Corrosion Part - II

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Lecture - 13
Area Effect of the Cathodic and Anodic Component - II

Hello everyone. Let’s start lecture 13.

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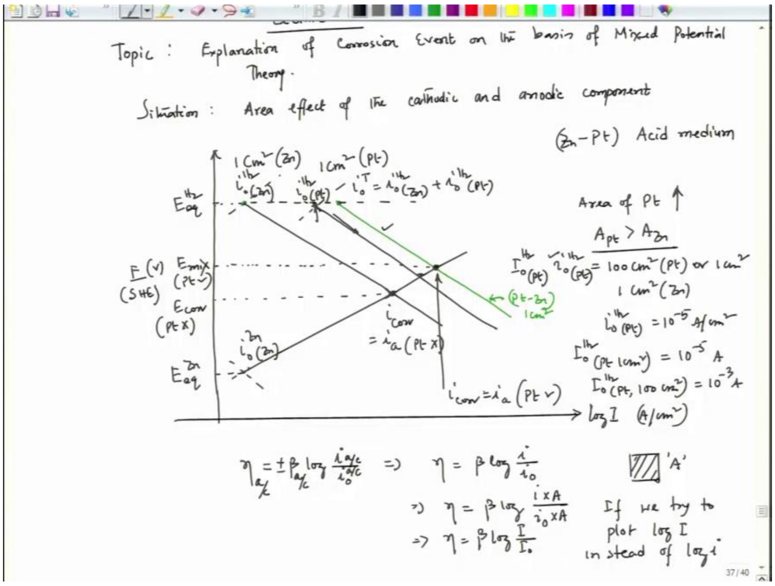

Topic : Explanation of Corrosion Event on the basis of Mixed Potential Theory.

Situation : Area effect of the cathodic and anodic component

($Zn-Pt$) Acid medium

Area of Pt ↑

$A_{Pt} > A_{Zn}$

$I_0^{H_2}(Pt)$ $i_0^{H_2}(Pt)$ = 100 cm² (Pt) or 1 cm²

1 cm² (Zn)

$i_0^{H_2}(Pt) = 10^{-5}\ A/cm^2$

$I_0^{H_2}(Pt\ 1cm^2) = 10^{-5}\ A$

$I_0^{H_2}(Pt, 100\ cm^2) = 10^{-3}\ A$

$$\eta_{a/c} = \pm \beta_{a/c} \log \frac{i_{a/c}}{i_0^{a/c}} \Rightarrow \eta = \beta \log \frac{i}{i_0}$$

$$\Rightarrow \eta = \beta \log \frac{i \times A}{i_0 \times A}$$

$$\Rightarrow \eta = \beta \log \frac{I}{I_0}$$

If we try to plot log I instead of log i

And topic explanation of corrosion event on the basis of mixed potential theory and we have started our discussion on this particular situation, area effect on the corrosion of active component when connected to a noble component. So there we started with this particular diagram and we realize, we have realized that we cannot explain this corrosion event if we consider current density instead of that we have to take current.

So once we take current so then this unit becomes A and this i zero point would change. Now here we are talking about everything in terms of capital I. So now if it is one centimeter square this is all the time one centimeter square this does not change, so this is also one centimeter square. So in case of one centimeter square I zero capital I zero that is current is equal to current density magnitude wise. so their units are different.

But magnitude wise they are same for example here we have given an example. So if i zero or small i zero is 10^{-5} ampere per centimeter square over platinum of that hydrogen evolution reaction. The capital i zero of the hydrogen evolution reaction on platinum with the same area would be same but the unit is one case ampere per centimeter square in other case it is ampere. Now I can term these values i can turn i can write this particular thing as capitalized I zero instead of small i zero and that unit becomes ampere. Now when we consider 100 centimeter square platinum connected to one centimeter square zinc, so the capital I zero over that 100 centimeter square area will shift to the right. So let me plot everything in blue color, okay. So that point will come here after multiplying area with that exchange current density of hydrogen evolution over platinum surface. Now it will also follow the same slope beta.

So will, so this is the individual that means the ic variation this is ic hydrogen, or sorry I should mention capital I hydrogen over platinum surface. Now we have to add this current density also as per the mix potential theory with this blue dotted line. So if we add that, so this addition will be this line so this is and this would extend definitely so this line is nothing but I or Ic total = Ic hydrogen over platinum or I should mention this.

So this is I total c = Ic hydrogen over platinum of 100 centimeter square + Ic hydrogen over zinc. So I can remove this terms of 1 centimeter square. Fine. I just I should mention side by Ic hydrogen and remember these are all capital I on zinc surface of one centimeter square, fine and this particular line also would be i zero only because this area is not changing its always remaining one centimeter square. Now where would it meet the criteria of mixed potential theory.

