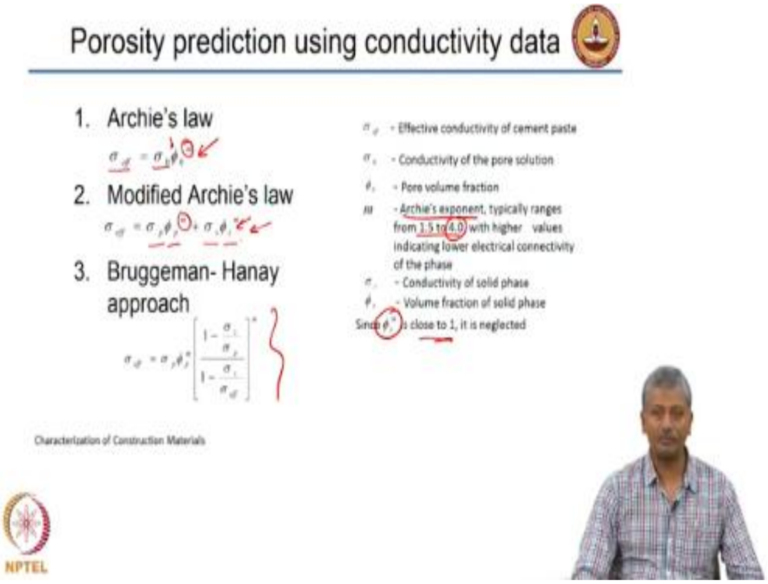

Porosity prediction using conductivity data

1. Archie's law

$\sigma_{eff} = \sigma_p \phi_p^m$

2. Modified Archie's law

$\sigma_{eff} = \sigma_p \phi_p^m + \sigma_s \phi_s^n$

3. Bruggeman- Hanay approach

$$\sigma_{eff} = \sigma_p \phi_p^m \left[\frac{1-\frac{\sigma_s}{\sigma_p}}{1-\frac{\sigma_s}{\sigma_{eff}}}\right]^m$$

σ_{eff} - Effective conductivity of cement paste

σ_p - Conductivity of the pore solution

ϕ_p - Pore volume fraction

m - Archie's exponent, typically ranges from 1.5 to 4.0 with higher values indicating lower electrical connectivity of the phase

σ_s - Conductivity of solid phase

ϕ_s - Volume fraction of solid phase

Since ϕ_s^n is close to 1, it is neglected

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There are studies previously conducted on porous solids by several investigators and one of the common methods of representation of porosity from conductivity data was proposed by Archie in the 1940s and this says that the effective conductivity of a porous system (σ_{eff}) is:

$$\sigma_{eff} = \sigma_o \phi_0^m$$

Where σ_o is the conductivity of the solution that is present in the pores

ϕ_0 is porosity

m is called Archie's exponent which typically ranges from 1.5 – 4; higher values generally indicate lower electrical connectivity of the phase. So, for rocks and for concrete generally we can use the higher values of 4 for the purposes of seeing whether the data agrees or not.

So here there is an indirect approach here which says that you can actually measure conductivity of the system and convert that to the porosity. Now there is also a modified form of Archie's law available which is:

$$\sigma_{eff} = \sigma_p \phi_p^m + \sigma_s \phi_s^m$$

Where σ_p is the conductivity of the pore solution

ϕ_p is the pore fraction of the pore solution

σ_s is the conductivity of the solid phase

ϕ_s is the pore fraction of the solid phase.

And there is also a more complicated version of the same approach presented by Bruggeman-Hanay. Also, ϕ_s^m is close to 1. So, it is almost a feature that can be neglected. We do not really need to consider that in the calculation of the effective conductivity.

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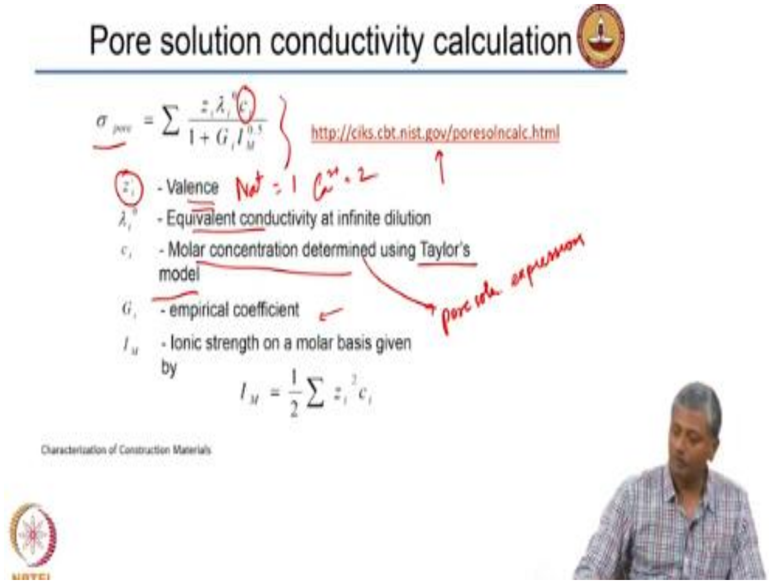

Pore solution conductivity calculation

$$\sigma_{pore} = \sum \frac{z_i \lambda_i^0 c_i}{1 + G_i I_M^{0.5}}$$

http://ciks.cbt.nist.gov/poresolncalc.html

z_i - Valence $Na^+ = 1$ $Ca^{2+} = 2$

λ_i^0 - Equivalent conductivity at infinite dilution

c_i - Molar concentration determined using Taylor's model

G_i - empirical coefficient

I_M - Ionic strength on a molar basis given by

$$I_M = \frac{1}{2} \sum z_i^2 c_i$$

pore soln. expression

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So, let us look at how this stacked up, for this of course you need to get an estimate of the pore solution conductivity σ_0. So now we have a method to do it. We squeeze out the pore solution and we measure its conductivity. That is not difficult at all. But in the past when we did not have that luxury, we had to use the software given by NIST - National Institute of Standards and Technology in the US. They actually have software that links the initial chemical composition of your cement and cementitious system to the final value of the pore solution conductivity that you will get from that system. And this is based on a database of pore solution expression analysis. But nevertheless what you have to do is get this conductivity of the pore solution (σ_{pore}) using this equation (given in slide) which deals with the concentration of the ionic species.

$$\sigma_{pore} = \sum \frac{z_i \lambda_i^0 c_i}{1 + G_i I_M^{0.5}}$$

Where z_i is the valence of the ionic species that you are trying to measure. For example, for Na^+ $z_i = 1$, for Ca^{2+} $z_i = 2$.

