Aqueous Corrosion and its Control

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Lecture – 08

DC polarization experiments and their relation to mixed potential theory/ Evan's diagram

Today we will look at the application of a mixed potential theory and in relation to the electrochemical testing for corrosion. You carry out electro chemical test in order to determine the electrochemical kinetics of corrosion. The, you one of the important the parameter that you might determine from this is the corrosion rate.

But there are other parameters we call them as electro chemical kinetic parameters, like the exchange current density, Tafel slopes. And in case the metal is passivating; what are the passive current density, critical current density, pitting potential, all these kinds of stuffs that you are going to determine using electrochemical experimental technique.

Now, we need to have a clarity in relating the data to the Evan's diagram. So, far we looked at the Evan's diagram. And we looked at in fact various parameters that affect the corrosion like; velocity, the effect of oxidizers, the Tafel slopes of the anodic reaction, cathodic reactions, exchange current density. We all saw in a theoretical manner how they affect the corrosion rate.

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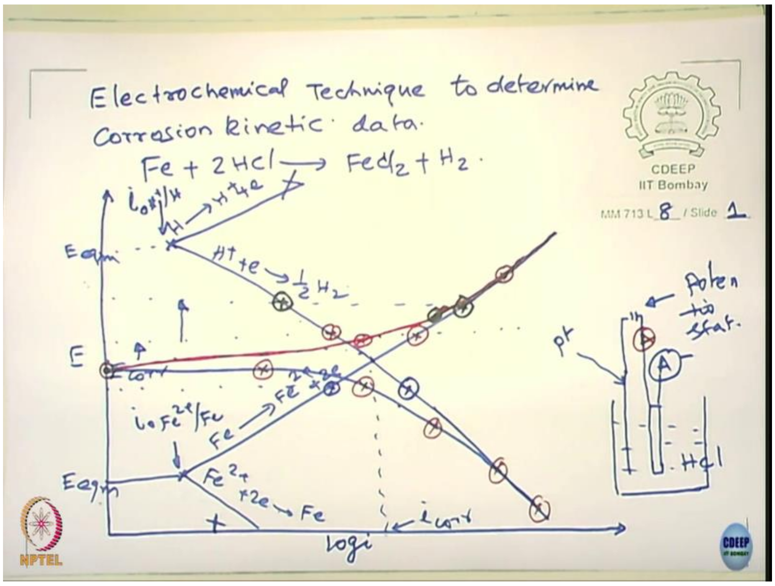

Electrochemical Technique to determine Corrosion kinetic data.

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

Now, you must have a method of determining all of them. How do you do it? It is not a very straightforward in the electrochemical technique. So, what we look at here is; the electrochemical technique to determine corrosion kinetic data. Now, let us start with the so-called Evan's diagram.

Let us take an example of iron corroding in hydrochloric acid. So, let us take this example of iron corroding in hydrochloric acid. It corrodes into a ferrous chloride then hydrogen is evolved

$Fe+2HCl \longrightarrow FeCl_2 + H_2$

We need to look at the corrosion kinetics of that. Now, for this you can write Evan's diagram right. How many equilibria you have in this to start with?

Student: Two.

Two; one is hydrogen gas is in equilibrium with hydrogen ions, the second is iron is in equilibrium with Fe^{2+} ions, there are two equilibria right. And you have corresponding exchange current density, Tafel slopes, equilibrium potential these factors. So, let us represent here in the diagram right.

So, you have a potential here, the log current density rather and you can represent the two equilibria that you have right. and these corresponds to what? $H \longrightarrow H^+ + e^-$.

Here, $H^+ + e^- \longrightarrow 1/2\ H_2$ right, what is this one? $Fe \longrightarrow Fe^{2+} + 2e^-$ and here the cathodic reaction

$Fe^{2+} + 2e^- \longrightarrow Fe$, here. And this is the equilibrium potential for hydrogen, and this is the equilibrium potential for iron in equilibrium with Fe^{2+}

Now, we all know in this case right this is your, i_{corr} and this is your E_{corr}. In the corrosion reaction here what are we governing relationship that affects the corrosion rate? These particular kinetic this particular kinetics, this does not really affect at all; this does not really affect at all they do not affect. Do they effect? They do not really affect at all.

Now, I need to determine the Tafel slopes, the exchange current density, the Tafel slope, exchange current density I need to determine. Of course, I need to determine of course, the i_{corr} and the E_{corr} value only. To start with let us look at a simple system I just draw schematically; suppose I have now represented this corrosion process using this schematic diagram.

