Characterization of Construction Materials
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Lecture -63
Principle and different methods - Part 2

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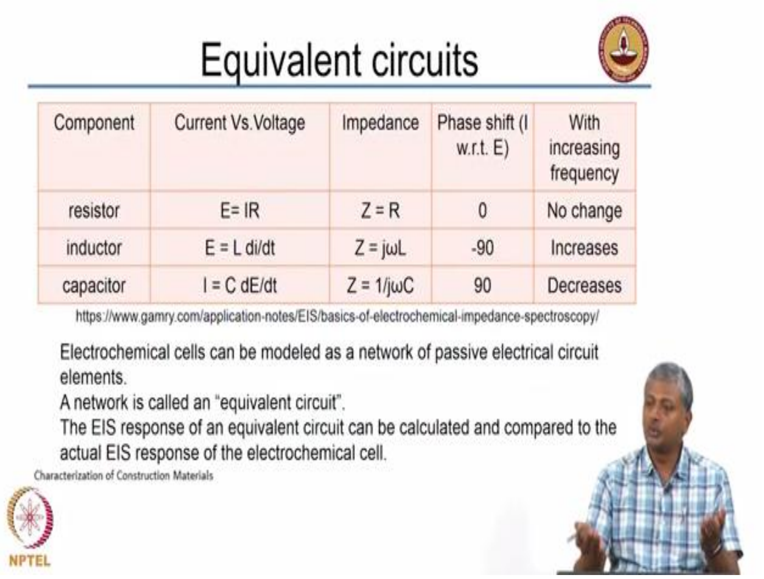

Equivalent circuits

Component	Current Vs.Voltage	Impedance	Phase shift (I w.r.t. E)	With increasing frequency
resistor	E= IR	Z = R	0	No change
inductor	E = L di/dt	Z = jωL	-90	Increases
capacitor	I = C dE/dt	Z = 1/jωC	90	Decreases

https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/

Electrochemical cells can be modeled as a network of passive electrical circuit elements.
A network is called an "equivalent circuit".
The EIS response of an equivalent circuit can be calculated and compared to the actual EIS response of the electrochemical cell.

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So now based on the type of circuit element that you have, that defines your material. Please remember you do not have a predefined notion of a circuit for your material. You need to do the test for your material.

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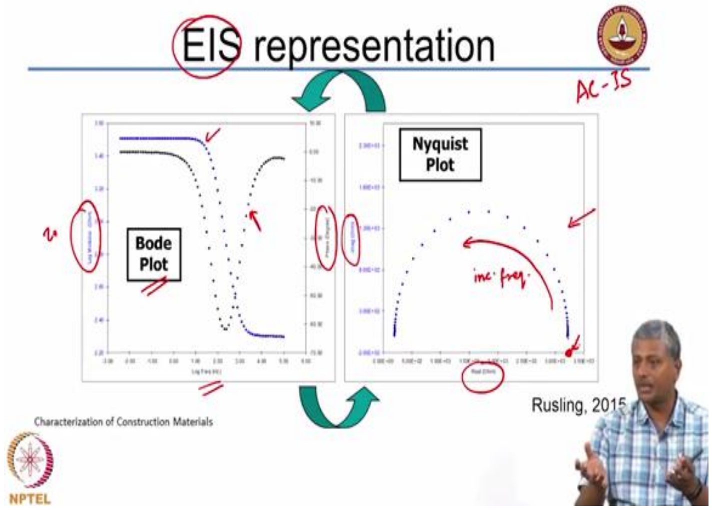

EIS representation

Rusling, 2015

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You need to get the Nyquist plot for your material and then idealize the material behavior in terms of an equivalent electrical circuit. For example, if you only get one point here for your material, that means it is only a resistor. So, you can approximate an equivalent circuit of just a resistor in your material. So, if your point is not changing with respect to frequency that means your current and potential are in phase and you are not going to get any change in the impedance. So, you will have an exact value which is again typical of your direct current measurements.

But the problem with direct current measurement is you would not get exactly this value because there will be a polarization potential that is against the applied electric field. So, you will not exactly get this value. But this is the true value that you want to actually use for your real resistance. So, you get that concept. So, we are testing any material which conducts and doing the Nyquist plot for that material and idealizing the Nyquist plot using an equivalent electrical circuit to get the actual electrical performance or actual electrical properties.