λ_i^0 is the equivalent conductivity at infinite dilution. So if you take a system and dilute it to an infinite level, the equivalent conductivity of that level is λ_i^0.

G_i is an empirical coefficient.

So, these are methods to actually determine the pore solution conductivity from the ionic concentration or molar concentration (c_i), which can be determined using pore solution expression, like I showed you earlier, or by using Taylor's model which relates the molar concentration to the initial chemical composition of your cement like the sodium oxide concentration, potassium oxide concentration, calcium oxide, silicon dioxide, and so on. So, you can get it in both ways. Ultimately, you are getting the σ_{pore}.

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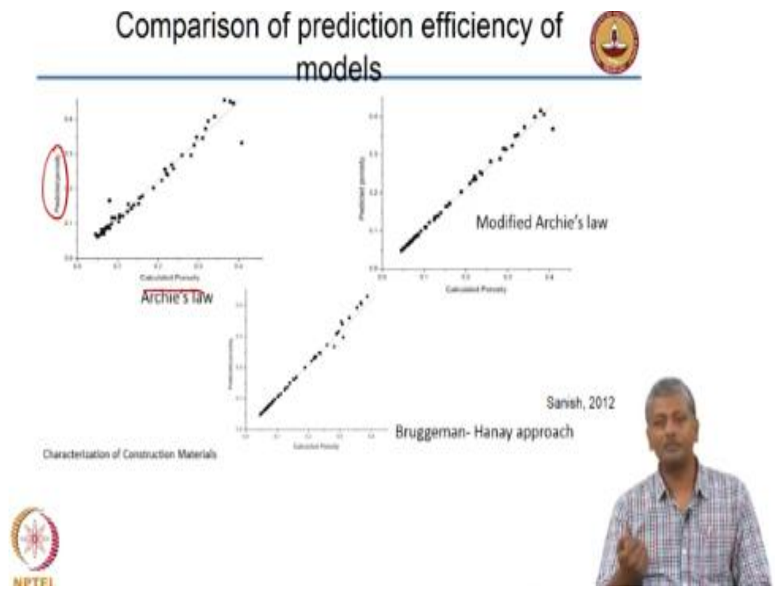

Comparison of prediction efficiency of models

Archie's law

Modified Archie's law

Bruggeman- Hanay approach

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So, we had the calculated porosities using Powers equation. We had the predicted porosities using the conductivity experiments. How is σ_{eff} obtained? From your experiment, the σ values that you get from experiment; (L/Ra) is your σ_{eff} because it is testing the entire system at once. σ_0 is obtained from the approach suggested by NIST.

And what is plotted here is the predicted porosity by conductivity measurements and the actual calculated, determined porosity from the system. You can see that for all 3 systems you have a very good agreement between the porosity that is determined from conductivity and the porosity that is calculated from fundamental principles from the approach suggested by Powers. So, this seems to indicate that there is a very good link between your electrical properties and the porosity in the system.

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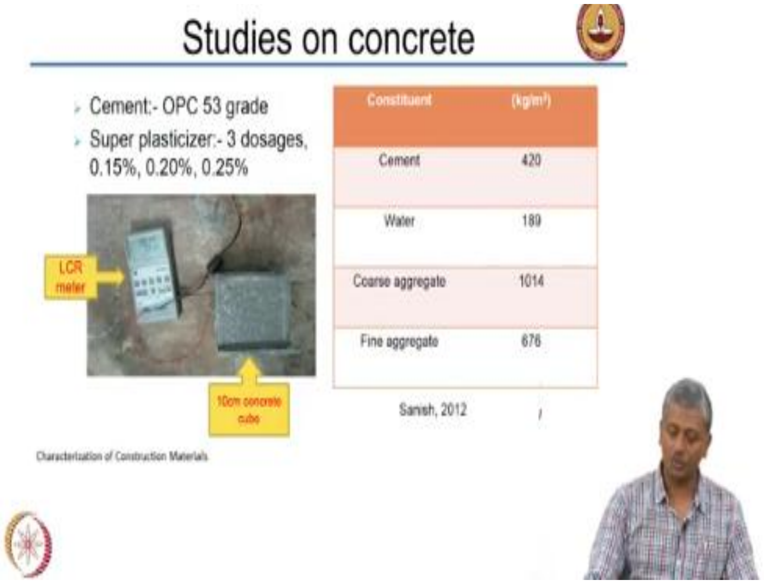

Studies on concrete

- Cement:- OPC 53 grade
- Super plasticizer:- 3 dosages, 0.15%, 0.20%, 0.25%

Constituent	(kg/m³)
Cement	420
Water	189
Coarse aggregate	1014
Fine aggregate	676

Sanish, 2012

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We repeated the same measurements in concrete. So here again, we did not use the impedance analyzer because at that time our lab did not have an impedance analyzer. The studies that I showed you previously were conducted by Sanish during a trip to Clarkson University in the US where one of our collaborators Professor Narayanan Neithalath had his own electrical impedance spectroscope and we actually did the measurements there and we came back and actually repeated the measurements on concrete using this simple LCR meter. LCR is basically an Inductance Capacitance Resistance meter which again operates on the same principles as an impedance spectroscope, except that here you have only the switching between frequencies, you can work at only one frequency at a time. So, you can switch between three values of frequency. I think it is if I remember it is 0.1,10,100 or 0.1 and 10 Hz in this case, something like that. I do not perfectly remember it. So we conducted the experiments at a single value of frequency, we chose the concrete mix as shown here.

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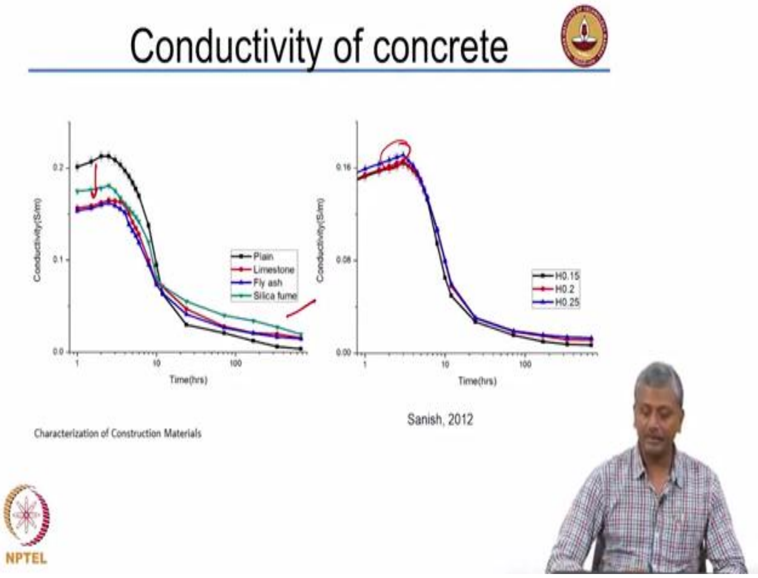

Conductivity of concrete

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And super plasticizer was also attempted at three dosages again; we tried to look at the effect of limestone, fly ash and silica fume. The same decrease in conductivity is being seen with respect to concrete also. Again, the influence of the water reducer was to increase the conductivity at the early ages and then compared to the OPC system, without admixture you see that there is a retardation in the effect. So, all the effects seen on the paste are also replicated in concrete.

