Characterization of Construction Materials

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Lecture -64

Electrical Impedance Analysis -Deliverables and Interpretation - Part 1

Hello everybody, in the last session we were talking about the principles of EIS and what sort of information we can actually achieve out of understanding electrical properties of construction materials. Primarily with respect to concrete and the porous building materials, we are interested in understanding the pore structure and that can be detected with the help of impedance spectroscopy because the interconnected porosity is what is responsible for conduction paths through the concrete.

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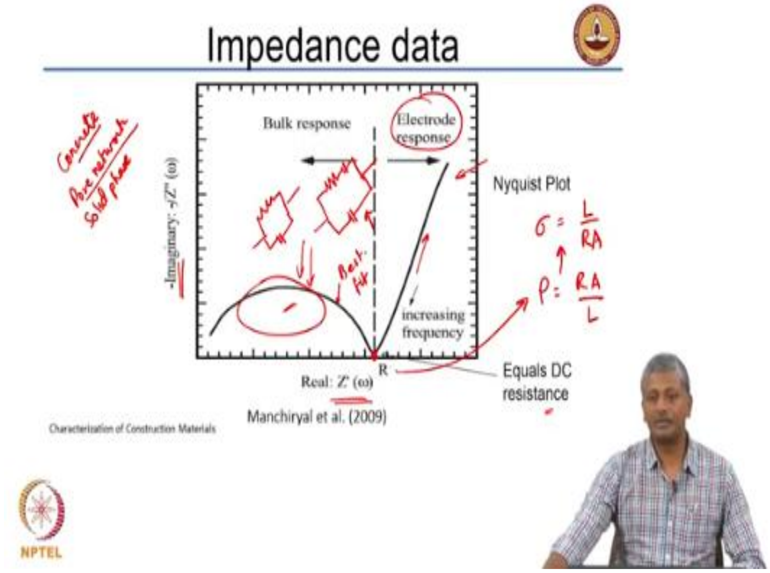

Impedance data

Manchiryal et al. (2009)

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So when we finished up yesterday, we were trying to see how impedance can be applied to the study of cementitious materials and how the data can be actually presented in terms of an equivalent circuit which helps us understand the resistance and capacitance properties of the material that we are trying to model.

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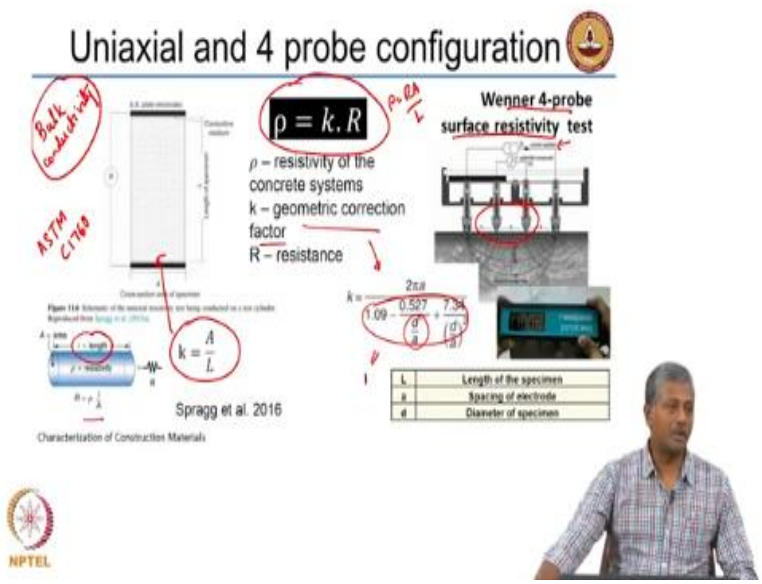

Uniaxial and 4 probe configuration

Bulk conductivity

ASTM C1760

$$\rho = k.R$$

$\rho = \frac{RA}{L}$

ρ – resistivity of the concrete systems

k – geometric correction factor

R – resistance

$$k = \frac{A}{L}$$

Wenner 4-probe surface resistivity test

$$k = \frac{2\pi a}{1.09 - \frac{0.527}{\left(\frac{d}{a}\right)} + \frac{7.34}{\left(\frac{d}{a}\right)^2}}$$

L	Length of the specimen
a	Spacing of electrode
d	Diameter of specimen

Spragg et al. 2016

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So, we looked at how the Wenner 4-probe resistivity test and bulk conductivity test can be used to determine durability related properties of concrete.

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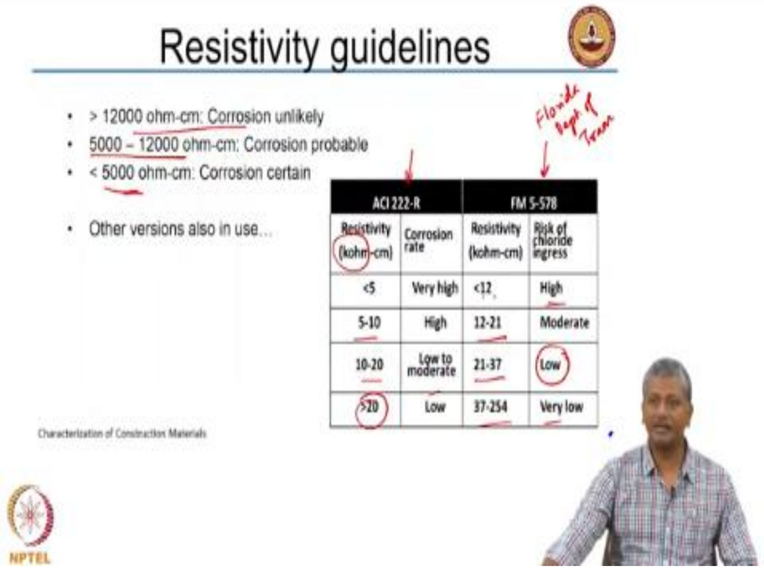