So, this is hydrochloric acid it is getting corroded simplicity it is deaerated right. If I measure the potential of this one, when it is corroding using a voltmeter or electrometer and using a reference electrode. What will be that potential called? Yeah use this diagram look at this diagram and tell me. In this case?

Student: Corrosion potential.

Which this is called as the corrosion potential. I can measure the corrosion potential much easily using a reference electrode and an electrometer. I want to also determine the i_{corr} value; can I measure here? I cannot measure here directly because no current is coming out of this metal now why? The rate of Fe oxidation = the rate of reduction of H^+ ions. The electrons liberated on the surface is consumed by the H^+ ions the no electrons they go out of the system.

Now, the current moves into the system. So, you cannot measure the i_{corr} value directly in here though I can measure E corr value you all with me. I cannot use ammeter right if you use ammeter what happens current does not flow out of this corroding system because the rate of oxidation here is equal to rate of reduction here at all. Or if I measure using ammeter suppose I measure using an ammeter some means what will be the current there? The current will be 0 am I right, the current will be 0; I cannot measure any current right.

So, at E_{corr} value the measurable current that is going out of this system is 0 can I say that; so that is the current. So, I just represent in this diagram what is the corresponding current? The corresponding current at E_{corr} =0 here agree right. Now, what I am going to do is now I am going to now apply a potential on this right I apply a potential on this. How do you apply a potential? I use another electrode here and this is it is going to be let us say a platinum electrode.

Now, I am going to apply using I use maybe a potentiostat or whatever I use a potentiostat, I will talk about what a potentiostat is later. So, what I am going to do is; now I am going to change this potential or this electrode I am going to now move from here towards a positive direction. Suppose I move towards like this suppose I move to let us say this potential I moved from here to this particular potential I moved.

Now, please look at this Evan’s diagram; what is the current that is corresponding to reduction? This is the reduction current and this is going to be your oxidation current. So, iron is getting oxidized more than hydrogen is getting reduced are you following me or not.

Student: Yes sir.

Right; that means, there is going to be net flow of current in the system am I right or not. That means, if I won’t rise it what happens now in this case now the iron is dissolving the electrons move out of the system like this electron move out and the current starts flowing like this.

Now, I may go to use an ammeter use an ammeter now here the ammeter start measuring the current what will be the current coming here. The current coming will be the difference between this current and this current right. For example, the iron is getting dissolved at this rate hydrogen is getting reduced this rate; what is the remaining electrons go out of the system right agreed.

So, the current will be between these two points ok. It is not going to exile like this so I subtract this current from this current ok. So, what happens now? You find that at this particular place the current is going somewhere here ok. The current starts increasing like that. Now, what I am going to do? I am going to raise the potential further I am going to raise it to this particular place. I am going to move this to another potential here. What happens in this case?

The rate of oxidation increases even more, and the rate of reduction is now decreasing am I right or not. So, this current will be very close to this now I come here this come very close to this because this current is less this is very high ok. Now, what happens now? Now, these currents will starts going close to this it should be here actually it should be here ok.

Now again if I again extend this further what happens now? Extend it further this curve will go and get merged with this because the reduction current is very small, the oxidizing current is more overall the current corresponds to oxidation current agree or not.

So, that means, this curve will go and almost start merging with this and go like this. Of course, here what happens? There is going to be one more oxidation thing will start moving you know differently. So, up to this point you will find you find that this curve is going to be merging with this Tafel line. Is it merging with my Tafel line or not? It is merging with this Tafel line here agreed. Anybody has any question?

Student: (Refer Time: 15:35).

Yes suppose, I will come to that point later what happens when decrease the potential right. Now, what happens now at least you have you agree, have you understood this behavior of potential current relationship; that it is initially 0 it increases it goes like this and at this point of time it is just following the Tafel behavior. Here it is not following the Tafel behavior not behaving the Tafel behavior and it starts behaving the Tafel behavior here is it ok, understood?

Student: Yes.

Right.

So, you ask the question what happens when I am going to bring the potential down in relation to E_{corr}, right when I bring it down what happens now? When I bring it down let us say to I am going to bring it down to this particular potential; the anodic reaction is rate is less and the cathodic reaction rate is going to be more agreed.

Student: (Refer Time: 16:44).

Ok. But here then what happens there is a net current, the net current is going to guy lie somewhere here only. So, what happens now? This guy will start following simply like this ok.