LCR meter still uses AC, it does not use DC. So, we do not have a back emf, because there is no polarization in this case.

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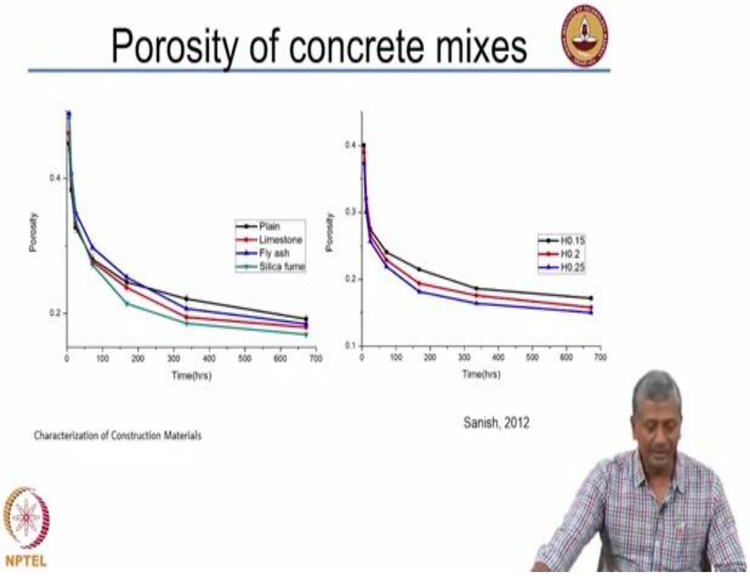

Porosity of concrete mixes

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So, porosity of concrete mixes was also determined using the same approach as I showed you earlier.

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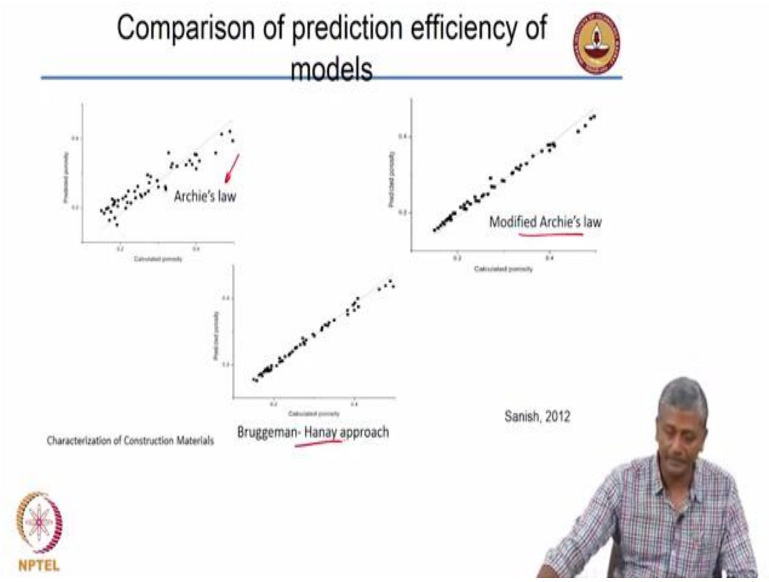

Comparison of prediction efficiency of models

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Then we did the same comparison of the prediction efficiency of the models. Now it looks like there is a greater spread in Archie's law in this case. Because here we have a system which is a composite of different sizes of materials, we not only have the paste, we have aggregates which are granular ingredients in different sizes, there will be an effect of the ITZ also. So, the solid phase conductivity may have a greater role to play in this system. That is why both your Modified Archie's law and Bruggeman-Hanay approach seem to work much better in the predictions as compared to your simple Archie’s law which only relies on the porosity and the pore solution conductivity.

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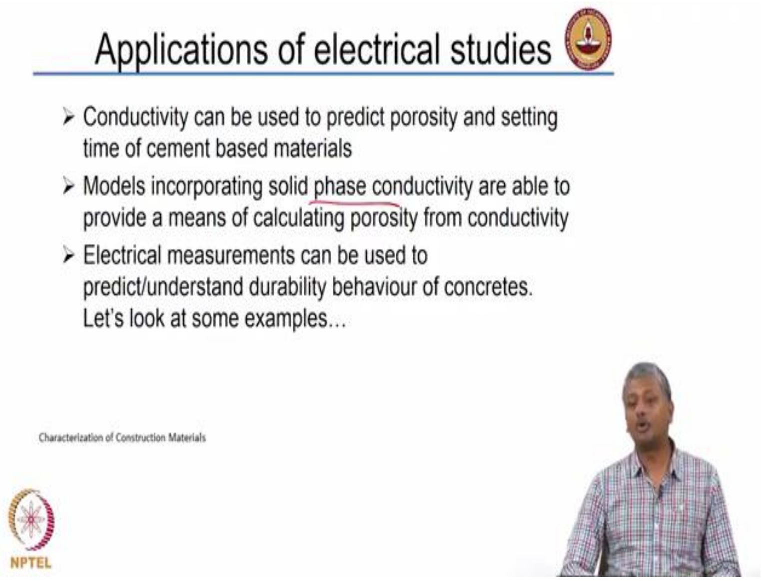

Applications of electrical studies

- Conductivity can be used to predict porosity and setting time of cement based materials
- Models incorporating solid phase conductivity are able to provide a means of calculating porosity from conductivity
- Electrical measurements can be used to predict/understand durability behaviour of concretes. Let's look at some examples…

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So, this is one aspect of the study - conductivity can be used to predict porosity. Models that incorporate solid phase conductivity help in actually achieving a better prediction for concrete. Now let us look at how to understand durability behavior of concrete based on electrical measurements, through some examples.