Where i could see that the charge balance is maintained. So i could see that the charge balance is maintained at this particular point. So what will be this situation at this point. I could see that equal to or I = Ia of zinc. So this is the condition and then what will be the mixed potential. So the mixed potential is this is the mixed potential. So E mix when this condition is meeting when zinc one centimeter square is connected to platinum 100 centimeter square.

Now if capital Ia is the new dissolution current of zinc remember we are saying current not current density and we know that the current density.

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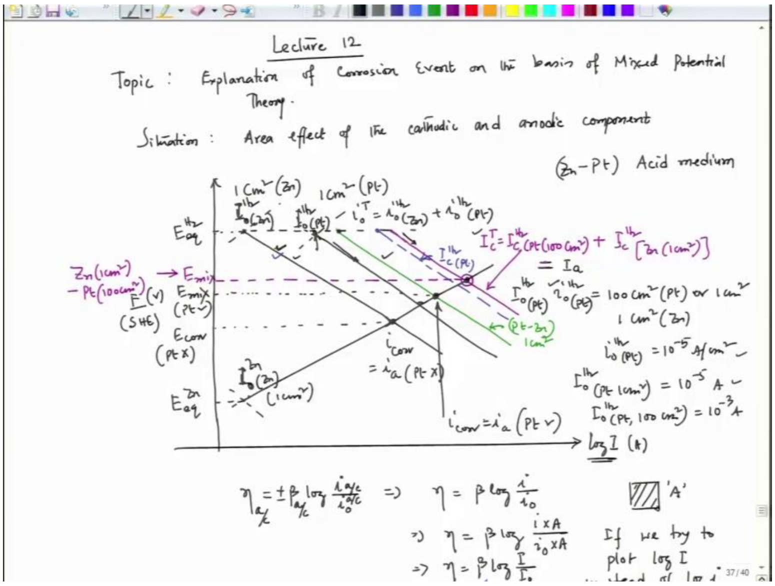

Lecture 12

Topic : Explanation of Corrosion Event on the basis of Mixed Potential Theory.

Situation : Area effect of the cathodic and anodic component

(Zn-Pt) Acid medium

$i_0^{T} = i_0^{H_2}(Zn) + i_0^{H_2}(Pt)$

$I_c^{T} = I_c^{H_2}(Pt(100\,cm^2)) + I_c^{H_2}[Zn(1\,cm^2)] = I_a$

$I_0^{H_2}(Pt)$ $i_0^{H_2}(Pt)$ = 100 cm² (Pt) or 1 cm² 1 cm² (Zn)

$i_0^{H_2}(Pt) = 10^{-5}\ A/cm^2$

$I_0^{H_2}(Pt\ 1\,cm^2) = 10^{-5}\ A$

$I_0^{H_2}(Pt, 100\,cm^2) = 10^{-3}\ A$

$\eta_{a/c} = \pm\beta_{a/c}\log\frac{i_{a/c}}{i_0^{a/c}} \Rightarrow \eta = \beta\log\frac{i}{i_0}$

$\Rightarrow \eta = \beta\log\frac{i\times A}{i_0\times A}$

$\Rightarrow \eta = \beta\log\frac{I}{I_0}$

▨ 'A'

If we try to plot log I

We know that the current is not proportional to corrosion rate, rather current density is proportional to corrosion rate. Since

$$\frac{W}{At} = \frac{I\,a}{nFA}$$

So where I is current in ampere, A is weight in gram, and n is equal to number of electrons, F is 1 Faraday which is 96500 Coulomb and A is equal to area.

So now we could see that if we consider the corrosion rate to be this then this quantity is not proportional to corrosion it because this can vary. But if we consider this quantity, that means I by A that is proportional to the corrosion rate. So we have seen that before, so now if Ia is equal to Ic hydrogen over platinum of 100 centimeter square + Ic of hydrogen over zinc of 1 centimeter square then I need to find out IA from this how do we find out now if I get to this same plot here same plot here.

Now since it is in log scale, now this particular line is farther left to this line, so the effect of that addition of this particular current for this particular current related to the hydrogen evolution over zinc surface on the total ic would be very minimum. We will see that later. So actually we can consider it to be Ic hydrogen over platinum one hundred centimeter square so ia would be Ic hydrogen over platinum hundred centimeter square divided by one centimeter square.