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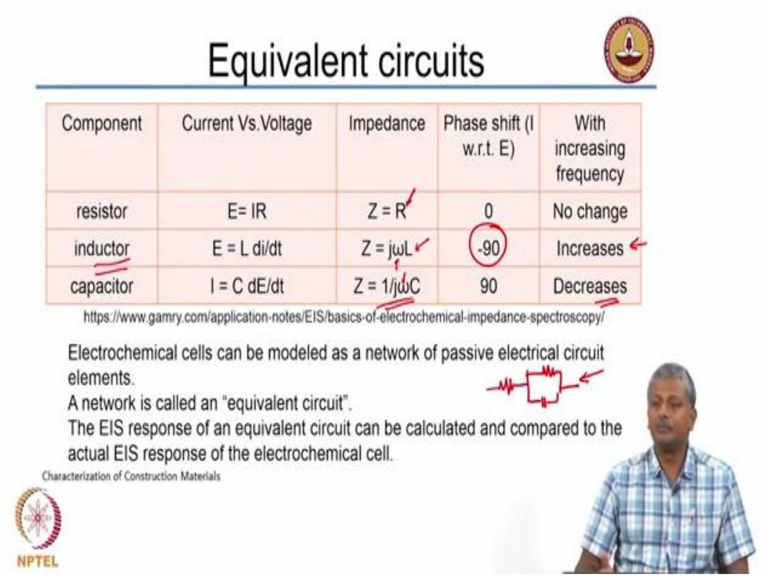

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So, in case of a resistor, impedance Z = R, in the case of a pure inductor, Z = jωL and as said earlier, it is shifted or it is lagging the potential. So, it is -90° out of phase with the potential. And what happens with increasing frequency is that the inductance value will increase. The capacitance on the other hand, Z= 1/ jωC and with increasing frequency the capacitance or impedance for a pure capacitor will decrease because obviously your ω is in the denominator and in the inductor, ω is in the numerator. So, it is a direct relationship for the impedance with respect to the frequency. For a pure inductor the impedance increases with increasing frequency. And for a pure capacitor the impedance decreases with increasing frequency.

So as I said again what you need to do is have these three basic elements and draw your own equivalent circuit for what you think best represents the electrical behavior of your system. So, for example, you can have a resistor and a resistor and capacitor in parallel (as shown in Figure 1). So that could be one of the representations of the kind of material that you are investigating.

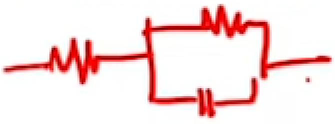

Figure 1 Example of an electrical circuit

You may get other systems also with an inductor, with a capacitor and inductor and so on and so forth. There are a lot of systems that conduct in different ways. For the most part we use this sort of a relationship to describe the situations in which you have steel embedded in concrete. I will show you why that happens?

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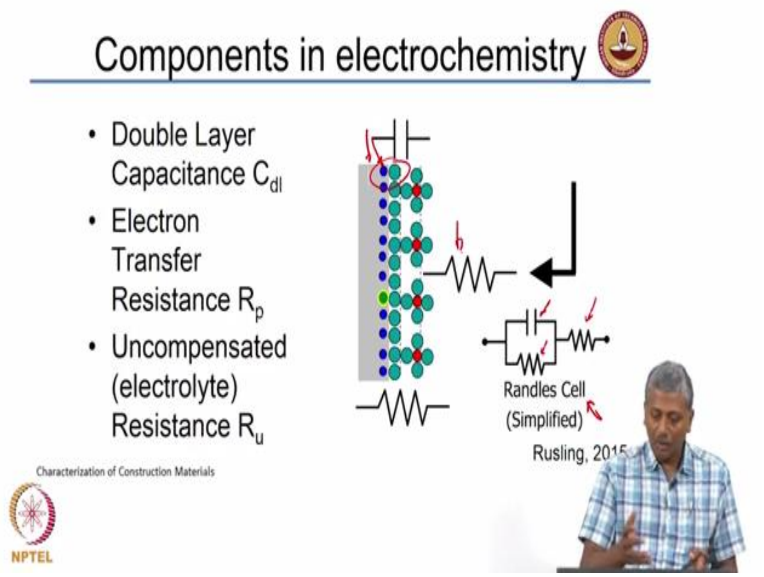