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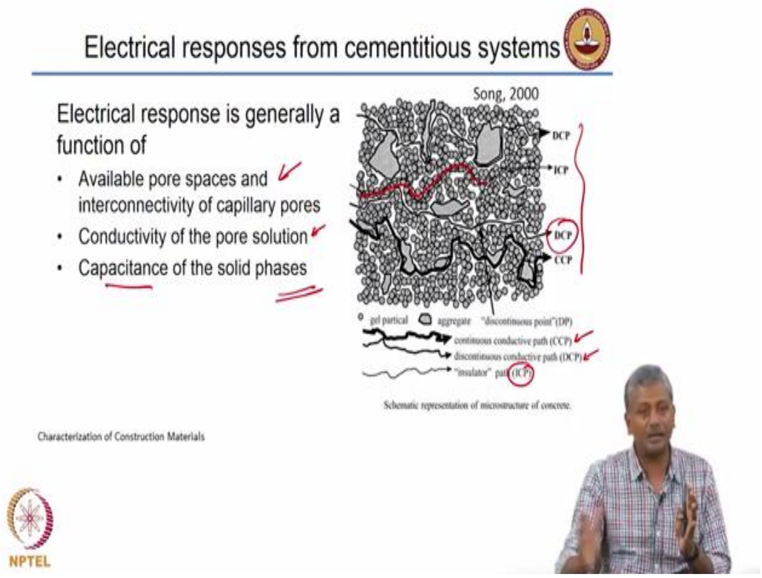

Electrical responses from cementitious systems

Electrical response is generally a function of

- Available pore spaces and interconnectivity of capillary pores
- Conductivity of the pore solution
- Capacitance of the solid phases

Song, 2000

Schematic representation of microstructure of concrete.

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So just to give you a picture of flow through concrete, so when you are measuring electrical response through concrete, it is a function of the available pore spaces and how these pores are actually connected. It also is governed by the conductivity of the pore solution and the capacitance or charge storage capacity of the solid phases. We saw earlier that these were very clearly governing the electrical response properties.

So again, here as far as the porosity is concerned, you can divide that into several types. One is a continuous pore path, i.e., continuous conductive path that means you have very large pores nicely connected to each other. Then you have a discontinuous conductive path in your system like you see is shown in the figure; it is still an interconnected porosity. Then you have an "insulator" path (ICP) which is basically through the grain to grain contact of the solid phases. That is basically responsible for the capacitance of the system. So, all these three types of systems will be conducting your charge through the concrete. What we need to do is now bring out the role of the interconnection of the porosity by the electrical measurements.

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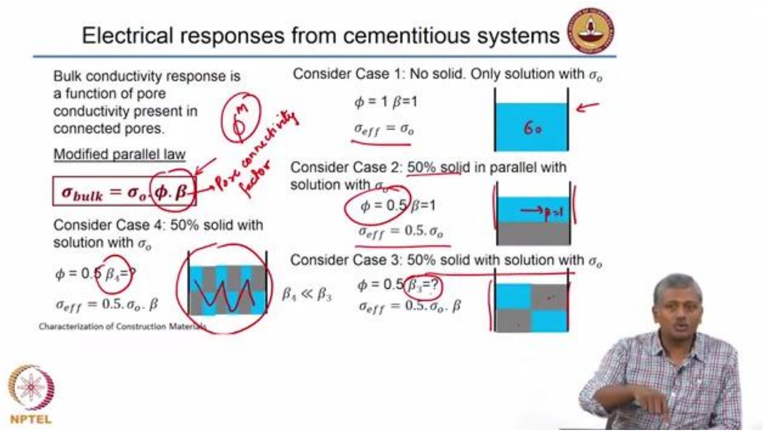

Electrical responses from cementitious systems

Bulk conductivity response is a function of pore conductivity present in connected pores.

Modified parallel law

$\boxed{\sigma_{bulk} = \sigma_o \cdot \phi . \beta}$

Consider Case 4: 50% solid with solution with σ_o

$\phi = 0.5\ \beta_4 = ?$

$\sigma_{eff} = 0.5 . \sigma_o . \beta$

Consider Case 1: No solid. Only solution with σ_o

$\phi = 1\ \beta = 1$

$\sigma_{eff} = \sigma_o$

Consider Case 2: 50% solid in parallel with solution with σ_o

$\phi = 0.5\ \beta = 1$

$\sigma_{eff} = 0.5 . \sigma_o$

Consider Case 3: 50% solid with solution with σ_o

$\phi = 0.5\ \beta_3 = ?$

$\sigma_{eff} = 0.5 . \sigma_o . \beta$

$\beta_4 \ll \beta_3$

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So here for instance, we can use the same relationship that we saw in the form of Archie's law in a slightly different approach. So, what we say here is the bulk conductivity response is a function of pore conductivity present in the connected porosity only. So, we are not considering solid phase to be responsible. So, we are saying again, we are restating Archie's law in a slightly different format. Earlier we said $\sigma_{eff} = \sigma_0 * \phi^m$. So, we are replacing ϕ^m by this multiple of porosity (ϕ) and the pore connectivity factor (β). This is another approach of restating the Archie's law.

Case 1: So just consider a case where your system is entirely liquid - that means full porosity, 100% porosity or porosity = 1, then pore connectivity is obviously equal to 1. All pores are connected. So, your $\sigma_{eff} = \sigma_0$ which is the conductivity of this solution that is here (in figure).

Case 2: You now have a 50% solid in parallel with the solution with σ_0. So, when you determine the electrical response by applying electrodes at the end you again have β=1. But the overall porosity is only half, because half of your material is solid. So, $\sigma_{eff} = 0.5\ \sigma_0$.

Case 3: Now you still have 50% porosity. But your phases are distributed like this now. So you need to determine your β, because β is not fixed in this case. That means by providing a solid phase that is dispersed in different directions, you have changed the β values; you will probably lead to a higher degree of tortuosity or disconnectedness of the porosity.

Case 4: Similarly here, you have a system where you again have 50% porosity, but your pores are such that they are more tortuous. So, increasing the path of flow is what is basically providing for the reduction in the conductivity of the system. So, your β values will keep on decreasing as you go from β_3 to β_4 to more complicated arrangements at the same level of porosity. So here this is a very interesting concept to show that even concretes which have the same porosities can show very distinct different electrical signatures because of the pore connectivity.