Because whatever this current requirement current is flowing is flowing between 1 centimeter square zinc and, so this is situation is like this, this is one centimeter square and this is one hundred centimeter square, this is one centimeter square so the current flow between this two so the same current is flowing over the smaller section so this is anode and this is cathode. And here it is platinum and here it is zinc so the same current is flowing so if the same current is flowing the current remains same but when we are considering converting into current density. We are seeing that we have to divide it by the area of the anode so area of the anode remains one centimeter square. So now you could see that the corrosion rate which is nothing but the i corr when zinc is connected to platinum over 100 centimeter square area okay, which is almost is much much higher than the corrosion rate of zinc when it is connected to one centimeter square area of platinum.

So this is the crux of the problem what we experienced in case of copper plate and iron rivet, so this is the problem what we experienced the iron rivet dissolves quickly quicker than the situation where area of copper and iron are same so here cathodic area is much higher so this is cathodic area and this is anodic area.

Since we have a big two plates, two plates so we have rivet small rivets this is iron rivet or steel rivet and this is copper so we could see that the current density related to the dissolution of iron over iron dissolution of an over iron becomes much higher than the situation which is proven here than the situation where the iron area and copper area both are same this is if these are same this is iron this is copper if they are same the situation would be much less aggressive.

This is proven here. For example, when one centimeter square area of zinc is connected to one centimeter square area of platinum the corrosion rate was here. Now once the platinum area is increased the corrosion rate, corrosion current has become here and the corrosion current density would also increase in relation to the area increment of that noble component and remember here as we have mentioned before the noble component or the cathodic component is decided by the reaction that means the cathodic reaction is taking place on that cathodic component.

Here also the cathodic reaction is hydrogen evolution reaction and that is taking place over the platinum surface and that so platinum becomes cathode and zinc becomes anode and in case of copper plate and iron plate, iron acts as anode and copper acts as cathode in seawater and that time cathodic reaction is

$$O_2 + H_2O + 4e = 4OH^-$$

and anodic reaction this is cathodic and this is going to be an anodic reaction.

So now this is the situation what we experience when we have active component having less area and noble component has higher area in a galvanic coupling and that is practically a very dangerous structure design. So we while designing structure on the basis of if we consider if we see that there is a chance of aggressive corrosion we should not keep any structure where cathodic area is higher than anodic area.

So our interest should be always the cathodic area should be less than the anodic area or rather if we can protect the cathode surface and leaving the anode surface exposed that would be great. For example, we if we recall in a lecture in a corrosion part 1 we discussed that in a tank if we have if we have coated, if we have added stainless steel at the bottom and the leaving some iron part on the top of the tank so then it is always better to coat the bottom surface that is the stainless steel so that the cathodic area is reduced.

So the design criteria is the cathodic area should be less than the anodic area and so that the area influence on the increase of the anodic dissolution rate should not be felt. We have seen that if we increase the area of cathodic region in a galvanic couple between an active metal and noble metal then the corrosion rate increases and the explanation for that we cannot explain it from the plot of potential versus log of current density rather we have to explain it from the plot of potential versus log of current.

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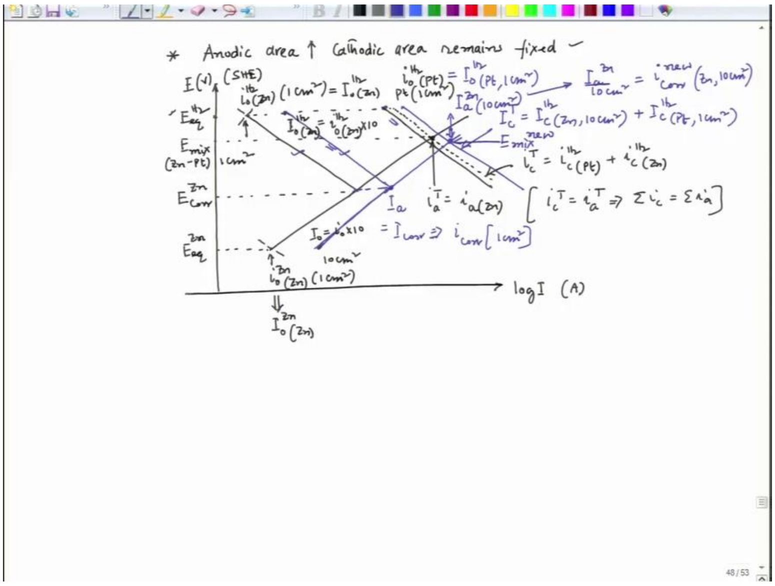

So the unit in the x axis changes from ampere per centimeter square to ampere, then only you will be able to appreciate the effect of increase in area of the noble part in that galvanic couple, now we also need to see that what would happen if we increase the anodic area keeping the cathodic area fixed. So in order to understand that we have to also use make use of potential versus log of current plot.