Resistivity guidelines

- > 12000 ohm-cm: Corrosion unlikely
- 5000 – 12000 ohm-cm: Corrosion probable
- < 5000 ohm-cm: Corrosion certain
- Other versions also in use…

Florida Dept of Tran

ACI 222-R		FM 5-578	
Resistivity (kohm-cm)	Corrosion rate	Resistivity (kohm-cm)	Risk of chloride ingress
<5	Very high	<12	High
5-10	High	12-21	Moderate
10-20	Low to moderate	21-37	Low
>20	Low	37-254	Very low

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And then we were trying to look at how the resistivity guidelines can be formulated to assess the performance of cementitious materials and different environments.

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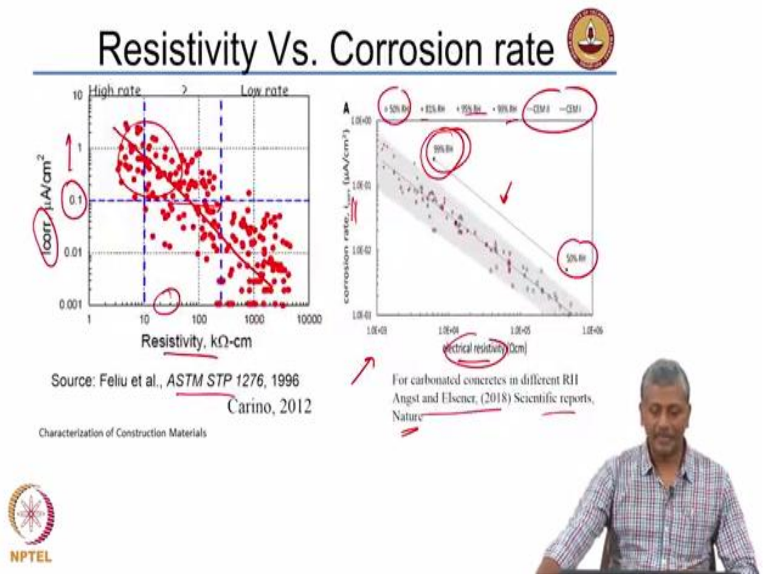

Resistivity Vs. Corrosion rate

Source: Feliu et al., *ASTM STP 1276*, 1996

Carino, 2012

For carbonated concretes in different RH Angst and Elsener, (2018) Scientific reports, Nature

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We also saw that the resistivity has been shown in literature to have a very good connection with the actual rate of corrosion experienced by steel in such concrete systems.

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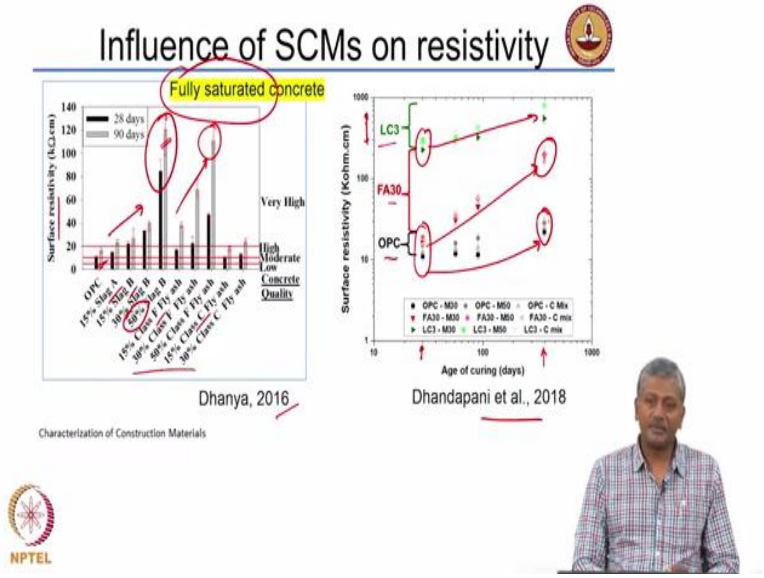

Influence of SCMs on resistivity

Fully saturated concrete

Dhanya, 2016

Dhandapani et al., 2018

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And today what I am going to talk about further is how the influence of binding materials on the resistivity of the concrete plays a great role in trying to enhance the durability of these kinds of special binder systems. So now these are some results from research studies that have been done in our lab. So this one is from the PhD thesis of Dhanya, where we were looking at what would be the influence of replacement of cement with slag and fly ash in different dosages for a range of mixture designs and mixture proportions with an attempt to bring out some sort of a durability specification for concrete construction.

So here this is presenting surface resistivity the Wenner 4-probe surface resistivity measurements with respect to the degree of replacement of ordinary Portland cement with two types of slag A and B and there was Class F fly ash and Class C fly ash which were also included in the experimental matrix. As you all know Class F fly ash refers to the low calcium fly ash that means it has got almost less than 5% CaO content; typically less than 5% but it could be up to about 10%. Class C fly ash is the high calcium fly ash which has more than 10% CaO present in the system.