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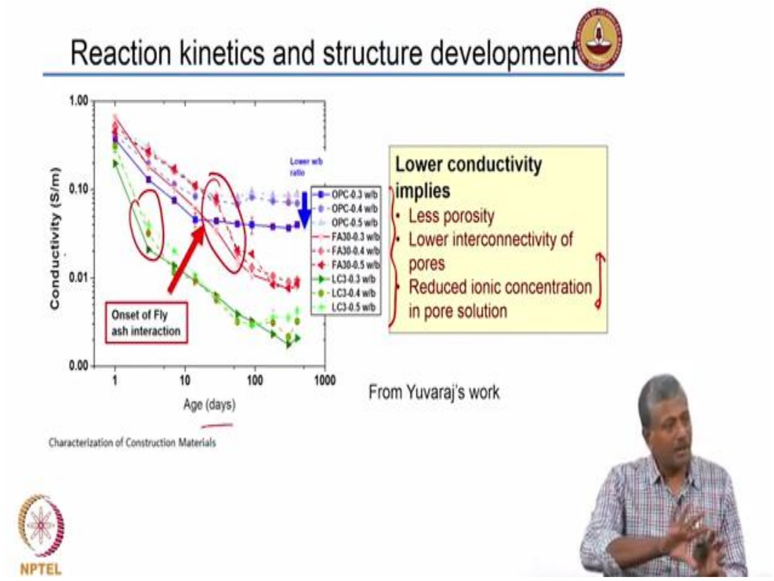

Reaction kinetics and structure development

Lower conductivity implies
- Less porosity
- Lower interconnectivity of pores
- Reduced ionic concentration in pore solution

Onset of Fly ash interaction

From Yuvaraj's work

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Now let us see how it actually looks at with respect to actual data from the lab. So again, conductivity here is plotted with respect to age for different cement paste systems. With ordinary Portland cement, 30% fly ash replaced paste and LC3 paste and you see very clearly, that as early as 3 days, you have a major reduction in conductivity of LC3 systems. In the case of fly ash the major reduction in the conductivity happens only in the long-term around 28 days. So, the fly ash interaction which is a delayed pozzolanic reaction contributes to this reduction in conductivity only at a later age.

So lower conductivity implies first of all less porosity, lower interconnectivity of the pores, it could also relate to reduced ionic concentration in the pore solution. We need now, a way to actually separate these two. We need to somehow bring out the effect of the pore solution concentration. To give some sort of a parameter that will only reflect the interconnectivity of the pore. That is quite easily done.

If you look at the approach of the law ($\sigma_{bulk} = \sigma_0 * \phi * \beta$), if you bring σ_0 to the other side, so that becomes a normalized sort of a conductivity with respect to the conductivity of the pore solution. And from that you can actually get an effective pore connectivity factor which will vary for your different systems, even at the same level of porosity.

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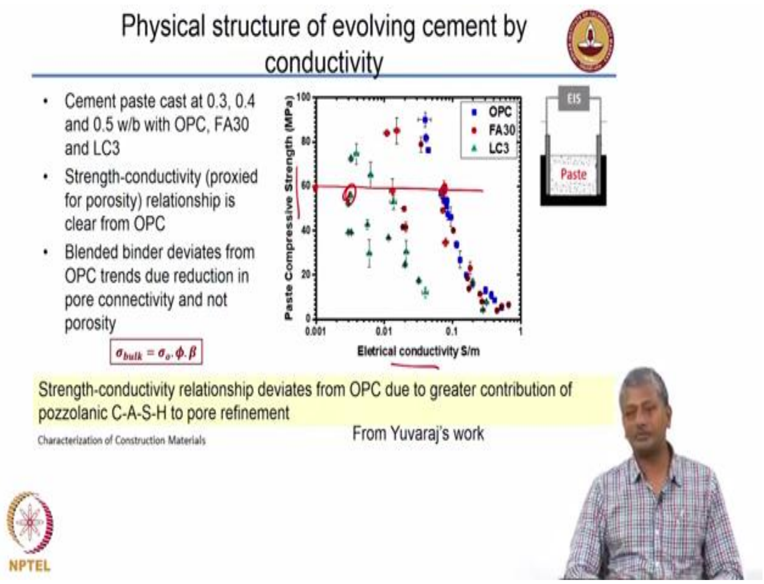

Physical structure of evolving cement by conductivity

- Cement paste cast at 0.3, 0.4 and 0.5 w/b with OPC, FA30 and LC3
- Strength-conductivity (proxied for porosity) relationship is clear from OPC
- Blended binder deviates from OPC trends due reduction in pore connectivity and not porosity

$\sigma_{bulk} = \sigma_o . \phi . \beta$

Strength-conductivity relationship deviates from OPC due to greater contribution of pozzolanic C-A-S-H to pore refinement

From Yuvaraj's work

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So that is what is exactly done in the approach that I am going to talk about. We talk about what is called the formation factor; of course before I get there again, the same sort of an understanding is given here in terms of the strength vs. conductivity relationships. What does strength depend on? Porosity, strength depends on overall porosity in the system, whereas the electrical conductivity depends on the pore connectivity.

So now if you look at a particular level of strength, let us say 60 MPa for the paste, you draw a line here, you see that the conductivity of OPC pastes is at a very high level, whereas your conductivity of your LC3 pastes is very low. So, the systems while showing the same strength indicative of the same porosity, the electrical conductivity response is quite different indicating a completely different pore connectedness. And that will have a clear bearing on the durability of the system, which we saw already in the resistivity values that I showed you earlier. Resistivity values of LC3 were an order of magnitude greater than the resistivity of the ordinary Portland cement.

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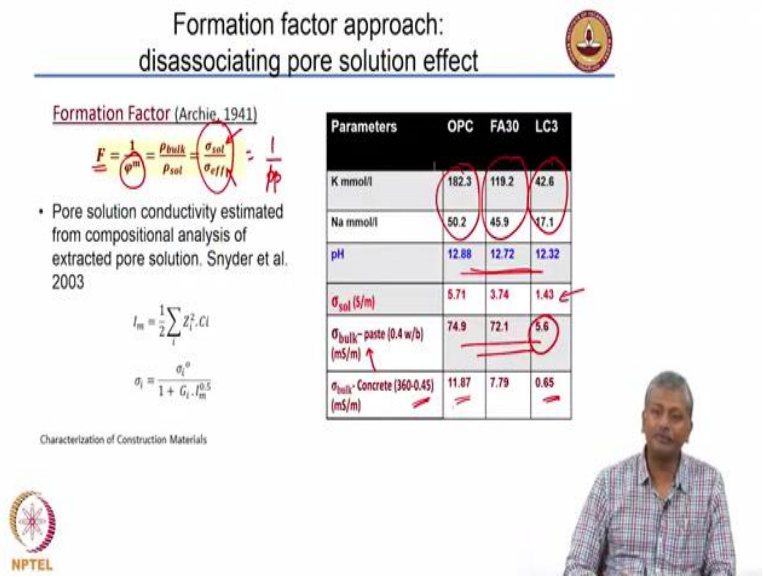

