Corrosion Part - II

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Lecture - 12
Area Effect of the Cathodic and Anodic Component – I

Hello everyone let’s start lecture 12.

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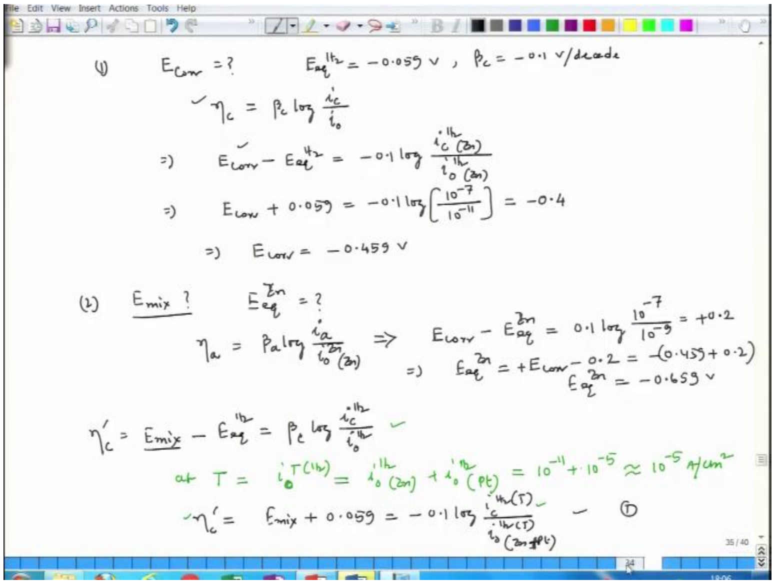

(1) $E_{corr} = ?$ $\quad E_{eq}^{H_2} = -0.059\ V$, $\beta_c = -0.1\ V/decade$

$\checkmark\ \eta_c = \beta_c \log \frac{i_c}{i_0}$

$\Rightarrow\ \overset{\checkmark}{E_{corr}} - E_{eq}^{H_2} = -0.1 \log \frac{i_c^{H_2}(Zn)}{i_0^{H_2}(Zn)}$

$\Rightarrow\ E_{corr} + 0.059 = -0.1 \log\left[\frac{10^{-7}}{10^{-11}}\right] = -0.4$

$\Rightarrow\ E_{corr} = -0.459\ V$

(2) $\underline{E_{mix}\ ?}$ $\quad E_{eq}^{Zn} = ?$

$\eta_a = \beta_a \log \frac{i_a}{i_0^{Zn}(Zn)} \Rightarrow E_{corr} - E_{eq}^{Zn} = 0.1 \log \frac{10^{-7}}{10^{-9}} = +0.2$

$\Rightarrow\ E_{eq}^{Zn} = +E_{corr} - 0.2 = -(0.459 + 0.2)$

$E_{eq}^{Zn} = -0.659\ V$

$\eta_c' = \underline{E_{mix}} - E_{eq}^{H_2} = \beta_c \log \frac{i_c^{H_2}}{i_0^{H_2}}\ \checkmark$

at $T = \ i_0^{T(H_2)} = i_0^{H_2}(Zn) + i_0^{H_2}(Pt) = 10^{-11} + 10^{-5} \approx 10^{-5}\ A/cm^2$

$\checkmark\ \eta_c' = E_{mix} + 0.059 = -0.1 \log \frac{i_c^{H_2(T)}}{i_0^{H_2(T)}(Zn + Pt)}$ — ①

So this equation comes out to be another tafel equation or I would say this particular line we have already mentioned this line we are considering, which is the parallel line of the individual tafel lines for hydrogen evolution reaction on zinc surface as well as platinum surface. And here neeta c is nothing but neeta c prime is nothing but this. So this is the neeta c prime.

So and here it is the total i c of hydrogen evolution which is nothing but the addition of 2 current densities corresponding to hydrogen evolution reaction for, on zinc as well as platinum surface and this is nothing but the over voltage. And here this E corr is nothing but the E mix, so we have mentioned that if we consider this particular plot. So this is the new E mix so instead of E corr I can write E mix, E mix I can write or I should write it in black E mix.