Components in electrochemistry

- Double Layer Capacitance C_{dl}
- Electron Transfer Resistance R_p
- Uncompensated (electrolyte) Resistance R_u

Generally when you have steel which is embedded in an electrolyte like concrete or an electrolyte like a pore solution for instance, you get the simplified Randles cell which approximates quite well the behavior of the steel embedded inside concrete or an electrolyte.

So, here you have these three components: you have a resistor component outside and then you have a resistance and capacitance in parallel. How is this arising? You have the double layer capacitance basically, which is on the surface of the steel where it is in contact with the electrolyte, you have what is known as double layer capacitance (C_{dl}). So, your ability to actually store charge is higher at the interface. You then have the electron transfer resistance (R_p), which is between the steel and the surrounding electrolyte and you also have an uncompensated resistance (R_u) or bulk resistance of the electrolyte, which is outside.

So whenever you have interfaces in materials, electrochemical impedance spectroscopy can actually help to bring out the characteristics of the interface quite clearly and when you actually go through the presentation by Sripriya, you will know how this can be actually used to study the properties of the steel-concrete interface and make some valid conclusions about when corrosion begins in concrete when steel is embedded in it.

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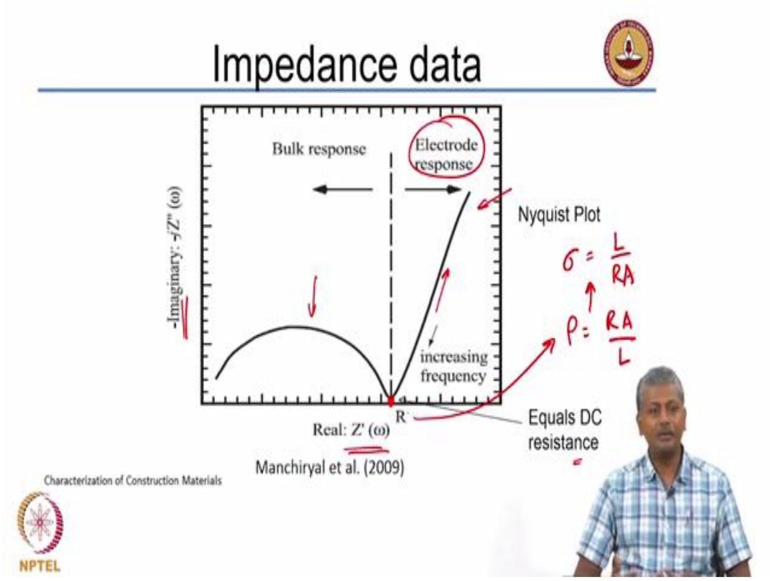

Impedance data

Nyquist Plot

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

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

Equals DC resistance

Manchiryal et al. (2009)

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But for now, what we do is we will use a very simplified approach of the impedance data and see how it works to explain the pore structure characteristics of concrete. So as I said, again, negative of the imaginary part is plotted on the Y-axis and positive of the real part is plotted on the X-axis and the point at which this arc touches the x-axis equals the actual DC resistance of your structural component or of your concrete for instance.

Now again, when you get an impedance data which is looking like this what we typically say is this part which is going up and for around 45° is because of the response of the electrode, whereas this arc that you get here is the response of the material that you are actually testing, when you are testing concrete for instance. So, what we get as a result of this test is the value of the DC resistance 'R' and this R can be converted into the resistivity 'ρ' by the formula: $\rho = \frac{RA}{L}$. Alternatively it can be used to determine the conductivity (σ) as $\sigma = \frac{L}{RA}$. So, all we are doing is taking inverse of resistivity and expressing as conductivity. So we can represent the data in both ways either as conductivity or as resistivity. So, let us look at how this is used in materials research?