Formation factor approach: disassociating pore solution effect

Formation Factor (Archie, 1941)

$$F = \frac{1}{\varphi^m} = \frac{\rho_{bulk}}{\rho_{sol}} = \frac{\sigma_{sol}}{\sigma_{eff}} = \frac{1}{\phi\beta}$$

- Pore solution conductivity estimated from compositional analysis of extracted pore solution. Snyder et al. 2003

$$I_m = \frac{1}{2}\sum_i Z_i^2 . Ci$$

$$\sigma_i = \frac{\sigma_i^o}{1 + G_i . I_m^{0.5}}$$

Parameters	OPC	FA30	LC3
K mmol/l	182.3	119.2	42.6
Na mmol/l	50.2	45.9	17.1
pH	12.88	12.72	12.32
σ_{sol} (S/m)	5.71	3.74	1.43
σ_{bulk} – paste (0.4 w/b) (mS/m)	74.9	72.1	5.6
σ_{bulk} - Concrete (360-0.45) (mS/m)	11.87	7.79	0.65

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So again the approach that I was talking about of removing the pore solution conductivity from the picture is called the formation factor approach, which just says that you divide your effective conductivity by pore solution conductivity or we define the formation factor 'F' as the conductivity of the pore solution divide by the conductivity of the entire system. That means it will be equal to what?

$$\sigma_{eff} = \sigma_{sol} . \phi . \beta$$

$$\rightarrow F = \frac{1}{\phi^m} = \frac{\rho_{bulk}}{\rho_{sol}} = \frac{\sigma_{sol}}{\sigma_{eff}} = \frac{1}{\phi . \beta}$$

So, F is your pore formation factor. In the older equations, it will be $\frac{1}{\phi^m}$ in the original Archies law expression. So again, pore solution conductivity can be estimated. We talked about the model earlier for estimating pore solution conductivity from either a pore solution, which is expressed out of the concrete or a pore solution that is calculated from the initial cement composition.

So again, here (in the table) this is giving you for the three different binder systems, what are the expected sodium and potassium concentrations of the system? What is the pH exhibited? Again these are pore solutions that have been expressed from the paste and these are the actual conductivities of the pore solution and what you get for the σ_{bulk} in the paste look at the variation here you get 5.6 mS/m as the actual conductivity of cement paste with 0.4 water-binder ratio for an LC3 as opposed to 74 mS/m for OPC. Similarly, in concrete which has 360 kg/m^3 binder content and 0.45 water-binder ratio, you get only 0.65 mS/m conductivity as opposed to 11.9 mS/m in the case of OPC. So, conductivities are off by a very large difference. In the same effect you saw earlier in the resistivity values. So electrical responses also are directly indicative of durability behavior of the concrete.

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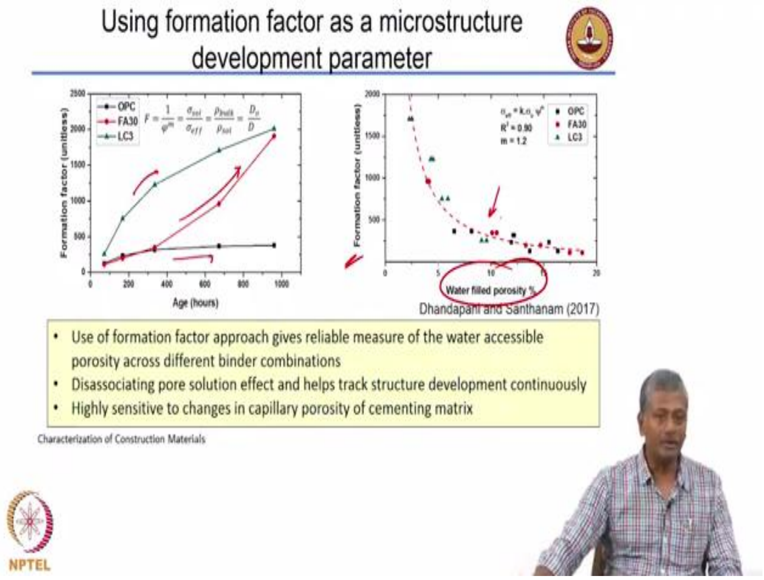

Using formation factor as a microstructure development parameter

Dhandapani and Santhanam (2017)

- Use of formation factor approach gives reliable measure of the water accessible porosity across different binder combinations
- Disassociating pore solution effect and helps track structure development continuously
- Highly sensitive to changes in capillary porosity of cementing matrix

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Again, formation factor, it can be quite clearly seen here develops very early for the LC3 system, for FA30 system it takes a longer time to develop, for OPC it develops to a certain stage and then there is no further development. It is also interesting to note that the formation factor seems to be quite well linked to durability parameters that are measured on a macro scale like water filled porosity of the system. You see here very clearly that irrespective of the binder type, the formation factor seems to be quite well linked to the water filled porosity of the system. So again, it is a very useful approach to actually determine the relative durability performance of your concrete systems by just measuring the electrical responses.

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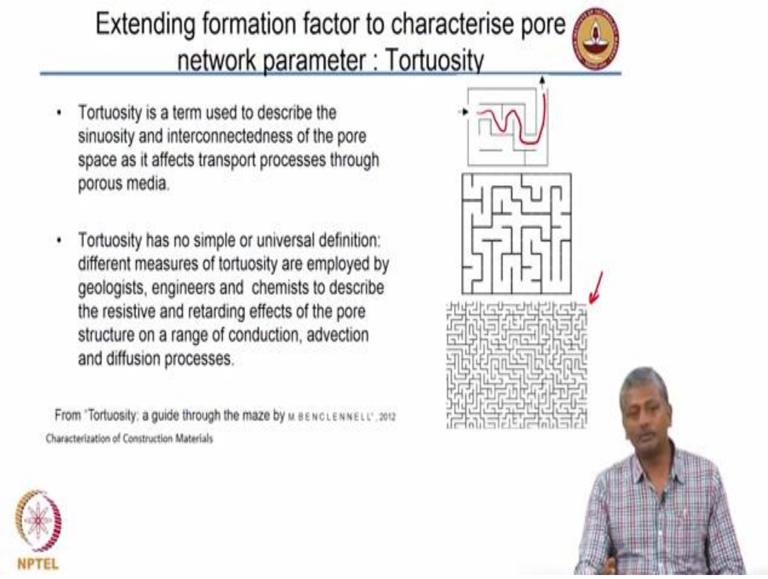

Extending formation factor to characterise pore network parameter : Tortuosity

- Tortuosity is a term used to describe the sinuosity and interconnectedness of the pore space as it affects transport processes through porous media.
- Tortuosity has no simple or universal definition: different measures of tortuosity are employed by geologists, engineers and chemists to describe the resistive and retarding effects of the pore structure on a range of conduction, advection and diffusion processes.