Now this equation 2 let's say and this is equation 1 this equation this becomes this is 1 equation. So, this is the equation 1 and let me find out one more equation for this one. So the equation becomes

$$\eta'_a = E_{mix} - E_{eq}^{Zn}$$

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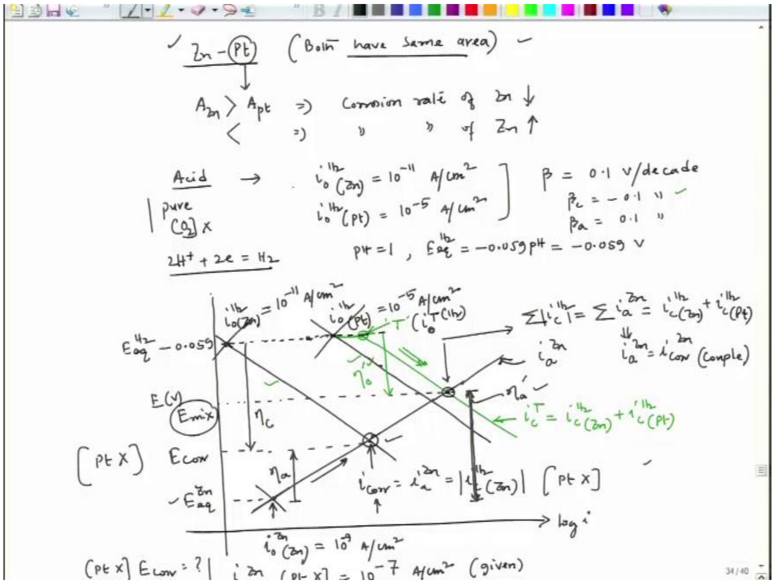

So this is E equilibrium of zinc so I am considering this much polarization equal to

$$\eta'_a = E_{mix} - E_{eq}^{Zn} = \beta_a log\frac{i_a}{i_{o,Zn}^{Zn}}$$

If I see so this is we are considering this line. Okay.

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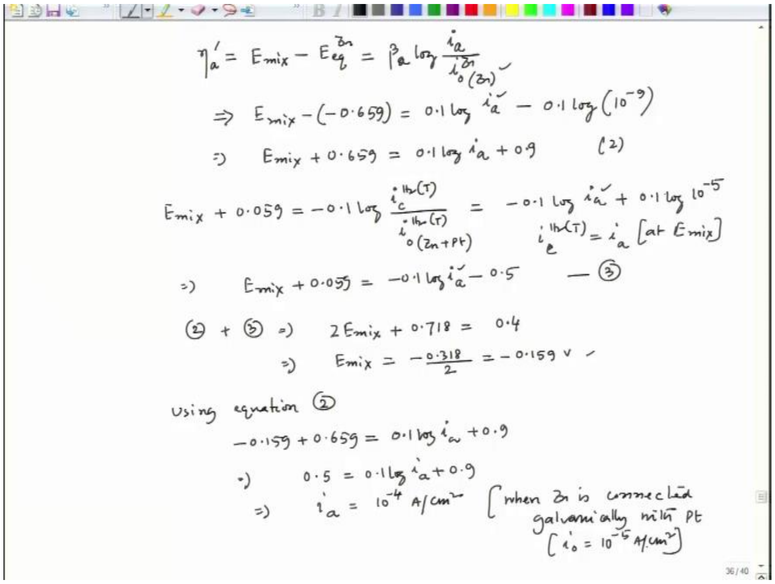

$$\eta'_a = E_{mix} - E_{eq}^{Zn} = \beta_a \log \frac{i_a}{i_{0(Zn)}^{Zn}}$$

$$\Rightarrow E_{mix} - (-0.659) = 0.1 \log i_a - 0.1 \log (10^{-9})$$

$$\Rightarrow E_{mix} + 0.659 = 0.1 \log i_a + 0.9 \qquad (2)$$

$$E_{mix} + 0.059 = -0.1 \log \frac{i_c^{H_2(T)}}{i_{0(Zn+Pt)}^{H_2(T)}} = -0.1 \log i_a + 0.1 \log 10^{-5}$$

$$i_c^{H_2(T)} = i_a \text{ [at } E_{mix}]$$

$$\Rightarrow E_{mix} + 0.059 = -0.1 \log i_a - 0.5 \qquad — ③$$

② + ③ $\Rightarrow 2E_{mix} + 0.718 = 0.4$

$\Rightarrow E_{mix} = -\frac{0.318}{2} = -0.159$ V

Using equation ②

$-0.159 + 0.659 = 0.1 \log i_a + 0.9$

$\Rightarrow 0.5 = 0.1 \log i_a + 0.9$

$\Rightarrow i_a = 10^{-4}$ A/cm² [when Zn is connected galvanically with Pt [$i_0 = 10^{-5}$ A/cm²]

So but this is the equation now one thing is very clear from this that at this mixed potential point I can say equal to ia which is valid for this point. This point this is valid. So in fact I can write it to be that means this is equation 2 which I can simplify -(- 0.659) = 0.1 log i_a and i_a - 0.1 log 10^{-9} because this value is 10^{-9}. So it becomes E mix + 0.659 = 0.1 log i_a - 0.1 or I can say this is + 0.9.