You can see here that values for a fully saturated concrete, please remember that we talked about this in the previous lecture, the resistivity is highly dependent on the moisture condition of the concrete, the more saturated the concrete the lower the value will be for the resistivity. So, for fully saturated concrete you can see that as you increase the degree of replacement of cement, you are causing a major increase in the resistivity of the specimens. Now, especially at 50% slag replacement you get resistivity values that are several times more than that which you see for cement. Similarly when you substitute with Class F fly ash at 15%, 30%, and 50%, you see that there is a major enhancement in the resistivity. And ultimately at 90 days of curing, that means potentially the longest possible curing period that you can imagine, the resistivity values with fly ash concretes at 50% replacement somewhat match those of slag concrete of at 50% replacement.

Now you all know that fly ash is a pozzolanic material, it has a slow reaction and that could take a prolonged duration to achieve completion. So, because of this the properties of fly ash concrete continue to develop slowly as we proceed with more and more curing. So, all these are fully saturated concretes which have been cured until the age of testing. So, 90 days also indicates that it is 90 days of curing. It is not 28 days curing followed by drying in the atmosphere. It is 90 days of curing. It is completely getting cured.

So, the question as to why do not we see the same effect with Class C fly ash as we see with the Class F fly ash on the surface resistivity? This is because Class C fly ash typically has around 30% amorphous silica whereas Class F fly ash has more than 50% amorphous silica. The siliceous compounds have a greater effect in actually binding alkalis, reducing their concentration in the pore solution. And secondly the late pozzolanic reactions of the Class F fly ash proceed to a much larger extent than you do with Class C fly ash, because whenever you have a faster reactivity, it slows down the later age development. So, Class C fly ash does give you a faster initial reactivity, so you see that at 28 days the results are comparable to your OPC and even comparable to Class F fly ash at that replacement level. But by 90 days, the benefit of additional curing is not felt by Class C fly ash like you do with class F fly ash because you have greater amorphous siliceous content in Class F fly ash.

Now in a more recent study by Yuvaraj in 2018, we compared the resistivity values for concretes prepared with ordinary Portland cement, 30% fly ash replaced concrete mixes (FA30) and LC^3 systems (limestone calcined clay cement based systems – LC3). What is interesting to note here is that as early as 28 days, your resistivity performance of OPC and fly ash are nearly the same but LC3 is in a completely different scale as compared to these two mixes. And you see that from 28 days, all the way up to 365 days (1 year), you do not see a major change in the resistivity values of LC3 concretes, indicating that at a very early age your systems have attained a pore structure that is discontinuous, resistivity is extremely high even at 28 days and there is not significant increase in the resistivity from 28 days to 1 year.

While I say it is not significant actually, if you look at it in terms of the actual numbers it is still significant. We are going from about 200 kΩ.cm to about 400 or 500 kΩ.cm in 1 year. But the scale is not as significant as you see for fly ash concrete, where we are at the 20 kΩ.cm region at 28 days and we are close to about 200 kΩ.cm at 1 year of curing. Again, these are concretes that have been completely cured until 365 days. We are not subjecting it to actual field curing, this is lab curing for the intended period of study. So, you can see that there is a great increase in the fly ash resistivity, which is indicative of the late reaction that fly ashes give in cementitious systems.

Ordinary Portland cement on the other hand does not enhance significantly from its 28 day value, because by 28 days, 90% of the reactions in cement are complete and the values you get at 28 days, you hardly double that value at about 1 year. So, from 10 or 15 kΩ.cm you are reaching the resistivity of about 20 to 30 kΩ.cm. So, the advantage of curing is maximum for fly ash based systems which increase by several times because of curing up to 1 year. LC3 systems at lesser ages itself indicate very high surface resistivities.

Now this surface resistivity being high could be indicative of two things. We saw earlier that the conduction in concrete is through the pore solution. So, the more the ionic concentration in the pore solution the greater will be the conduction. Now cement has a composition in which there are a lot of alkali based compounds which dissolve immediately when cement reacts with water. That raises the alkali concentration of your pore solution and in fact you all know very well that the pore solution as it evolves, in the long-term the pore solution has only the alkali species from the cement which are available.

In the case of pozzolanic additives there is a tendency, generally to reduce the alkaline component in the pore solution because you are diluting the cement; you are reducing the amount of cement by substituting it with the mineral admixture and that dilutes the amount of alkali that you can have in your system. So, if you have lesser alkali in your pore solution, obviously the conductivity will also be lower. So, one reason for the higher resistivity could also be because of simply the difference in the conductivity of the pore solution itself. However, the other reason which is more interesting or important to investigate is the presence of a discontinuous pore structure and that is what we will see in the forthcoming slides.

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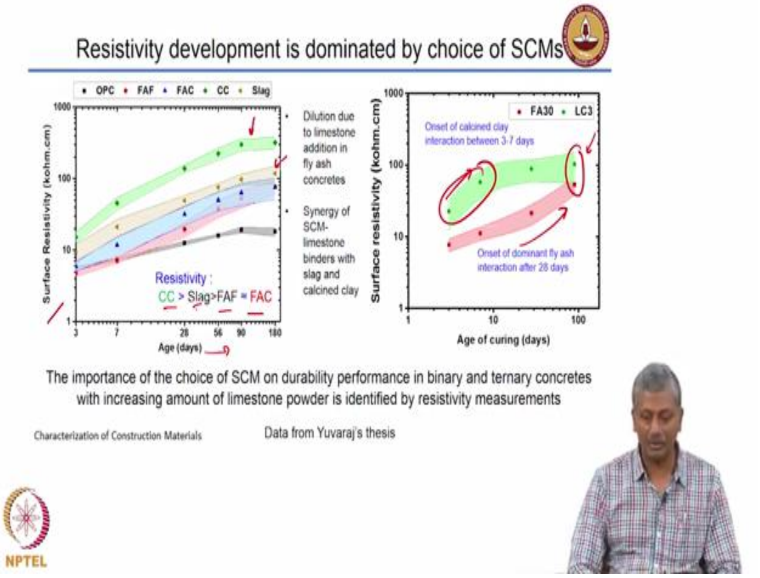