So, I would get I would obtain you know the points will lie along this I am reversing it. So, that it will become easy for you to understand. So, this is what you will get in a actual experiment. In actual experiment you carry out in the laboratory you measure E_{corr} first, you move from E_{corr} either way you can move either towards cathodically first and then you can start moving anodically later you will able to get this particular plot you get this particular plot here.

So, this is how things will look like in all your experiment, in all your experiments now. And you using this you should able to now reconstruct the diagram now ok. So, if I have this polarization curve; this polarization curve, how do I get; how would I get i_{corr}? How do I get it?

Simple right.

Student: Tangent (Refer Time: 18:10).

You draw a tangent right; your where do you draw a tangent do i draw a tangent here; no you draw a tangent here because it forms a Tafel equation. So, the Tafel behavior is coming here the Tafel behavior is not here, the Tafel behavior is not here. So, you draw a tangent from here, tangent from here, and extrapolate the tangent the intersection point gives you what is called as $\log(i_{corr})$ The intersection point ideally will give you the corrosion potential E_{corr} agreed or not agreed.

Student: Yes sir.

Now, I want to get the exchange current density right. How do I get exchange current density? I want to get exchange current density for hydrogen H^+ equilibrium right; how do I get it? I have only this line and I have only this line how do I get; how do I get exchange current density? Ok.

Can you identify which is the; which is the exchange current density in this in this Evans diagram? Where is it? This one right. So, this corresponds to $i_{0H+/H}$ and this corresponds to $i_{0Fe2+/Fe}$ ok. So, how do I; how do I get this exchange current densities? Right. It should be much easier right it is anybody’s guess.

Student: (Refer Time: 19:46) E equilibrium is known we can find.

Yeah. So, you need to calculate the E equilibrium. And extrapolate the tangent to the E equilibrium potentials I mean why are your hesitant right. I mean you should not be hesitant at this stage you extrapolate to their particular place you get exchange current density and you get exchange current density.

So, how do I calculate the equilibrium potential? Is there a way to calculate? Come quick. Suppose I say iron is here in the solution I you know in a hydrochloric acid and I say that the ferrous ion concentration is 10^{-6} moles. Now, you tell me is there a way to calculate the equilibrium potential can you or not?

Student: (Refer Time: 20:35).

Quick.

Student: (Refer Time: 20:37).

Can you how?

Student: Nernst equation.

Nernst equation right. So, you can use the Nernst equation and calculate this, and you will able to get the equilibrium potentials. Then you can able to get exchange current density you can get all these values. Why are these important? It is important because the exchange current density decides what should be the corrosion rate. Of course, you have Tafel slopes you have other factors.

So, you can determine that you will see over a time period how we use this to design a new alloy system you want a less exchange current density. For example, if I move assume that the Tafel slope is same right, if I lower the exchange current density what will happen to corrosion rate the Tafel slope is same, the equilibrium potential is same, if I lower the exchange current density for this. So, what will happen to i_{corr} value? Quick. It will decrease, right.

So, these are the things that that is what I meant the mechanisms of corrosion in this case. So, it is possible for us to determine all the electrochemical parameters using the so called the polarization diagram ok. So, this is an important thing and you might have done already I suppose this experiment, if not you might be doing these very shortly.

And in this case, you will only get you will get only these lines then only these lines you are not going to get this. It is not possible; why? The moment you immerse steel in hydrochloric acid you are not having any more equilibrium here, you are not going to have any more equilibrium here. In fact, this half of it this part of it you never able to get it at all you will only get only this part of it right you only get this part of it. And you extrapolate and you can get the electrochemical parameters understood ok.

Now, let us go little further into it and try to use the so-called Butler-Volmer equation and try to understand why it really happens, ok. I move to now you know a right a briefly what the Butler-Volmer equation is.

