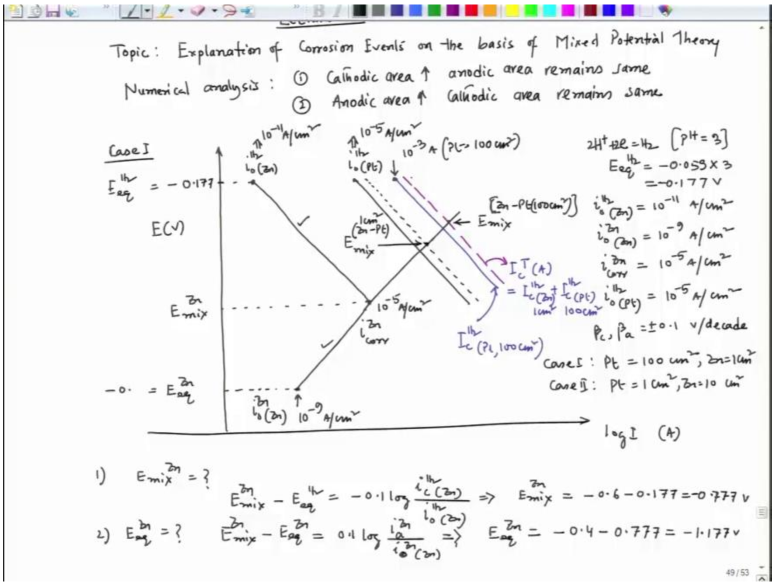
Corrosion Part - II

Prof. Kallol Mondal
Department of Material Science and Engineering
Indian Institute of Technology - Kanpur

Lecture - 14
Explanation of Corrosion Processes on the basis of Mixed Potential Theory: Numerical Analysis

Hello everyone, let’s start lecture 14.

(Refer Slide Time: 00:20)



And our topic remains same, on the basis of mixed potential theory. This explanation of corrosion events on the basis of mixed potential theory that is the topic and today we will consider some numerical analysis for two situations. One is when cathodic increases, remain same and second thing is increases but. So these two situations. We will solve some problems okay. Now if we try to solve the first case.

And remember the data will take in such a fashion that they will be related, both the problems will be both the cases will be related. Now if we try to draw the diagram, in fact here we have to draw a log I capital I. Remember here we have to consider in the form of current in order to understand the area effect and our choice of solution of course hydrogen evolution is our reduction reaction, pH 3 and so if pH is 3 so this

$$E_{eq}^{H_2} = -0.059\,pH$$

= 05 and pH is nothing but 3.

So I can multiply by 3 which is becoming - 0.774 and our consideration is the pressure of hydrogen remains one atmosphere. Now if we arbitrarily choose i zero hydrogen over zinc surface = 10^{-11} ampere per centimeter square. i zero zinc over zinc = 10^{-9} ampere per centimeter square. Now, i corr of zinc when zinc = one centimeter square equal to.

Anyhow when you are talking about small I It's every time it is with reference to one centimeter square unit area is 10^{-5} ampere per centimeter square then i zero hydrogen on platinum = 10^{-5} ampere per centimeter square. beta a = 0.1 as well as beta c the only thing is their signs will change. In case of beta c there will be - and in case of beta a there will be positive so I am just writing +/- volt per decade of current density and then and these two values will not change.

When we converted it into log current scale then that means this becomes volt per decade of current change. Now if we try to plot them so this becomes i zero hydrogen over zinc and this becomes i zero zinc over zinc so this is 9 so this point will be relative position will be like this. And then, this point becomes my i zero hydrogen over platinum. Now if we try to see so this is i corr zinc when it is, in the immersed in that acid without connecting it to the platinum area platinum.

And if we connect it with the platinum so it will also have its own plot and then we have to add as per the mix potential theory we have to add it. This is the total i am not indicating that because you please go back and then check how we have drawn this. So now this will be extended so this point becomes my E mix zinc platinum one centimeter square area. Now once we changed it to 100 centimeters area so that say if I change it to 100 centimeter square in case of platinum.

See one case platinum = 100 centimeter square another case it become and zinc one centimeter square this case one. Case two platinum = one centimeter square and zinc 100 centimeter square okay. So, or let's say I make it different little different so I make it 10 centimeter square okay. So once we do that the case one case so if it is if this value is 10^{-5} ampere per centimeter square so this point would become 10^{-3} ampere when platinum = 100 centimeter square.

Please make sure that please look at the unit what we are using so it is here it is ampere. Now when you do that we have its own plot. This is Ic total in ampere = Ic hydrogen over sink of 1 centimeter square + Ic hydrogen over platinum 100 centimeter square. Sorry this is not that part, it is rather this is the this is Ic hydrogen over platinum 100 centimeter square and then if I do it with the different color so this becomes my this is the total part.