Resistivity development is dominated by choice of SCMs

- Dilution due to limestone addition in fly ash concretes
- Synergy of SCM-limestone binders with slag and calcined clay

The importance of the choice of SCM on durability performance in binary and ternary concretes with increasing amount of limestone powder is identified by resistivity measurements

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Data from Yuvaraj's thesis

Now as we saw in the previous slide, the results indicate that the resistivity development is dominated by the choice of the supplementary material that you are using to replace the cement. So the more the reactivity of the supplementary material, the faster will be the development of surface resistivity and that is what is being shown here. Surface resistivity is being plotted with respect to age for different types of mineral additives: calcined clay, slag, F type fly ash and C type fly ash. So in this set of results you can again see that the calcined clays give you a range of resistivity values that are much higher than that of fly ashes or much higher even than that of slag and slag is higher than fly ash.

So again, there are clear indications that there is either a reduction in pore solution conductivity or an improvement in the disconnectedness of the porosity or both, and we need to actually investigate what is the real cause. Again, in this case fly ash and LC3 systems which are shown in the previous graph are again getting compared and you see primarily that the major enhancement is happening as early as seven days in the case of the LC3 systems, whereas, in fly ash systems the major enhancement happens only at later ages indicating that fly ash based concretes need a greater degree of curing as compared to the LC3 based systems for achieving a certain level of durability. Now of course at 90 days which is the comparison here, there is not distinct difference in the bands of the LC3 and the fly ash systems. The bands are almost overlapping. That means that you get nearly the same level of increase in resistivity by about 90 days, but the difference in early ages is quite drastic.

So, comparing this to a field situation now, in the field you have projects where curing is done sometimes for 3 days for 7 days. So, the kind of concrete that will be susceptible to the effect of lack of curing would be the fly ash concrete and not the LC3 concrete in such cases.

In the graphs, the band is just the spread of the results; the point is the average and the band is just the spread. Over a range of concretes, this is not just one concrete this is over a range of different concretes at different water-binder ratios and different binder contents. This is not for one concrete, this is just presenting the band over a range of water-cement ratios and binder contents.

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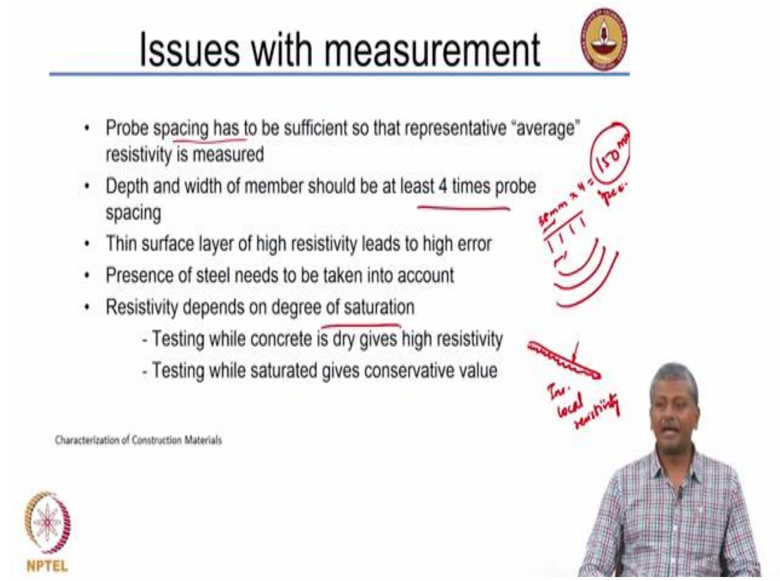

Issues with measurement

- Probe spacing has to be sufficient so that representative "average" resistivity is measured
- Depth and width of member should be at least 4 times probe spacing
- Thin surface layer of high resistivity leads to high error
- Presence of steel needs to be taken into account
- Resistivity depends on degree of saturation
  - Testing while concrete is dry gives high resistivity
  - Testing while saturated gives conservative value

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Now we talked about this briefly earlier, but again just to reiterate, there are several issues with measurement of resistivity. One is that your probe spacing has to be sufficient so that representative "average" resistivity is measured. So, you have your probe with the four electrodes, the spacing between the electrodes should be sufficiently large, so that the flow lines are going through a larger section of the concrete. So, the spacing should be at least large enough to cause the flow lines to go through a larger section, we do not want only the surface 5 mm or 10 mm to be assessed; we want a representation of a larger segment.

At the same time when the probe size becomes large, the size of the specimen you have to use also become larger. So, depth and width of the member should be at least 4 times the probe spacing. So that is another limitation - you cannot do this on small specimens; you need to have a specimen that is at least 4 times the probe spacing. Once again, as I said, the commercial instruments have a probe spacing of 38 mm. So, multiply that by 4, your specimen size should be at least 150 mm. You need to use at least a 150 mm specimen to be able to use a resistivity measurement.