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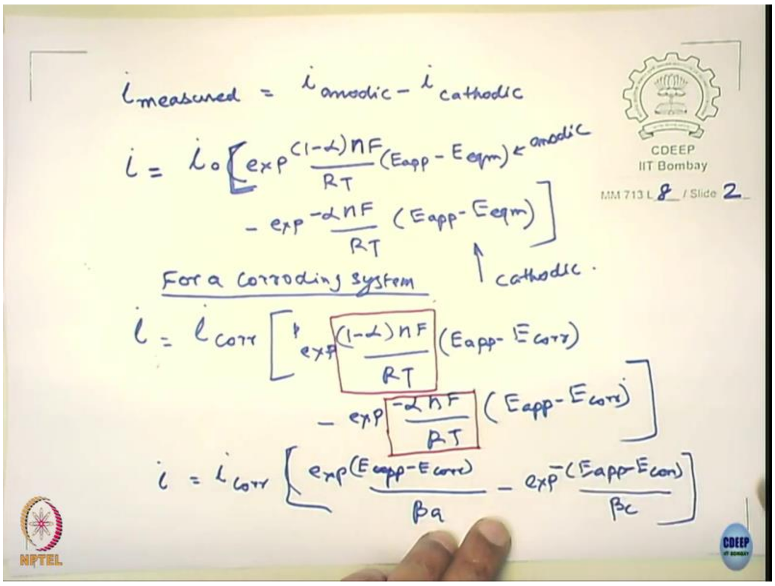

$$i_{measured} = i_{anodic} - i_{cathodic}$$

$$i = i_0 \left[\exp \frac{(1-\alpha)nF}{RT}(E_{app} - E_{eqm}) \leftarrow \text{anodic} - \exp \frac{-\alpha nF}{RT}(E_{app} - E_{eqm}) \right]$$

↑ cathodic.

For a corroding system

$$i = i_{corr} \left[\exp \boxed{\frac{(1-\alpha)nF}{RT}}(E_{app} - E_{corr}) - \exp \boxed{\frac{-\alpha nF}{RT}}(E_{app} - E_{corr}) \right]$$

$$i = i_{corr} \left[\exp \frac{(E_{app} - E_{corr})}{\beta_a} - \exp \frac{-(E_{app} - E_{corr})}{\beta_c} \right]$$

Now, now we have seen the current that is flowing in a system,

$i_{measured} = i_{anodic} - i_{cathodic}$; please understand current as a sign. So, as a potential it is not independent ok. Cathodic current is generally negative and anodic current is generally positive; because why in anodic current what happens in anodic current why does it.

So, why does you call this anodic current? You take a metal right you take a metal there and when it dissolves the assume in the case of iron right. I have an electrode here iron dissolves as Fe^{2+}. The current moves away from it when H ok. Whereas, when H^+ is getting reduced the current moves in the counter directions. So, the current flow at the interface is different this anodic current or a cathodic current ok.

So, the net current is given as anodic current minus the cathodic current that is the convention. We have seen earlier the so called Butler-Volmer equation where i which is measured normally given as what is related thing, anybody still remember i_0 exponential what?

$i=i_0[\exp(1-\alpha)nF(E_{app}-E_{eqm})/RT\ -\ \exp(-\alpha)nF(E_{app}-E_{eqm})/RT\ ]$

Student: Yes sir.

We can use this bracket here and the first one what is this? This is your anodic and this is your cathodic you can go back to your notes and check.

Now, in over here I am going to now put back this. The Butler-Volmer equation talks about this and talks about this and talks about this I am going to apply this to corrosion also corrosion not equilibrium still you can apply this. So, I am going to apply to this particular line here this particular line here the same Butler-Volmer equation ok. How do you do that? Actually it is changes into this equation slightly change as.

Student: (Refer Time: 26:54).

$i = i_{corr}[\exp(1-\alpha)nF(E_{app}- E_{corr})/RT\ -\ \exp(-\alpha)nF(E_{app}- E_{corr})/RT\ ]$ do this. What I have done here? Instead of equilibrium potential. I made as E_{corr}, instead of exchange current density I made as i_{corr}; from there only I am deviating right I am deviating from there right.

So, I have moved from here to this for a; this is for a corrosion system. So, this is for corroding system. Now, you tell me what does this correspond to? Yeah.

Student: (Refer Time: 28:48).

Is it is inverse or Tafel slope $RT/\alpha nF$,is Tafel slope it is a inverse of Tafel slope right. So, I write this equation like this;

$i = i_{corr}[\exp\ (E_{app}- E_{corr})/\beta_a\ -\ \exp-\ (E_{app}- E_{corr})/\beta_c\ ]$

Let us now look at this equation I hope you guys are following right. Let us look at this equation ok.