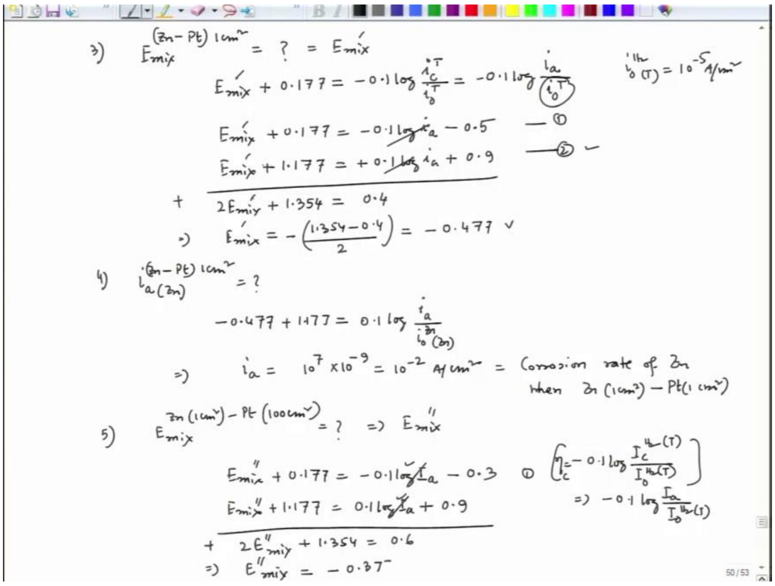
Now if we extend this one so it will cut here this becomes my E mix zinc platinum 100 centimeters square and zinc here we are not changing. Now those values if we try to indicate this is 10^{-5} ampere per centimeter square and this is 10^{-11} ampere per centimeter square this is 10^{-9} ampere per centimeter square and we have already indicated everything and that this value corresponds to - 0.177 volt. Now we have to find out E mix zinc.

So now if you want to mix I try to find out so the first thing let's find out E mix zinc. In order to do that we just take this line if we take that line so E mix - E, so this is nothing but equilibrium hydrogen, this is E equilibrium zinc, equilibrium hydrogen = - 0.1 log of ic hydrogen over zinc divided by i zero hydrogen over zinc. Now if we solve it by putting all the values we will get E mix would be = - 0.6 - 0.177 = - 0.1777.

This will be the E mix zinc. Now if we try to solve, now we have to find out E equilibriums zinc which can also be find out found out we have to find out that part. So E mix zinc - E equilibrium zinc = 0.1 log of we have to take this particular line ia zinc i zero zinc over zinc surface would be = E equilibrium zinc would be = - 0.4 - 0.777 = - 1.177. So that will be the value, Okay.

So we have found out this point so i can mention it to be - 0.7. So these points i can change it becomes - 1.177 and this would be this would be - 0.777 okay. So now if we try to find out now let's find out, this point. This point if i need to find out so let's find out E mix zinc platinum when it is one centimeter square, if we try to find out we have to solve two equations.

(Refer Slide Time: 14:22)



We have to find out this point. So this point would become 10^{-11} + 10^{-5} which is nothing but 10^{-5} ampere per centimeter square. If we solve that so two equations if I indicate in this fashion E mix single prime. So single prime - 0.177 + = - 0.1 log ($i_{c\ total}/i_{o\ total}$). I can write in this fashion 1 log of ia divided by i zero total, the way we have done previously so it becomes so this becomes a mix prime + 0.177 = - 0.1 log of ia +.

And then this value is nothing but 10 to the power hydrogen total is nothing but 10^{-5} ampere per centimeter square, we have seen already so this becomes 0.5 sorry this becomes 0.5 and for the anodic part if we consider + 1.177 = - 0.0 this is + log ia + 0.9. Because we are considering this line and this line. So if we solve that this is equation 1 this is equation 2.

So it if we add them prime + 1.354 equal to these two would get cancelled and then we are getting 0.4. So E mix prime becomes 477. So this becomes this value becomes - 0.477 volt. Now we can calculate ia zinc when for this couple of one centimeter square we can do that so if we take equation 2 so - 0.477 + 1.7177 = 0.1 log ia by 10^{-9}. Because i zero here I have to take i zero of zinc over zinc surface.

So if we solve this this is for solve this will get ia would be = 10^{-7} into 10^{-9}. So this becomes 10^{-2} ampere per centimeter square. So this is the corrosion rate of zinc when is galvanically coupled zinc one centimeter square is galvanically coupled to platinum one centimeter square.

Now when we increase the area of the platinum so we have to find out so if we correspond to this particular point because this so this becomes 10^{-3} because we are not changing i zero capital

I zero because zinc area we are not changing so 10^{-11} ampere + 10^{-3} ampere. Which is roughly = 10^{-3} ampere because -11 because when we change everything to ampere instead of ampere per second ampere per centimeter square and then this particular value we can calculate.