Now supposing you had something like carbonation happening of your concrete. Carbonation means the influence of atmospheric CO_2 to convert the lime that is there in the cement to calcium carbonate. Now, if you have a surface of the concrete, you have a surface zone where calcium carbonate is getting deposited. The presence of calcium carbonate will increase the local resistivity and that may actually lead to some error with the measurement of surface resistivity.

Again saturation is probably the most important characteristic. Remember that if your systems are fully saturated you get a conservative value and if your systems are dry you will get a very high value of resistivity, which is not indicative of the true connectivity of the porosity.

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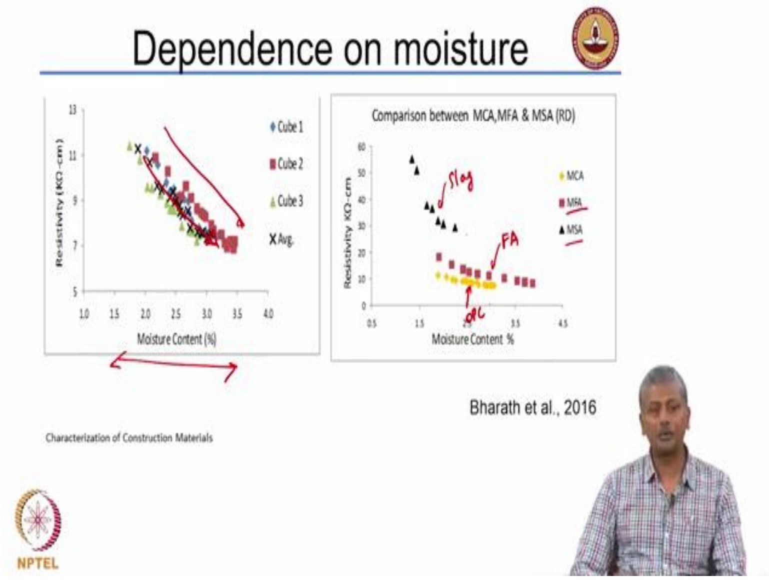

Dependence on moisture

Bharath et al., 2016

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Now again, this is something that we had investigated in our lab also, with simple cubes on which resistivity measurement was done. So here it is clearly showing that there is a distinct dependence on the moisture content for concrete resistivity. So again, these moisture contents are determined based on surface moisture meters. There are surface moisture meters that help in detecting the moisture content. Again, we discussed earlier that one of the common methodologies of measuring moisture involves nuclear magnetic resonance, but surface moisture meters can also use electrical properties to actually measure the moisture. So, you can have either magnetic resonance based moisture meters or electrical capacitance based moisture meters. So, this is a capacitance based moisture meter which was used to detect the surface moisture.

Alternatively, what you could also do is once you measure the resistivity on the saturated sample, you can put that in the oven and dry it for 24 hours and then measure the dry mass. So that means all the moisture has been driven out, you can get the moisture content from that simple experiment also, if you do not have a moisture meter.

What is indicated here is that the resistivity declines significantly when moisture increases. Even for a change of 2% of the moisture, you have a decline of resistivity which is nearly 50%. And now you see here that with different types of systems (in Figure on the right), this is slag (MSA), MFA indicates fly ash and MCA is for OPC. For different types of systems, the dependence on moisture could be different. You see here that while fly ash and OPC systems are equally sensitive to the change in the moisture content, slag systems are very sensitive to the change in moisture content as far as resistivity measurement is concerned. So, the challenge here is whenever you measure resistivity, you need to bring all your specimens down to the same level of moisture preferably a complete saturation has to be done before you do the measurement. Otherwise we will get highly erroneous values.

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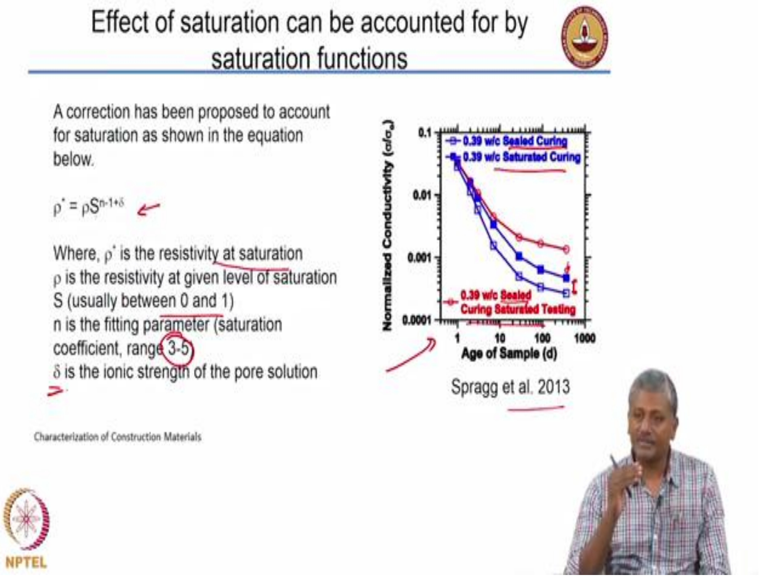

Effect of saturation can be accounted for by saturation functions

A correction has been proposed to account for saturation as shown in the equation below.

$\rho^* = \rho S^{n-1+\delta}$

Where, ρ^* is the resistivity at saturation
ρ is the resistivity at given level of saturation
S (usually between 0 and 1)
n is the fitting parameter (saturation coefficient, range 3-5)
δ is the ionic strength of the pore solution

Spragg et al. 2013

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Now there are studies in literature which indicate that you can actually use saturation functions to correct for the level of saturation. What we saw previously was only an indicative response, but this is actually a much larger set of database collected by Spragg, which talks about how conductivity can be normalized with respect to the degree of moisture that is present?