From "Tortuosity: a guide through the maze by M. BEN CLENNELL", 2012

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Now again more details are provided here. In, this case what I am going to show you here is basically the tortuosity calculation from the pore parameters. So, tortuosity is nothing but how disconnected the pores are or what is the path of flow? So, if this is a maze for instance, your flow has to happen through the maze like this. That is the path of flow from one point to the other.

Now, why is this important? In concrete we know that durability characteristics are governed by the permeability of the concrete. How easily can water or ionic species penetrate into concrete? And the more tortuous the path is more difficult it will be for flow to happen. Now this tortuosity can be indicated by the electrical properties also. The factor β or pore connectivity factor can be indicative about the tortuosity.

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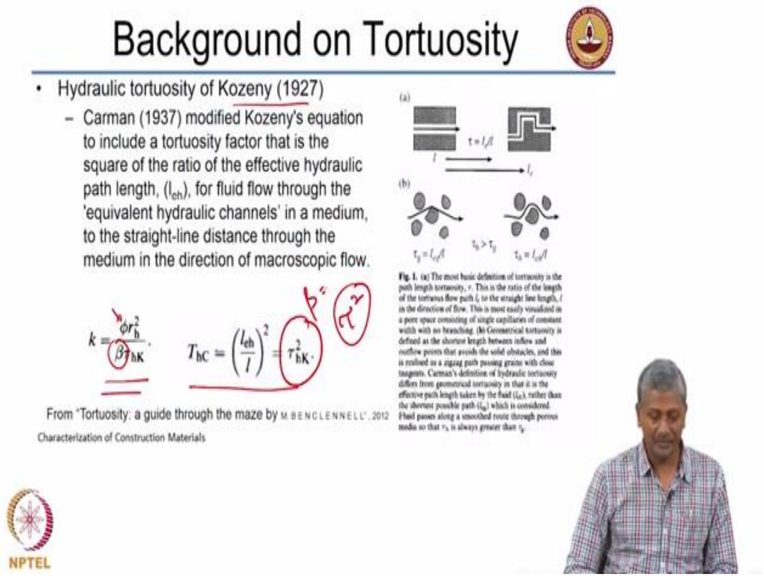

Background on Tortuosity

- Hydraulic tortuosity of Kozeny (1927)
  - Carman (1937) modified Kozeny's equation to include a tortuosity factor that is the square of the ratio of the effective hydraulic path length, (l_{eh}), for fluid flow through the 'equivalent hydraulic channels' in a medium, to the straight-line distance through the medium in the direction of macroscopic flow.

$$k = \frac{\phi r_h^2}{\beta \tau_{hK}}. \qquad T_{hC} = \left(\frac{l_{eh}}{l}\right)^2 = \tau_{hK}^2 .$$

$\beta =$ τ^2

Fig. 1. (a) The most basic definition of tortuosity is the path length tortuosity, τ. This is the ratio of the length of the tortuous flow path l_t to the straight line length, l in the direction of flow. This is most easily visualized in a pore space consisting of single capillaries of constant width with no branching. (b) Geometrical tortuosity is defined as the shortest length between inflow and outflow points that avoids the solid obstacles, and this is realised as a zigzag path passing grains with close tangents. Carman's definition of hydraulic tortuosity differs from geometrical tortuosity in that it is the effective path length taken by the fluid (l_{eh}), rather than the shortest possible path (l_{eg}) which is considered. Fluid passes along a smoothed route through porous media so that τ_h is always greater than τ_g.

From "Tortuosity: a guide through the maze by M BEN CLENNELL", 2012

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So how is that parameter defined? Of course, there are different ways of defining it; you can actually define the geometrical tortuosity, which is nothing, but the effective length of travel divided by the total length between two points. You can also have diffusional tortuosity or hydraulic tortuosity, which is defined by Kozeny. I am just giving you these details so that you can do additional understanding of this aspect of tortuosity. We do not really have to discuss in detail here, but just so that you get an idea.

So here the coefficient of permeability as per Kozeny's equation is related to the porosity and this system tortuosity. So here tortuosity is defined by the square of the effective length over the actual distance measured between two points, i.e., $\left(\frac{l_{eh}}{l}\right)^2$ and that is given as τ^2. So, τ is tortuosity; pore connectivity factor $\beta = \tau^2$.

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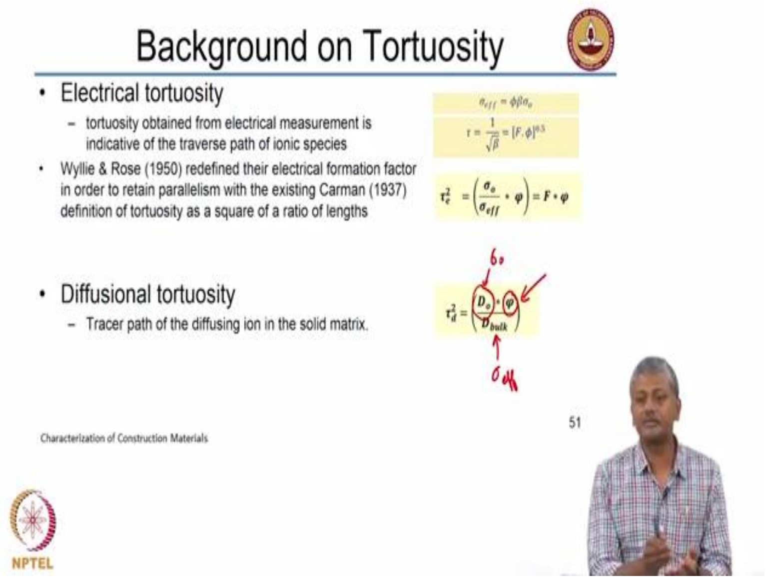