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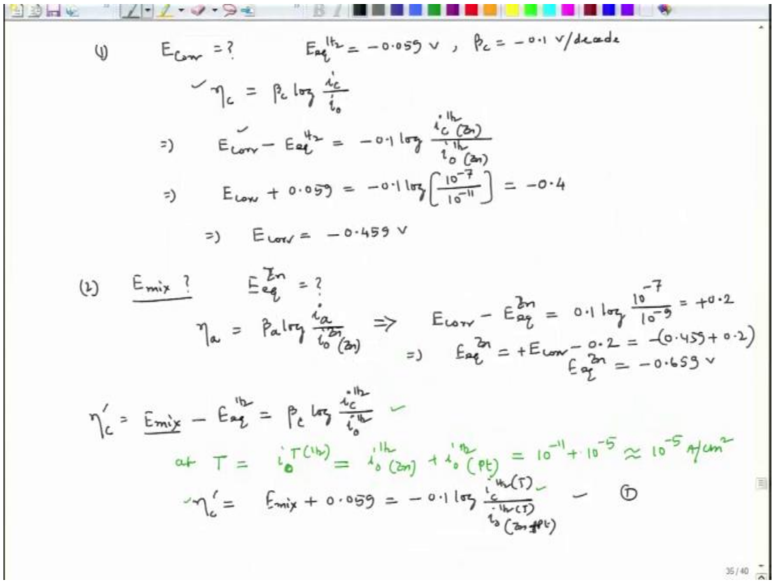

(1) $E_{corr} = ?$ $\quad E_{eq}^{H_2} = -0.059$ V, $\beta_c = -0.1$ V/decade

$$\eta_c = \beta_c \log \frac{i_c}{i_0}$$

$$\Rightarrow E_{corr} - E_{eq}^{H_2} = -0.1 \log \frac{i_{c(Zn)}^{H_2}}{i_{0(Zn)}^{H_2}}$$

$$\Rightarrow E_{corr} + 0.059 = -0.1 \log \left[\frac{10^{-7}}{10^{-11}}\right] = -0.4$$

$$\Rightarrow E_{corr} = -0.459 \text{ V}$$

(2) $\underline{E_{mix}\ ?}$ $\quad E_{eq}^{Zn} = ?$

$$\eta_a = \beta_a \log \frac{i_a}{i_{0(Zn)}^{Zn}} \Rightarrow E_{corr} - E_{eq}^{Zn} = 0.1 \log \frac{10^{-7}}{10^{-9}} = +0.2$$

$$\Rightarrow E_{eq}^{Zn} = +E_{corr} - 0.2 = -(0.459 + 0.2)$$

$$E_{eq}^{Zn} = -0.659 \text{ V}$$

$$\eta'_c = \underline{E_{mix}} - E_{eq}^{H_2} = \beta_c \log \frac{i_c^{H_2}}{i_0^{H_2}}$$

at T = $i_0^{T(H_2)} = i_{0(Zn)}^{H_2} + i_{0(Pt)}^{H_2} = 10^{-11} + 10^{-5} \approx 10^{-5}$ A/cm²

$$\eta'_c = E_{mix} + 0.059 = -0.1 \log \frac{i_c^{H_2(T)}}{i_{0(Zn+Pt)}^{H_2(T)}} \qquad — ①$$

This is equation or let's say let me put this one as equation 2 and from the equation 1, I can write E mix + 0.059 = - 0.1 log $i_{c\ total}$ or let me put the same notation. This is the notation we have used hydrogen total divided by i zero hydrogen. The notation what we have used is basically the total again over zinc platinum. So I used + so this is +. So that means this i zero is the addition of this particular current density and this particular condition which is giving this current density

So now I have seen that at this mixed potential point, I can have this condition meeting, so I can easily write this is to be - 0.1 log i_a + 0.1 log 10^{-5}. Since we have seen that this fellow which is i zero total hydrogen is nothing but another - 5 ampere, so ampere per centimeter square. So this becomes E mix + 0.059 = - 0.1 log i_a - 0.5. So this let’s say equation 3.