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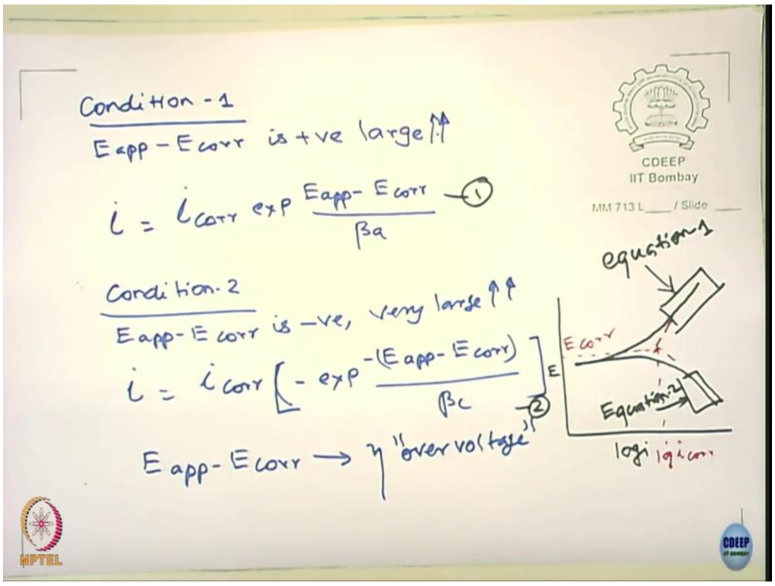

Condition - 1

$E_{app} - E_{corr}$ is +ve large ↑↑

$$i = i_{corr} \exp \frac{E_{app} - E_{corr}}{\beta a} \text{ — ①}$$

Condition. 2

$E_{app} - E_{corr}$ is −ve, very large ↑↑

$$i = i_{corr} \left[- \exp \frac{-(E_{app} - E_{corr})}{\beta c} \right] \text{ — ②}$$

$E_{app} - E_{corr} \rightarrow \eta$ "over voltage"

Now look at this condition 1; $E_{applied}$ -E_{corr} is positive and large let us say very large quite large quite large. So, what equation look at your equation tell me what happens? I think I made a mistake here please go back to this.

Go back to this equation yeah. See there is a mistake here please correct it

$i = i_{corr}[\exp (E_{app} - E_{corr})/\beta_a \ - \ \exp- (E_{app} - E_{corr})/\beta_c \ ]$

yeah please look at that please make this change.

So, having this let us go to the condition 1, $E_{applied}$ - E_{corr} is positive and quite large. So, what will happen to this equation? The equation will be equal to

$i = i_{corr}[\exp (E_{app} - E_{corr})/\beta_a]$ ………….1, understood.

Condition 2; $E_{applied}$ - E_{corr} is negative and very large ok. What happens to i_{corr}?

$i = i_{corr} \exp- (E_{app} - E_{corr})/\beta_c$ ……….2 what happens? Minus exponential minus ok. So, this is a very interesting thing.

What is what can you say about see you can also say $E_{applied}$ - E_{corr} can be considered as overvoltage here. You know in a sense of over voltage. I do not want to call in that true sense it is it is over voltage in a different sense of that deviation from E_{corr} actually. So, this is what is this relation called? Anybody? This is called a Tafel equation this is called a Tafel equation right.

So, go back to this diagram go back to this diagram or. So, this is the Tafel equation it is Tafel 1. So that means, if I represent this go back to the go back to the; I am going to make a small diagram here I versus E like this, this is your experimental data right. This is your experimental data please go back and see your diagram I have not given the Evan's diagram completely, but these are the measured values.

Now, equation 1 and the equation 2; equation 1 is applied here right, the equation 2 agree. And it is not valid here not valid here; that means, where do I extrapolate? I extrapolate from this point to this continuously and I extrapolate from here and get this. If I do any extrapolation in these regions that becomes wrong because it is not valid equation you understood. Not understood?

Student: Yes sir.

Ok. So, that is why when you carry out an experiment you normally get E versus logi curves. And in order to get i_{corr} value you make a Tafel extrapolation when; when is the condition? The condition is $E_{applied}$ - E_{corr} is large please look at this $E_{applied}$ - E_{corr} is large and negative you get this here. So, it has to be higher value then only you can able to extrapolate and get this thing here. So, you can extrapolate, and you can get; E_{corr} and i_{corrs}.

So, any other place extrapolation is incorrect you must clear your doubts here if you are not you going to have perennial problem in understanding polarization curves. Anybody has any questions? Do not be hesitant you will just tell me I am ready to spend some more time and make it clear to you that what it really means.

So, do not draw a tangent anywhere you want you should draw a tangent where the over voltage is higher ok; because that is where the Tafel relation is valid other places it is not really valid ok. That is the important thing and you should keep in mind.