Background on Tortuosity

- Electrical tortuosity
  - tortuosity obtained from electrical measurement is indicative of the traverse path of ionic species
- Wyllie & Rose (1950) redefined their electrical formation factor in order to retain parallelism with the existing Carman (1937) definition of tortuosity as a square of a ratio of lengths

$$\sigma_{eff} = \phi\beta\sigma_o$$

$$\tau = \frac{1}{\sqrt{\beta}} = [F.\phi]^{0.5}$$

$$\tau_e^2 = \left(\frac{\sigma_o}{\sigma_{eff}} * \varphi\right) = F * \varphi$$

- Diffusional tortuosity
  - Tracer path of the diffusing ion in the solid matrix.

$$\tau_d^2 = \left(\frac{\overset{\sigma_0}{D_o} * \varphi}{\underset{\sigma_{eff}}{D_{bulk}}}\right)$$

Let us bring that back into our current discussion. So here we define the diffusional τ_d^2 as:

$$\tau_d^2 = \left(\frac{D_0 * \phi}{D_{bulk}}\right)$$

where D_0 is the diffusion coefficient of a system with infinite dilution

ϕ is the porosity

D_{bulk} is the diffusion coefficient of the actual system that you are trying to measure.

Now convert this to an electrical response. D_0 will be σ_0 and D_{bulk} will be σ_{eff}. All these are again playing with the same sort of relationships that we talked about earlier based on Archie's law.

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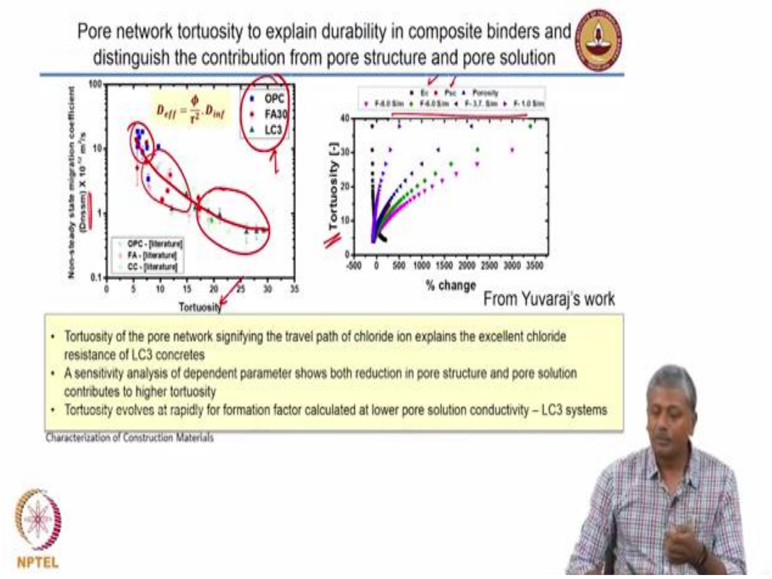

Pore network tortuosity to explain durability in composite binders and distinguish the contribution from pore structure and pore solution

From Yuvaraj's work

- Tortuosity of the pore network signifying the travel path of chloride ion explains the excellent chloride resistance of LC3 concretes
- A sensitivity analysis of dependent parameter shows both reduction in pore structure and pore solution contributes to higher tortuosity
- Tortuosity evolves at rapidly for formation factor calculated at lower pore solution conductivity – LC3 systems

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So, what is being plotted next is the tortuosity for different cementitious systems and how well it describes a durability parameter like the non-steady state migration coefficient. Now those of you have learnt this before, know that this migration coefficient is a very important parameter that is used in several project specifications to define the durability of the concrete. So, this is actually an electrical migration test where chlorides actually are made to migrate through the concrete under an applied electrical potential. You measure the depth of the chloride penetration and then convert that to an equivalent migration coefficient.

What is clear from here is that there is a clear dependence of this migration coefficient on the tortuosity of the system irrespective of the binder type. But what you also see is that these green points are basically all your LC3 systems the blue is OPC and the red are your fly ash based systems. So very clearly, we can see that the higher the tortuosity of the system, the lower the migration coefficient or lower the propensity for chloride migration through your cementitious system from happening.

Now what is also seen from Yuvaraj's study is that the sensitivity of your tortuosity is much greater on the actual conductivity of the pore solution and the electrical conductivity of the system. So, what he also was trying to do is sensitivity analysis as to the factors that affect this tortuosity value and what is seen is the pore solution conductivity values that we assume in the relationship can have a major significant effect on the change in tortuosity.

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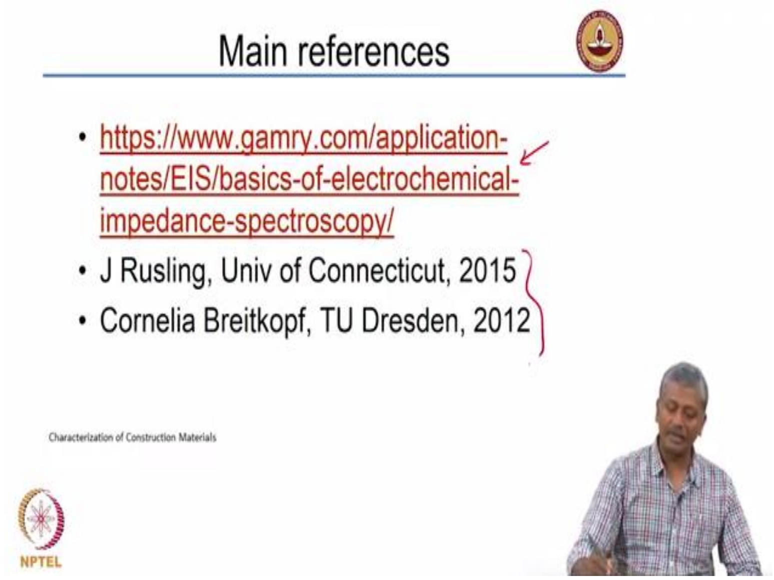

Main references

- https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/
- J Rusling, Univ of Connecticut, 2015
- Cornelia Breitkopf, TU Dresden, 2012

So that was just to give you an idea about how well we can actually progress from simply an understanding of the porosity of the system to defining aspects about pore connectivity which are primarily responsible for addressing the durability characteristics of concrete systems.

So, there are several differences that you can look at. This first reference is very interesting because you can learn about electrical properties and the measurement of electrical responses quite significantly from this; most of the illustrations that I chose in the early part were from this website. And there is also a couple of lecture notes which are available on the web by Rusling and Breitkopf which can also give you a much better understanding of Electrochemical Impedance Spectroscopy.