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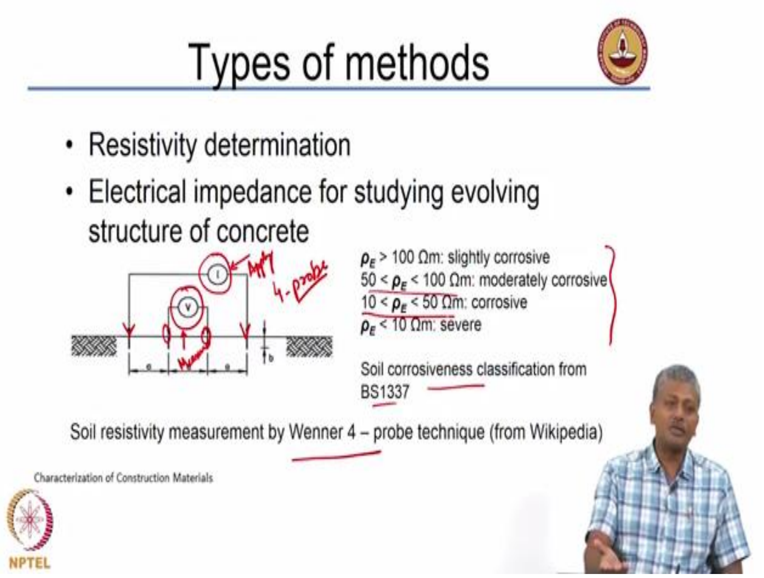

Types of methods

- Resistivity determination
- Electrical impedance for studying evolving structure of concrete

$\rho_E > 100$ Ωm: slightly corrosive
$50 < \rho_E < 100$ Ωm: moderately corrosive
$10 < \rho_E < 50$ Ωm: corrosive
$\rho_E < 10$ Ωm: severe

Soil corrosiveness classification from BS1337

Soil resistivity measurement by Wenner 4 – probe technique (from Wikipedia)

So, one of the common methods which we apply both in soils and in concrete is the determination of the resistivity of the material. Now we use electrical impedance to study the evolving structure of concrete because as the concrete structure evolves the pores become more and more disconnected. When pores get more disconnected, what happens to the resistivity? It will increase. So, you can measure electrical properties using impedance and track the development of your pore network or the increasing disconnectivity of your pore network can be detected.

So here for instance a typical measurement is done using a 4-probe technique which is also known as a Wenner 4-probe technique, which previously is developed for measuring soil resistivity characteristics. What is done here is, we have an AC current source which is supplying current to two outer electrodes and you also have two inner electrodes in the system across which you actually measure the potential difference. You apply an electrical current and you measure the potential. And from the measured potential you convert the value to an equivalent resistivity of the system.

Now there are several scales for what the resistivity actually denotes. For example in the case of soil corrosiveness classification from British Standards BS 1337, it says that if the soil has a resistivity of 100 Ωm or more it is only slightly corrosive, that means it is not really having a characteristic that will be harmful, between 50 and 100 Ωm it is moderately corrosive. As it becomes lesser and lesser in resistivity, the corrosion or corrosive nature of the soil gets enhanced. Now what is causing this corrosive nature of the soil? Obviously the presence of ionic species in the soil, like sulfates, chlorides for instance. So, all those ionic species are contributing to reducing the resistivity or increasing the conductivity of the soil for a given porosity present in the soil.

Now if you take the soil and you compact it by vibration compaction. What do you think will happen to the resistivity value? Resistivity will increase because more compact soil implies, you have lesser porosity, automatically you get lesser interconnected porosity, and so your resistivity obviously will go up as you compact the soil.