Now, the question now that comes is how much you can do that ok. How much that you can do? Let us look at some complications here ok.

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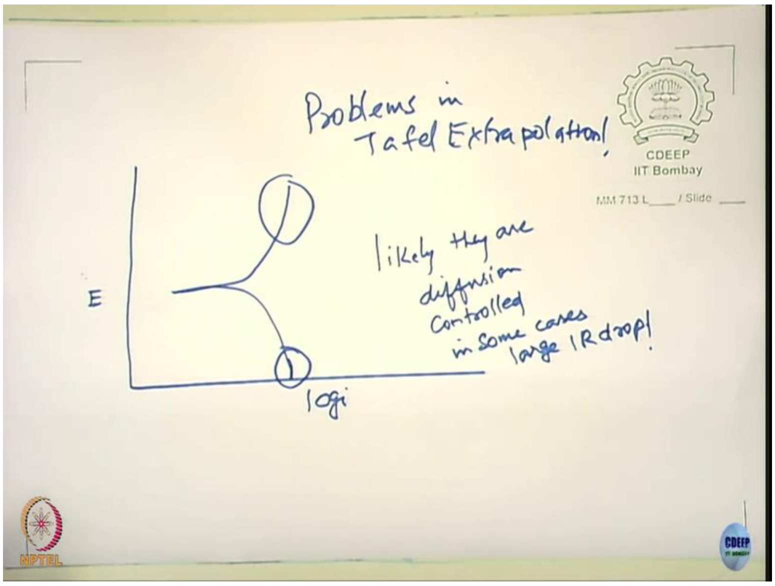

Now it goes something like that now it goes like this can you do this here, can you do it here? You cannot do because very likely they are diffusion controlled. In some cases large IR drop; I am not going to talk about right now IR drop and let us not worry about right now.

So, you cannot do either at two large you need a value because the Tafel equation is not valid anymore. So, it is valid so you should not look at which region the Tafel equation is valid. And you should make extrapolation that is a very important thing getting the electrochemical kinetics of corrosion ok.

So, I think this you should keep in mind when I talk about when I talk about ok; problems in Tafel extrapolation. So, it is not that simple I mean you have to be you have to know what is going on. If you do not know what is going on in the system you simply cannot use these plots to extrapolate the way you need it; need to do that ok.

Student: (Refer Time: 40:00).

Yeah.

Student: It is (Refer Time: 40:01).

Yeah, right now we will not talk about it and it is now it is going to take you know quite a bit of time it will lot of digression. Maybe at some other point we will discuss otherwise you will be discussing this in the other course experimental techniques for corrosion there you might discuss in detail. Just note down that or we can discuss off the class ok. It is a big subject by itself ok.

Let me go back to this equation again and see what it really means actually ok. I go back to this equation otherwise e let me put this equation here.

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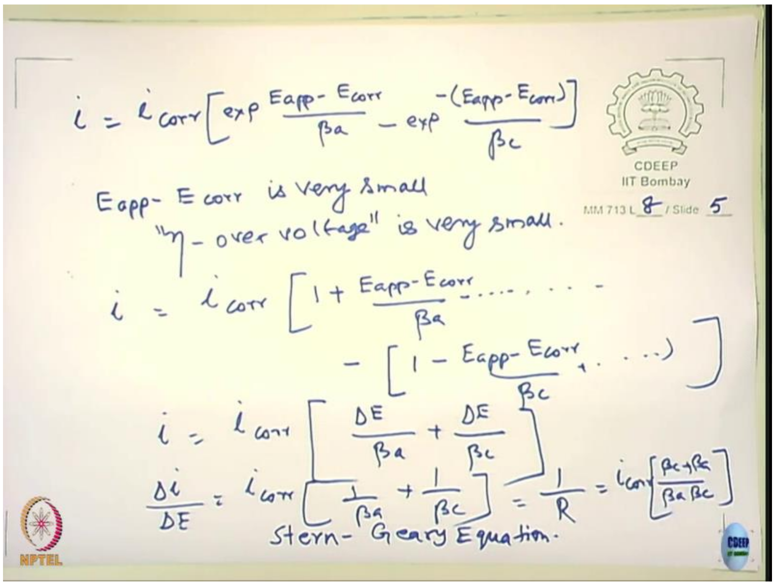

$$i = i_{corr}\left[\exp\frac{E_{app}-E_{corr}}{\beta_a} - \exp\frac{-(E_{app}-E_{corr})}{\beta_c}\right]$$