So here these are results presented for sealed curing and saturated testing. And the blue is for just saturated curing or sealed curing separately. So, you can see here that the effect of the saturation changes the level of the conductivity. So, your normalized conductivity values are higher when you saturate your system. So, in sealing also you may actually tend to lose some of your moisture that is responsible for this difference in conductivities.

So here the equation which is proposed is given as:

$$\rho^{*} = \rho S^{n-1+\delta}$$

ρ^{*} is the effective resistivity at saturation

ρ is the resistivity which is tested at the given level of saturation.

S is the saturation level between 0 and 1; 0 means it is completely dry, 1 means it is completely saturated.

'n' is the fitting parameter which can be obtained from experiments like what is shown here, which is otherwise also known as the saturation coefficient which can have a range between 3-5.

δ is the ionic strength of the pore solution. We need to consider that also because that has a direct bearing on the resistivity too.

So, this is an interesting approach to actually translate resistivities collected at different moisture levels to the actual resistivity value that you expect for a saturated condition. So, that all the comparisons between mixes can be made only in the saturated state. It is very important to do that.

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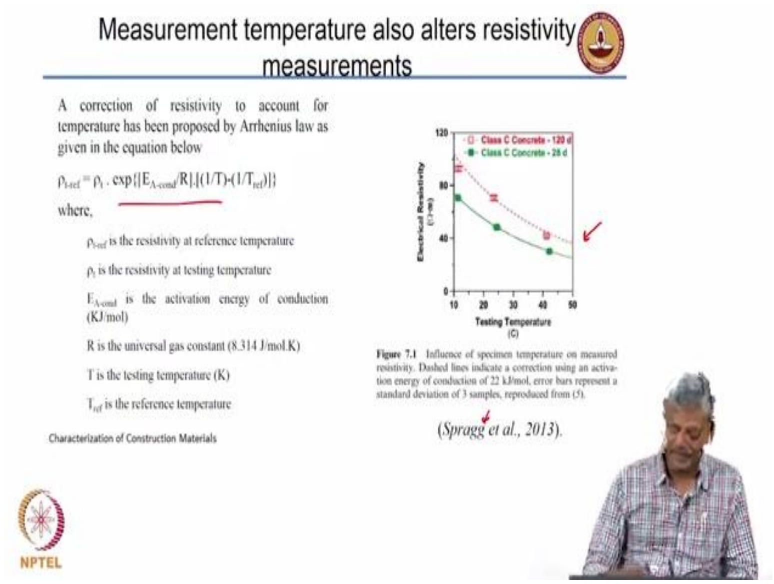

Measurement temperature also alters resistivity measurements

A correction of resistivity to account for temperature has been proposed by Arrhenius law as given in the equation below

$\rho_{t\text{-}ref} = \rho_t \cdot \exp\{[E_{A\text{-}cond}/R].[(1/T)-(1/T_{ref})]\}$

where,

$\rho_{t\text{-}ref}$ is the resistivity at reference temperature

ρ_t is the resistivity at testing temperature

$E_{A\text{-}cond}$ is the activation energy of conduction (KJ/mol)

R is the universal gas constant (8.314 J/mol.K)

T is the testing temperature (K)

T_{ref} is the reference temperature

Figure 7.1 Influence of specimen temperature on measured resistivity. Dashed lines indicate a correction using an activation energy of conduction of 22 kJ/mol, error bars represent a standard deviation of 3 samples, reproduced from (5).

(Spragg et al., 2013).

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Now the other aspect that can affect resistivity measurements is the measurement temperature. Now, just like any other temperature-dependent process, you can apply the Arrhenius relationships and determine again the effect of the temperature on the resistivity. So here (in graph in slide) you can see that resistivity generally tends to decline with increase in testing temperature. So, we need to do a correction for the resistivity with respect to temperature. And you can do that with the help of this Arrhenius relationship that has been suggested again by the same literature - Spragg et al, 2013.

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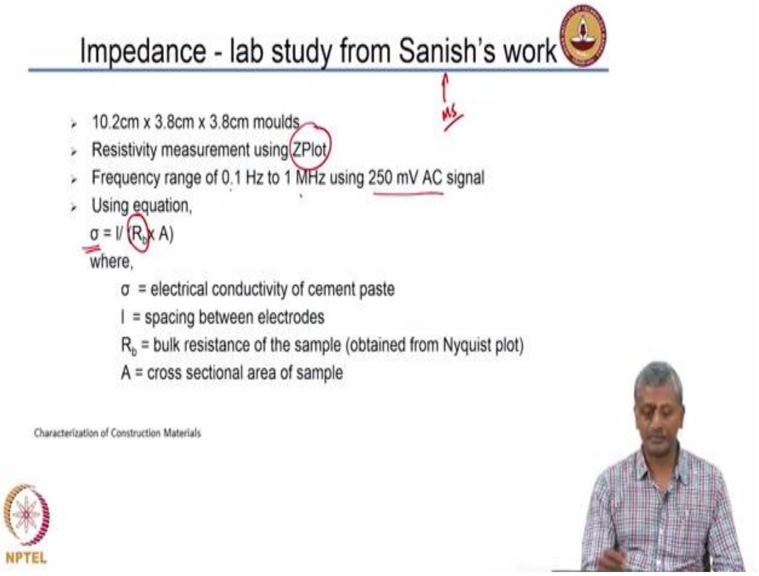