The similar practice we can do. So if we try to find out E mix zinc 1 centimeter square platinum 100 centimeter square area. So we have to find out if we assume this is to be E mix. double prime, so again we can follow the similar equation solving mode so

$$E''_{mix} + 1.177 = -0.1 log I_a - 0.3$$

because here equation becomes 0.1 log Ic hydrogen I would say total + I zero hydrogen total so this is = c.

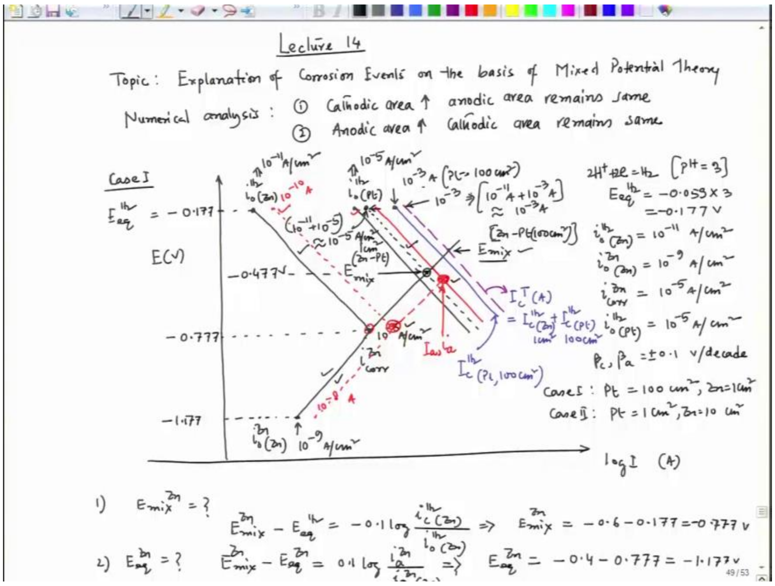
So I can change it to - 0.1 log Ia divided by I zero hydrogen total so this I zero hydrogen total is nothing but 10^{-3} ampere. So this is one equation then another equation if we consider the anodic apart 0.1 log Ia - this will become +. And since the zinc area is not changing so i zero small i zero nothing but the capital I zero in terms of magnitude. So if we solve this again if we add them so 2 E double prime mix + 1.354 for this two will get cancelled.

So we are left with 0.6. So E double prime mix = - 0.377 volt, 377 volt. Now this is I am talking about this point this is the value we have calculated. Now if we want to calculate Ia this is 5 this is 6, Ia when zinc one centimeter square is connected to platinum 100 centimeter square. If we want to calculate so

$$E''_{mix} + 1.177 = 0.1 \, log \, log \, \frac{I_a}{I^{Zn}_{o\,(Zn)}}$$

So this becomes 10^{-1}.

(Refer Slide Time: 23:07)



If we do that you will get another - one because this is 10^{-1}. So this becomes my corrosion current when zinc 1 centimeter square is connected to platinum 100 centimeter square. Now if I try to calculate the current density the current density, or corrosion current density of zinc so this will be = 10^{-1} ampere 1 centimeter square because the zinc area has not changed so this becomes the 1 ampere per centimeter square.

So now you could see that, when if we try to compare this value and this value I could see that the corrosion rate has increased one order magnitude. Now this is the part 1 or case 2, this is case one case two if we try to see where zinc area is 10 centimeter square and platinum area is 1 centimeter square that case if we plot everything in the red color so this point will not change for one centimeter square area but once we change to zinc is changed to 10 centimeter square.

So this way will come here. So this becomes 10^{-8} ampere since zinc is now 10 centimeter square so this is to be 10^{-9} into 10 becomes this and this will also become 10^{-10} ampere. So if we continue this so they will connect here at the same so here it will connect. Now this line we have to consider addition of this line and this line we have to consider so this will shift little bit on the right side.

And we have to continue that 10 centimeter square line to this. So now we are getting new point this and so let’s find out all those two points and try to find out what could be the corresponding Ia and ia. These two values let’s find out because this will be the mix values mix potential as per the the mix potential this the theory will be met at this point at this point it will be met. So let's find out that. Now in order to find out first we have to find out this particular point and then we go ahead with this.

So if I try to find out the first point so now you will be considering everything in terms of i capital I and E of course so now first part is we have to solve in order to get this point we have to solve two equations what are those two equation I will just a bit of jump I'll do first part is E mix star, let's say this point is E mix star. So if I try to find out this E mix star - 0.177 because this value will not change this value will remain fixed volt this is volt = 0.1 if we take this line.