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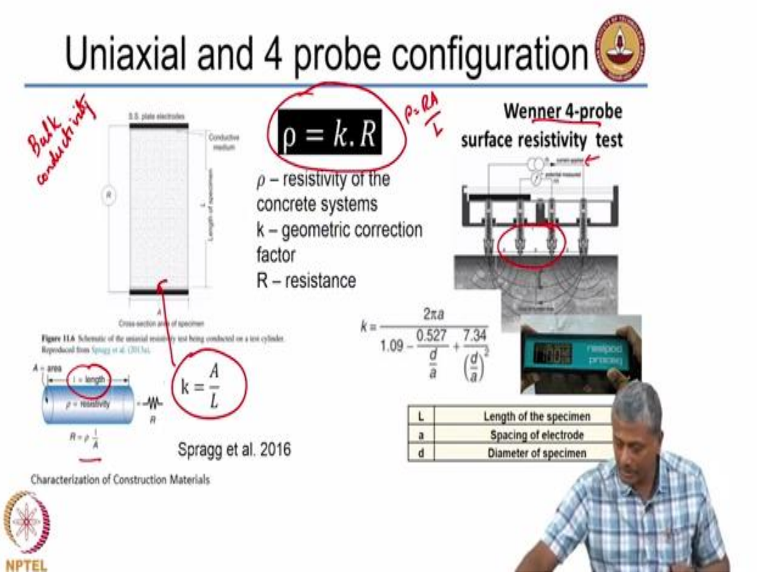

Uniaxial and 4 probe configuration

Bulk conductivity

$\rho = k.R$

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

ρ – resistivity of the concrete systems

k – geometric correction factor

R – resistance

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

Figure 11.6 Schematic of the uniaxial resistivity test being conducted on a test cylinder. Reproduced from Spragg et al. (2013a).

Spragg et al. 2016

Wenner 4-probe surface resistivity test

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

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

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Now the same concept applies in concrete also, but in concrete we have two different methods or two different configurations: one is the Uniaxial configuration which is used in bulk conductivity measurements or we have the same Wenner 4-probe surface resistivity test. Now bulk conductivity we say because we take concrete specimens and we have the positive and negative electrodes directly attached to the ends of the concrete specimen like a cylinder, for instance and then we simply measure the bulk electrical response when we apply alternating current. So, here for instance your length is clearly defined. Your area across which the current is passing is also clearly defined because you have a perfect cylindrical specimen, so you get your resistance (R) = ρl/A.

So here you can have a generic relationship between your resistivity ρ and the resistance R by a factor ‘k’ as: ρ = k.R. Now in this case, of course your ‘k’ is very simple because your part of flow of the electric charge is perfectly maintained. So, you have this k represented just as the area divided by the length (k=A/L).

In the case of a surface resistivity test, it is a little bit more complicated because while you are applying an electrical current across the two outer electrodes, you are trying to measure the potential drop across the two inner electrodes. We will come back to this picture again later.

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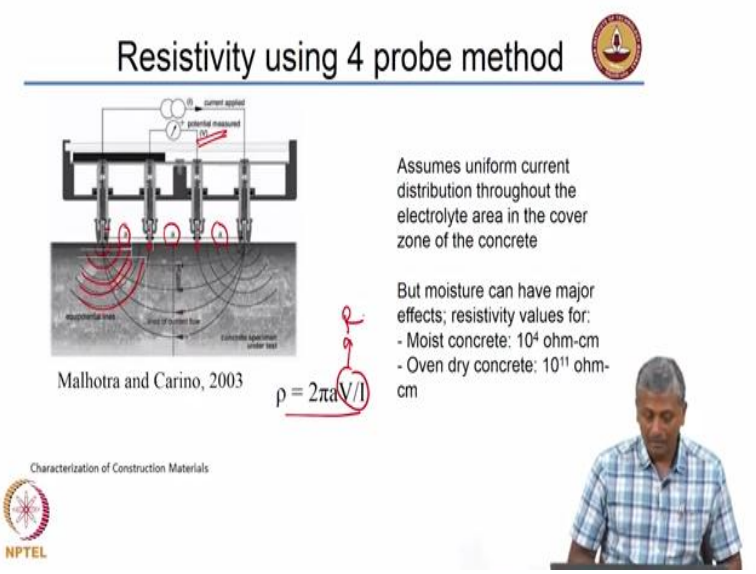

Resistivity using 4 probe method

Malhotra and Carino, 2003

$\rho = 2\pi a V/I$

Assumes uniform current distribution throughout the electrolyte area in the cover zone of the concrete

But moisture can have major effects; resistivity values for:
- Moist concrete: 10^4 ohm-cm
- Oven dry concrete: 10^{11} ohm-cm