$E_{app} - E_{corr}$ is very small

"η - over voltage" is very small.

$$i = i_{corr}\left[1 + \frac{E_{app}-E_{corr}}{\beta_a} \ldots - \left[1 - \frac{E_{app}-E_{corr}}{\beta_c} + \ldots\right)\right]$$

$$i = i_{corr}\left[\frac{\Delta E}{\beta_a} + \frac{\Delta E}{\beta_c}\right]$$

$$\frac{\Delta i}{\Delta E} = i_{corr}\left[\frac{1}{\beta_a} + \frac{1}{\beta_c}\right] = \frac{1}{R} = i_{corr}\left[\frac{\beta_c+\beta_a}{\beta_a\beta_c}\right]$$

Stern- Geary Equation.

Let us look at the equation one more time

$i = i_{corr}[\exp (E_{app}- E_{corr})/\beta_a\ -\ \exp- (E_{app}- E_{corr})/\beta_c\ ]$

let us see. Let us look at this equation now; let me just put another condition right; $E_{applied} - E_{corr}$ is very small. So, what does it mean? η over voltage is very small.

So, what do you think will happen? You guys are you know experts in mathematics right; if this is small it could be either positive or negative whatever it is very small what happens. So, you have a series right. So, this can be written as

$i = i_{corr}\ [1 + (E_{app}-E_{corr})/\beta_a \ldots\ldots\ldots.-[1-(E_{app}-E_{corr})/\beta_c]$, I can keep having the series right. And I can have this then I have minus of then what happens? 1 minus square now goes right like this isn't it goes like that I am right.

So, what will happen now? If I make this is delta now what I do; then

$$i = i_{corr}[\Delta E/\beta_a + \Delta E/\beta_c]$$

am I right. It can also be i. So, when I put a see when I have a ΔE and what will happen to this i also becomes $\Delta i/\Delta E = i_{corr}[1/\beta_a + 1/\beta_c.]$ What is i / E, generally?

Student: R

R right ok. So, is equal to 1/R?

Student: (Refer Time: 44:50)

i_{corr}, is it right?

Student: Yes.

Look at the now the relation between E and i are linear; now look at this is linear relationship or not? And this is called as it is called as Stern-Geary equations equation. Now, what is β_a, β_c? They are all constants ok. These are constants and R and I mean i_{corr}, R interrelated to each other actually ok.

So, this is other way of determining the i_{corr} value ok. So, how to do this here? How does it work?

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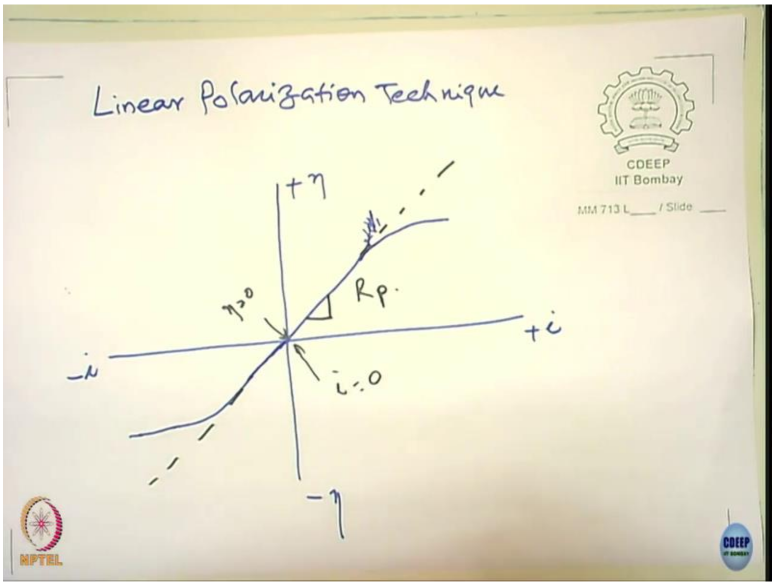

It work this way this is called as linear polarization technique right. One second, yeah. Sorry oops yeah. Please notice here we have plotted not on the log scale we have plotted in simply linear scale, linear current, in a voltage. And you see that there is a region over this place is its over voltage is 0 here right, η=0 here, i= 0 here right.

So, origin goes from the origin here ok. And of course, here it becomes the exponential and it becomes exponential and that is how the equation is valid. Now, the Butler-Volmer equation is valid all through please look at if you use a Butler-Volmer equation it is valid everywhere. The Tafel equation is valid here the Stern-Geary equation is valid here because they are all special case of the over voltage ok. So, the slope of that is what this is what gives you; what is slope? Is equal to.