Impedance - lab study from Sanish's work

- 10.2cm x 3.8cm x 3.8cm moulds
- Resistivity measurement using ZPlot
- Frequency range of 0.1 Hz to 1 MHz using 250 mV AC signal
- Using equation,

$\sigma = l / (R_b \times A)$

where,

σ = electrical conductivity of cement paste
l = spacing between electrodes
R_b = bulk resistance of the sample (obtained from Nyquist plot)
A = cross sectional area of sample

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Now I will show you some larger data for impedance measurements, not just resistivity measurements, and how we can actually relate this to the development of the pore structure. So, this is from a previous MS work at IIT Madras by Sanish and here he had used prismatic moulds of 10.2 cm x 3.8 cm x 3.8 cm and the resistivity measurement was done using a frequency response analyzer and plotted using software called ZPlot. And the frequency range of 0.1 Hz to 1 MHz was used with an AC signal of 250 mV amplitude.

So what he is trying to simply do is get the Nyquist plot, get the value where the Nyquist plot crosses the X-axis, which is your bulk resistance value (R_b) and use that bulk resistance value to determine the conductivity of your system (σ).

$$\sigma = \frac{l}{(R_b * A)}$$

Where l=spacing between electrodes; A = cross-sectional area of the sample.

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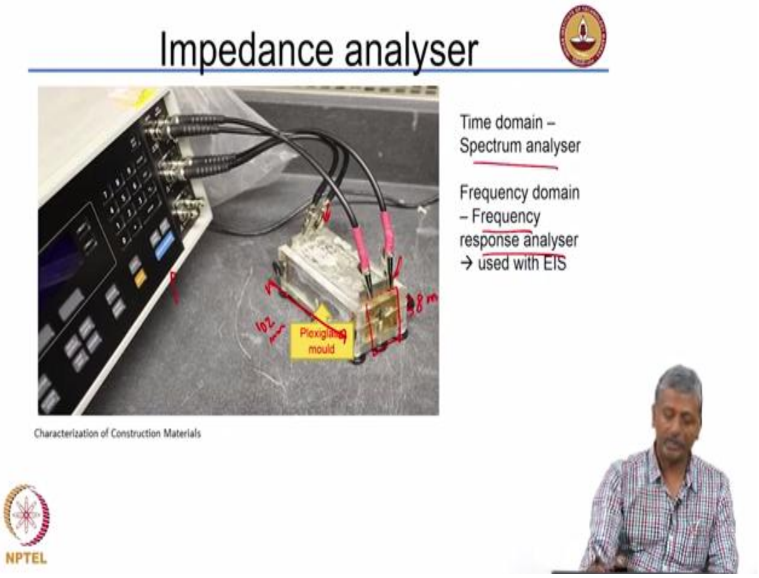

Impedance analyser

Time domain – Spectrum analyser

Frequency domain – Frequency response analyser → used with EIS

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So, this is the picture of the experiment being conducted. This is the frequency response analyzer you have the electrodes which are connected to the ends of the specimen, the length is 102 mm. And the cross-section is a square of 38 mm.

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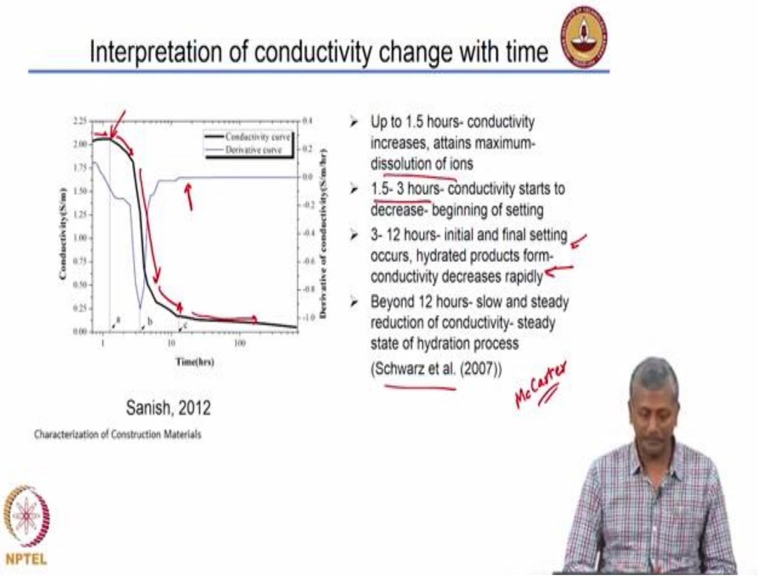

Interpretation of conductivity change with time

- Up to 1.5 hours- conductivity increases, attains maximum- dissolution of ions
- 1.5- 3 hours- conductivity starts to decrease- beginning of setting
- 3- 12 hours- initial and final setting occurs, hydrated products form- conductivity decreases rapidly
- Beyond 12 hours- slow and steady reduction of conductivity- steady state of hydration process (Schwarz et al. (2007))

McCarter

Sanish, 2012

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So now what he did in his work was to look at: Can conductivity change be a representation of the setting process inside the cementitious system? There has been previous work also in this regard by Schwarz et al. (2007) and also a lot of electrical response based work was done by McCarter in the UK which talks about use of electrical properties to determine early-age behavior of cementitious mixes.