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So, if you look at the more detailed drawing of this resistivity, these are the four probes that are sitting directly in contact with the surface. The distance between the probes is constant ‘a’, in all the cases. Now if you look at the lines of current flow, they are defined by these isopleths that are drawn in this figure. However, the equipotential lines are what are emanating from the source of the current. So, where the equipotential lines define the potential, at this point and this point (inner electrode points), that is what we are trying to measure, using the potentiostat between the two inner probes. And that we are using to calculate the resistivity in terms of this equation:

$$\rho = \frac{2\pi aV}{I}$$

Now V/I is nothing but R, but where this 2πa come from? It comes from this expression here, that I showed you previously for resistivity of concrete systems ρ = k * R, where k is a geometric correction factor, which we need to apply in this case. It is a little bit more complicated than what we had in the case of the bulk conductivity experiment where the path of flow is perfect. In this case, we need to consider the effect of the size of the specimen and the spacing between the electrodes.

Now what happens is generally we apply this to systems where the size of the specimen is much larger as compared to spacing between electrodes. So, when you apply this equation, what will happen? (d/a) will be a very large number because d is very large compared to a. So, in other words the entire thing (in denominator) will go up to about 1. That is why we have the numerator typically used for calculation as simply 2πa. Now you need to remember that very often we do not really conduct the experiment on infinite or rather very large thickness. We have specimens that have finite thickness. So, you may actually have effects built in because of those finite thicknesses, which is why we need to use specimen sizes which are, at least three to four times the spacing between the electrodes. So, the commercially available instruments have a spacing ‘a’ of 38 mm or 50 mm typically. So, if you say 38 * 4 you are talking about a minimum size which is at least 150 mm or at least the length of flow should be 150 mm. In one direction at least you should have a spread that is equal to about 150 mm.

So, when you start using this resistivity test on smaller specimens, you need to take the result with a pinch of the salt. It is not perfect when you take it on small specimens when you measure on a very large block of concrete, you can be fairly certain that your calculation, which is given as this $\rho = \frac{2\pi a V}{I}$ will be more or less accurate for a very large block. The smaller the specimen, you have a problem.

So, of course this assumes uniform current distribution throughout the electrolyte area in the cover zone of the concrete. Why are we worried only about the cover zone? Because when we are actually placing this resistivity probe on top of the concrete surface, the current flow is actually happening only in the cover zone of the concrete. We are not getting any current flow in the bulk of the concrete, and that is why the name is surface resistivity. Whereas in this case, we call it bulk conductivity or bulk resistivity. In ASTM C1760, you can actually refer to the standard and check for yourself. It is a bulk conductivity determination standard and it is quite commonly used these days, as a good durability parameter that can be measured fairly easily. You need only a few minutes to do this test. Before your strength determination on cylinders, you can determine the bulk conductivity and then determine the strength. So, very useful test to do for regular quality control purposes also.

However, given the fact that the Wenner 4-probe can also be used in the field, people generally tend to have this equipment quite handy in most labs and because of that it is quite useful to actually conduct the conductivity or resistivity determination with the Wenner 4-probe equipment also. One major issue is the presence of moisture the concrete. You have to remember that when you are doing laboratory investigations using resistivity, you need to make sure that all your samples, or all your specimens are completely saturated. Because when you have drying, it can play havoc with the kind of data that you can obtain from resistivity measurements. For moist concrete it is 10^4 Ω.cm, and for oven dry concrete 10^{11} Ω.cm. So that is absolutely, not comparable you have seven orders of magnitude difference in the resistivity data. So use of this resistivity probe on-site needs to be done with a lot of care, because if you cannot ensure that your surface that you are measuring the resistivity on is completely moist, or if you can determine the moisture content there, you should report it for that moisture content.

But on site you need to contend with one more problem - there is going to be steel under the surface and very often the current flow lines can actually end up intercepting the steel also, in which case you will get completely erroneous readings. You want to check the conductivity of the concrete or resistivity of the concrete and not the entire system. So, the presence of steel will obviously lead to errors in field measurements. But more than that, the presence of moisture which plays havoc with the measurement of resistivity in concrete systems.