Student: (Refer Time: 49:12).

And this is where supposed to go the wave should go so it goes here. Now why do you use a linear polarization technique as compared to Tafel technique, ok. Let us go to the now what are the advantages and disadvantages of this technique ok.

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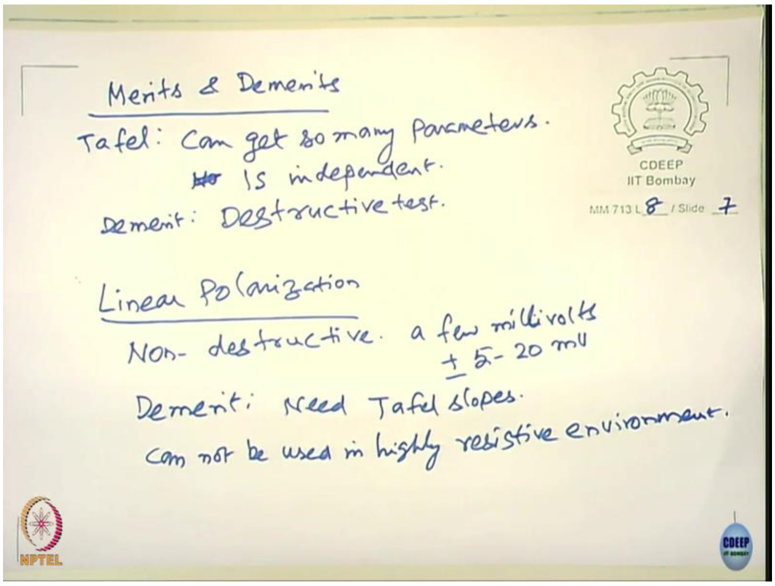

Merits & Demerits

Tafel: Can get so many parameters.
~~Ho~~ is independent.
Demerit: Destructive test.

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Linear Polarization

Non- destructive. a few millivolts
± 5- 20 mV

Demerit: Need Tafel slopes.
Can not be used in highly resistive environment.

Merits, demerits, Tafel can get so many parameters is independent is. What is the demerit? It is a destructive test. If I do for if I want to follow the corrosion rate with the time. So, sometimes the metals may not corrode the same way you know with the time the corrosion rate may increase or decrease you cannot use the Tafel slope; because once you polarize the metal corrodes the surface getting destroyed it is a destructive technique right.

We go to linear polarization; it is non-destructive why we apply only a few millivolts. The range is the range of 5-20 millivolts you apply this is plus or minus 5 to 20 millivolt you apply actually. So, the corrosion is so small the sample is not really changing it is characteristics this is nondestructive technique. What is the demerit? The demerit is you need Tafel slopes. One more I just mentioned I am not going to discuss too much and cannot be used in highly resistive environment. What I mean the conductivity of the electrolyte is very small you will not get it. Again, I will not discuss it required some other background.

So, for the time being it is sufficient to understand and be aware that linear polarization cannot be used in some conditions. I am sure of course; the next course you are taking electrochemical techniques there these things will be discussed more in details ok.

So, I think we have discussed so far, the relation between experimentally obtainable polarization data. And how you can use that to determine the electrochemical parameters; like corrosion current density, E_{corr} values, exchange current densities, Tafel slopes and all this like that we can able to get this. And I also it is necessary to connect them to Evan's diagram because you need to get a clear picture about what are the mechanisms are happening so that we have done it.

We also seen that they are related to the mother equation, we call it. The mother equation is a Butler-Volmer equations. We have not derived that those who are interested you can read Buckhannon and or maybe you read the Bockris and Reddy book they are very nice you know derivations are given there.

But you know that if you know that the Tafel equation and what are the significance of that you can see how from that equations the Tafel relationship emerges, from that equation how these Stern-Geary equation emerges. And the merit and demerit of these equation see the point again is clear.

They are special case of Butler-Volmer equation; that means, the electrochemical data should be properly interpreted you cannot diverse that from the Tafel relationship or the

Stern-Geary because there are certain regions; they are applicable, certain regions they are not applicable.

So, then only you can able to get a proper data otherwise you get some i_{corr} value you may not even know whether it has any relevance at all ok. With this I think we will finish the discussion related to i_{corr}, E_{corr} other electro chemical parameters and ok.