So if we try to see the situation if we try to see the anodic area increases, cathodic area remains as fixed, so how to explain that situation in that galvanic couple. So we have to plot, log I. Now it is interesting to note that we are using capital I so that means the unit becomes ampere and this becomes potential which is in volt. Now we have already mentioned that we'll be talking in terms of standard hydrogen electrode, so now if we try to see the hydrogen evolution reaction that means if that couple that cathodic and anodic area considering this situation.

If we dip that particular couple in an acid where if we consider that hydrogen evolution reaction is my cathodic reaction so that would happen on both anodic and cathodic surface. So now this is E equilibrium of let’s say we are considering zinc and then this is this potential is decided by the pH of the solution. So when we consider mixed potential theory, so this point is i zero zinc of zinc and this point is i zero hydrogen over zinc. Now if we consider there to be 1 centimeter square.

So here we are considering 1 centimeter square so this is with reference to 1 centimeter square and this becomes my E corr of zinc. Now if we try to change that current density into current if area remains 1 centimeter square so then that would also be I zero because this in multiplied by 1 centimeter square becomes my current corresponding to exchange current density so now this is also becoming this would also become I zero hydrogen over zinc because we are considering 1 centimeter square.

Now when we couple platinum of 1 centimeter square, this value will not change because that is decided by the pH but we will have i zero hydrogen over platinum surface of one centimeter Square area and then as for the mix potential theory the way we have done previously so we will do and then we have to add it because we have to consider the mix potential so we continue this this becomes my E mix when we are connecting zinc and platinum of one centimeter square each.

And i zero of hydrogen over platinum surface is very high and this is nothing but ic total which is ic hydrogen over platinum surface + ic hydrogen over zinc surface and this particular current density is ia total equal to ia zinc because here only one anodic reaction is taking place and so these 2 are ic total equal to ia total we are expressing in the form of ic equal to ia. Now last time we have increased platinum area and then without changing the zinc area.

Now if we change the zinc area so let's say zinc area has been changed to some arbitrary 10 centimeter square okay, so now 10 centimeter square if we do it so I zero would become then I zero into 10. So then this point will come here. Similarly, this also have equal change I zero hydrogen over zinc surface equal to I zero hydrogen into 10. So now we can draw that line, like this, so this becomes my E corr and interestingly we will see later on with the calculation that this point does not change.

Even if we increase the area because the slope remains same so this point will move right side only thing that change will happen but remember again, this change this becomes my Ia equal to I corr but it will be also equivalent to i corr when 1 centimeter square area. There is nothing we are changing only changing because both the I zeros will change in a in a multiplied manner.

Now when we talk about platinum now so this point would not change this would remain as I zero hydrogen over platinum one centimeter square. This point will not change but now we have to add this line and this line so if we add them that comes let's say it comes here because since this point is shifted to this point after considering capital I so now it will also shift little bit so it will come like this okay. Now we have to continue this particular plot okay. So it will come and meet this point.

So this line is nothing but I total c equal to Ic hydrogen over zinc of 10 centimeter square area + Ic hydrogen over Platinum 1 centimeter square area and the new E mix is this point so this is E mix new. So my corrosion rate has come to we do not know the corrosion rate rather we know the current. So if we try to see what is the current corresponding to dissolution so this is nothing but Ia of zinc of 10 to a centimeter square area, so now in order to find out corrosion rate because of the increased in anodic area.

This would become Ia zinc by 10 centimeter square equal to i corr for μ when zinc is 10 centimeter square when the zink is 10 centimeters square. So that will be change in the overall diagram but by looking at this apparently it looks like the corrosion rate of zinc should increase, but if we follow if we do some numerical analysis we will see interestingly the corrosion rate of zinc does not increase rather it is lower than the corrosion rate of zinc when the equal area of zinc and platinum are connected.

We will see with an example, and remember one condition is to be met that every time when we are talking about this potential log current or current density plot we are assuming that uniform dissolution is taking place and uniform reaction of cathodic and anodic reactions over cathodic and anodic surfaces are taking place. This uniformity is one of the major criteria for drawing this particular diagram.

Then only we will see that yes increase in anodic area rather decreases the overall corrosion rate of zinc compared to the situation where equal area of anode and cathode are connected, and in other situation where cathodic area increases as compared to the anodic area corrosion rate of anodic region will increases to a great extent. So let’s stop here we will continue our discussion in our next lecture, thank you very much.