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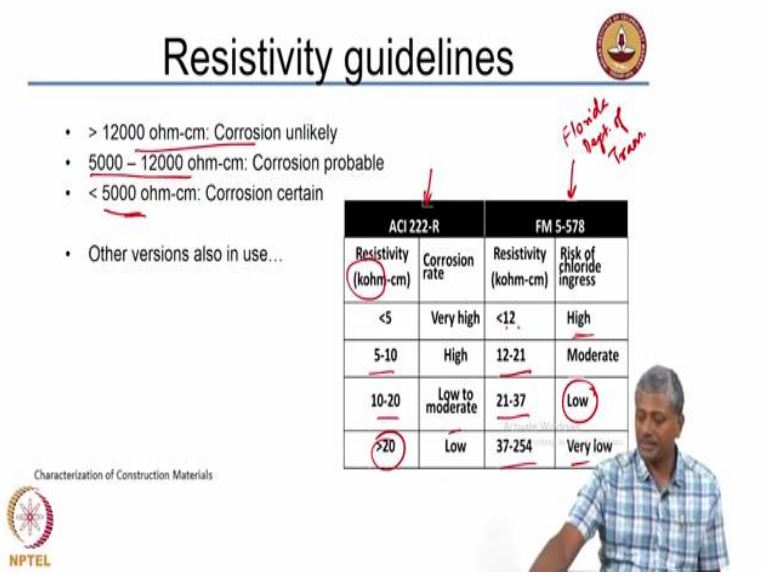

Resistivity guidelines

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

Florida Dept. of Trans.

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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But anyway, what we will do in the next part of this lecture is look at how this is applied to do various kinds of research studies, but before that I just wanted to talk about the guidelines that are typically used for resistivity to define the performance of concrete in the event of corrosion. Generally it is well understood that more resistive the concrete, the more resistance it will offer to the passage of ionic species within it. That means the ionic flow will be restricted in concrete that is highly resistive and you know very well that corrosion propagation generally happens when you have ionic flow happening through the concrete, basically your Fe^{2+} and OH^- ions move through the concrete and any resistance to the movement of those ions will result in better performance as far as corrosion is concerned.

So generally the corrosion related criteria are drawn up based on resistivity in this fashion. For example, one of the versions says that if you have a resistivity of concrete more than 12000 ohm-cm (Ω.cm) corrosion is unlikely; between 5000 – 12000 Ω.cm it is probable and less than 5000 Ω.cm, you are certain to have corrosion in your system.

There are other versions also in use. I will show you an example of ACI 222-R. I think this is the committee that deals with corrosion or corrosion inhibiting admixtures. So ACI 222-R report says that again for 5 kΩ.cm (kilo ohm-cm) you have a very high corrosion rate. So, it is the same as this 5000 Ω.cm. 5 - 10 kΩ.cm it is high; 10 - 20 kΩ.cm is low to moderate and > 20 kΩ.cm is low corrosion rate.

But a more sophisticated model is proposed by the Florida Department of Transportation. In their document FM 5-578, it says that resistivity values of < 12 kΩ.cm indicate a high risk of chloride ingress. Now please remember that your resistivity is in no way linked to the actual physical ingress of the chlorides. Your resistivity is just defining the interconnectivity of the pores, but you all know very well that the more interconnected the porosity, the greater the risk of ionic species coming in from the outside. So again, there are various ways in which the data is interpreted and none of these can be entirely accurate. So, what this says is for < 12 kΩ.cm, the risk of chloride ingress is high; 12 - 21 kΩ.cm, risk is moderate; 21 - 37 kΩ.cm, the risk is low and for 37-254 kΩ.cm, the risk is very low. Now of course where did these numbers come from? These came from a very large data set of testing which they were able to actually get these values from to see how the resistivity is actually matched with the actual corrosion potentials in these concretes.