So here what is plotted is the conductivity curve, which is in black and the first derivative of the conductivity curve which is in blue, with respect to time (time is plotted on a log scale). So you see here that the conductivity curve can be broken up into several regions:

- One is you have a minor rise in the beginning in the conductivity which happens up to about 1.5 hours and that could be because your ions present in your cementitious system are taking some time to dissolve into the pore solution.
- Between 1.5 to 3 hours there is a conductivity decrease that starts at that point, and that is the second stage.
- At 3 to 12 hours, you have a rapid decrease in your conductivity. This rapid decrease is because your hydration products are forming at that stage, because you know that the dormant period typically gets over by about 3 to 4 hours and then your setting process actually starts to initiate and your hydration products form rapidly. As your structure becomes more and more disconnected, initially the connection was completely there because of water, as the structure becomes more disconnected because of the presence of hydrated compounds, you have a reduction in conductivity.
- Beyond this (12 hours) you have a very slow reduction in conductivity because your system has developed to a certain stage and incremental development is only taking place beyond that point.

So now you have four different stages, can we get some information on the setting behavior of the system from these or at least empirically correlate what is happening here with the measurement of the setting time.

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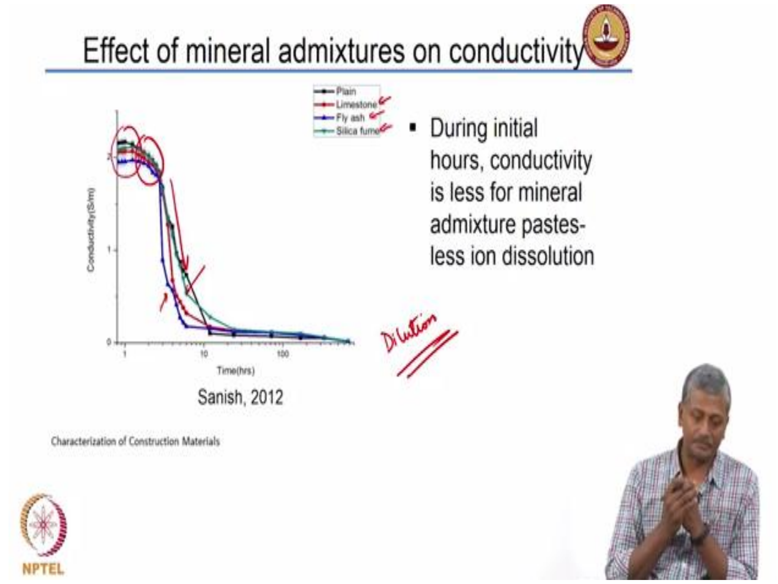

Effect of mineral admixtures on conductivity

- During initial hours, conductivity is less for mineral admixture pastes- less ion dissolution

Sanish, 2012

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So that is what was attempted; first of all, in this study the effects of mineral admixtures were also investigated. So, limestone, fly ash and silica fume were used as additives in this system. So, some differences could be seen at the early conductivity values. Generally, the conductivity at very early stages was brought down as cement was replaced by limestone, fly ash, and silica fume. Why is that decrease in conductivity happening? It is just simply the dilution of the cement. Effect of dilution of the cement, you have lesser cement, so you have lesser conductivity, that is all.

Now what happens beyond this, the rate at which this conductivity drops in the next stage is indicative of the contribution of the materials to the system. You see very clearly here that your contribution from fly ash is significant in reducing conductivity, primarily because fly ash substitution is typically done at the level of 30% whereas limestone and silica fume will be maximum about 10%. Silica fume systems do not seem to show much of a difference as compared to cement, because you do not get that effect of a pozzolanic reaction that early. So why is fly ash giving you this decline? Because it is able to take up more of the alkali within the glass very quickly. So, alkali gets contained within the unreacted silica glass of the fly ash very quickly and that reduces the conductivity rapidly.

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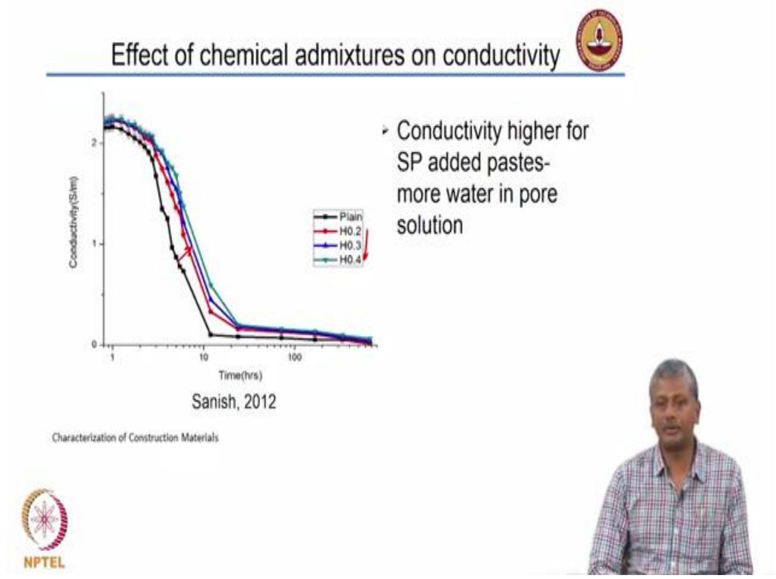

Effect of chemical admixtures on conductivity

- Conductivity higher for SP added pastes- more water in pore solution

Sanish, 2012

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Now again with respect to chemical admixtures here: it is a water reducer at different dosages. You do not see that much significant difference except that you push the curves up. What it means is that you have retarded your mix a little bit as compared to the plain cement. So, there is higher conductivity for the superplasticizer added pastes in the decline period indicating that there is a retardation happening in the system.