So it will be in terms of area in terms of current Ic hydrogen over zinc surface I zero hydrogen over zinc surface zinc. So I can replace it with Ia log Ia and this one I note in 10 so this become 1.0 and corresponding

$$E_{mix}^{*} + 1.177 = 0.1 log I_a + 0.8$$

So if we add them this will get cancelled so this become 0.2. So E mix star 2 = - 1.554 so E mix star = - 0.777.

So interestingly we could See that even if we increase the area this E mix is nothing but the same value. Now we have to find out Ia which can be found out by taking this equation so Ia if you calculate you will see that Ia value comes out to be 10^{-4} ampere. Now corresponding, ia if I try to find out 10^{-4}/10 centimeter square = 10^{-5} ampere per centimeter square and so this is the corrosion rate of zinc of 10 centimeter square when zinc only is dipped in acid.

Now we have to find out then this particular point which let's say make it double star. So if we do that then this is let's say 1 then 2 same I will go by I will try to solve in this case we solve this line and this line and now in this case will solve this line and this line now we have already found out that this point will be this point will be 10^{-5} ampere only

Because if we add this value and I zero when platinum is 1 centimeter square which is this point if we correspondingly I zero with the same value because we are not changing platinum area. So if we add this and quantity which becomes to - 5 ampere. So that case we have to again constitute two equations in order to do that.

So E mix double star so if I try to solve this line and this line then I have to again constitute another equation this is stage 2, E mix we are trying to find out E mix and Ia first I will try to find out Ia when zinc 10 centimeter square is connected to platinum 1 centimeter square. So if I try to do that so

$$E''_{mix} + 0.177 = -0.1 log I_a - 0.5$$

I'm not because when we tried to the same way when we try to solve draw a equation.

An equation for this line this line so we are assuming that a current value does not change because it is roughly same value as we have seen that this quantity and this quantity if we add it becomes roughly and under the - 5 so that does not change. So and at the same time we are seeing that at this point rate the current corresponding to the total evolution of hydrogen is = the total current corresponding to the dissolution of zinc.

So if we do that log Ia and here I zero total is nothing but - 5 so it becomes so I zero total = $10^{-10} + 10^{-5} = 10^{-5}$ ampere so 0.5 E mix + 1.177 = 0.1. This is here I am replacing Ic total so here it will be this is in the anodic part this is the cathodic part + 0.8.

Because here I have to consider this line so here the point has 10^{-8}. So if we add them + 1.354 = this two would get cancelled so this becomes 0.3. So

$$E^{**}_{mix} = \frac{-1.054}{2} = -0.527$$

o this is the E mix thing then we can take this equation to find out Ia.

So 527 if we take if we try to find out Ia. So we can solve equation 2. This equation we can solve so

$$-0.527 + 1.177 = 0.1 log \frac{I_a}{10^{-8}}$$

which becomes 10 to the power of 1.5 - 1.5 ampere. So now this is the corrosion current when zinc is 10 centimeter square.

So in a corresponding Ia if we try to find out $10^{-1.5}$ divided by 10 centimeter square which becomes $10^{-2.5}$ ampere per centimeter square. This is the corrosion density. When 10 centimeter square is connected to platinum one centimeter square. Now let's get back to the corrosion current density when zinc one centimeter square is connected to platinum one centimeter square.

That value was we have calculated before so that value was 10^{-2}. That value was let me see what was the value calculated, yes this was the value we have calculated. So it was 10^{-2}. So I could see that Ia zinc one centimeter square Platinum one centimeter square is less is greater than Ia zinc ten centimeter square and platinum one centimeter square.

So it is very clear that the corrosion current density of zinc, if we increase the anodic area decreases with reference to the value what we have found out when zinc of one centimeter square area is connected to platinum upon one centimeter square area. So the zinc corrosion rate actually decreases because of increase in anodic area but if I try to find out corrosion current density when zinc one centimeter square and platinum 100 centimeter square.

These were the situation that time corrosion current density was ampere to the - one ampere per centimeter square which is much higher so that means I could see that the corrosion rate of anodic region increases because of connection of that anodic region to a cathodic region of higher area.

But the zinc corrosion rate decreases when it is connected to when its own area increases with reference to the cathodic area and remember every time we are assuming that it is uniform dissolution. That situation and the assumption is this is one important assumption all those problems it is uniform distribution of cathodic and anodic reactions over cathode and anode area and we are considering uniform dissolution.

So that case we could see that increase in cathodic areas need not good for the structural design rather if we have increase in anodic area with reference to the cathodic area that solves better because the dissolution rate decreases. So from this numerical solving, the problem solving mode we could see the effect of area factor in a area factor in a better fashion and appreciate it better. Let's stop it and we will continue our discussion in our future lectures, thank you.