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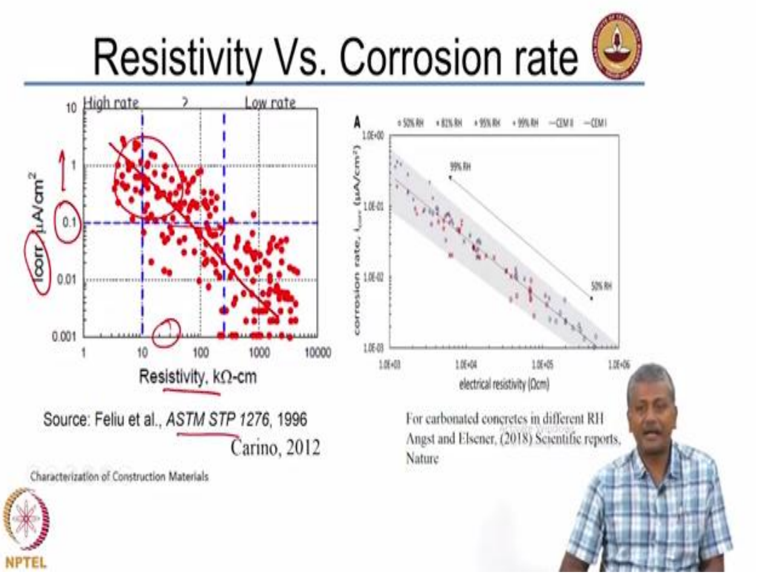

Resistivity Vs. Corrosion rate

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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Again, this is another picture from an ASTM Special Technical Publication, which looks at the corrosion current, I_{corr} (μA/cm^2) plotted on the Y-axis versus resistivity of the concrete in kΩ.cm. What you can see very clearly is a distinct trend which shows that as the resistivity becomes more and more the corrosion current in the concrete is less and less, and that is only expected because the higher the resistance the greater will be the potential to resist the charge flow through the concrete. So, because of that the corrosion charge or corrosion current reduces with increasing values of resistivity.

Now generally when we do corrosion studies, 0.1 μA/cm^2 corrosion current density is said to be a critical value of density which defines the state of passive corrosion and active corrosion. Anything more than 0.1 μA/cm^2 indicates active corrosion in your system. So, you can see that for levels of resistivity which are greater than about 10 to 20 kΩ.cm, most of these values here are more than about 20 – 30 kΩ.cm, for instance. Most of those concretes are in the passive condition, whereas anything which is < 20 kΩ.cm is mostly in the active condition. So, if you come back to this Florida Department of Transportation, more or less it matches with what we are actually seeing as far as the corrosion current density behavior is concerned.

Your resistivity indicated by the experiment will get reduced when steel is present in the vicinity because charge is getting carried much easier. So, because of the presence of steel, actually show a lesser resistivity in your system. So, maybe you can say that is a more conservative approach to have the steel inside.

See again we are talking about ideal situations for an electrolyte alone like just a pore solution, for instance. But when you are considering a solid phase which is present inside the concrete like aggregate or cement paste even, you have the hydrated cement paste, which is a solid phase and that will lead it to actually have an impedance, you will actually go away from the idealized resistor type of an arrangement and you will also get some charge storage capacity. The greater the extent of solid phase the more will be the storage capacity. So, capacitance will play a larger role in the case of a concrete.

So, I will just stop with this graph here to the right. Again, it is the same sort of a graph with corrosion rate I_{corr} versus electrical resistivity; this is taken from actually a paper published in 2018 in a Scientific Report in the Nature journal. So, it is quite well cited obviously. So here it shows you the effect of the relative humidities, as you go for the lower and lower relative humidities, obviously your electrical resistivity that is shown is very high. Whereas when you go for almost saturated concretes the electrical resistivity becomes very low and your corrosion rates are much higher as the electrical resistivity reduces.

So that seems to match well with our understanding of corrosion, because the corrosion rate is going to be high in a very moist environment. When the environment becomes drier and drier your corrosion rates are not going to be as high because there is no easy path for the flow of your charges. So, this holds a lot of importance with respect to understanding how corrosion propagates in concrete systems, which have different types of binders. Like if you have slag or silica fume and the kind of resistance that offers to the actual flow of charge in your system can define to a large extent how the system will perform in a real corrosion experiment.

So, in the next part of this chapter we will look at how actual data can be interpreted to make some distinct understanding of your pore structure and whether that representation of the electrical properties derived pore structure is able to accurately quantify the durability performance of concrete.