So then by adding equation 1 and 2 and this current density and this current density they are same. Since ic hydrogen total = ia at E mix. So now if we add equation 2 and 3 we get 2 E mix + 0.718 = 0.4. So E mix = - 0.318/2 = - 0.159 volt so E mix turns out to be this E mix this value turns out to be 0.159 volt. Now once we know a mix we wanted to find out i corr zinc when the Platinum is present.

So now we have to find out ia, this ia I have to find out. So once we know we can use using equation 2. I put those values

$$-0.159 + 0.659 = -0.1 log i_a + 0.9$$

So we are getting this is

$$0.5 = -0.1 log i_a + 0.9$$

So I am getting ia to be 10^{-4} ampere centimeter square, when zinc is connected galvanically with platinum where i zero = 10^{-5} ampere per centimeter square.

So it is very clear that, I am having if without galvanic coupling my corrosion rate was 10^{-7} ampere per centimeter square and now after coupling so what was without coupling say ia, and in fact this is nothing but i corr when platinum is connected and i corr, when platinum is not there, is = 10^{-7}. So, there is order of magnitude increase in the corrosion rate when an active metal is connected to a noble metal with much higher exchange current density of hydrogen evolution on that noble metal surface.

And also the E mix moves up that means if we see this the E corr when platinum was not there so E corr was positioned here. But after it is connected to platinum with higher exchange current density of hydrogen evolution on that surface the corrosion potential or the E corr or E mix has moved up but the corrosion rate of that active component, that is zinc has gone up orders of magnitude. So this is one numerical problem which talks about how we can get all those values.

In fact, now these 2 values one can easily find out though will not do it here I am leaving it to you because now if we see this particular line particular line which is the E corr line and now that line connects cuts the hydrogen evolution reaction on zinc surface at this point and hydrogen evolution reaction on the platinum surface at this point in fact this reaction is hydrogen on zinc and this point is i zero so it is ic hydrogen reaction on platinum.

So these two points can be easily found out how we have to just consider this line for finding out this particular current density. And that time my over voltage would be prime similar over voltage will be will have to be applied for this particular line. So then you will get both those current densities. So this is about a situation when we connect an active component with a noble metal with a higher exchange current density of the cathodic reactions over that noble metal.

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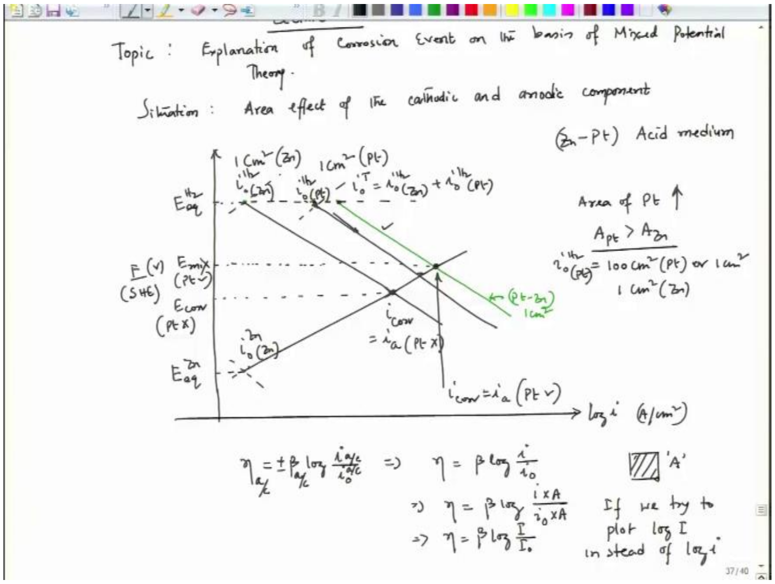

Topic : Explanation of Corrosion Event on the basis of Mixed Potential Theory.

Situation : Area effect of the cathodic and anodic component

(Zn–Pt) Acid medium

Area of Pt ↑

$A_{Pt} > A_{Zn}$

$i_0^{H_2}(Pt) = 100\ cm^2\ (Pt)$ or $1\ cm^2$

$1\ cm^2\ (Zn)$

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

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

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

▨ 'A'

If we try to plot log I instead of log i

And then we see that how the corrosion potential as well as corrosion current density increases and our topic of course we are continuing our discussion on explanation of corrosion event on the basis of mixed potential theory and today we will consider a situation which talks about area effect of the cathodic and anodic component. So when we have a kind of electrochemical reaction like dissolution of active component we have already seen from the discussion in lecture 10 and 11.

That the exchange current density has got a huge implication on the rate of corrosion of the active component. And the exchange current density over the noble component in that galvanic coupling does play a huge role. We have shown an example like the exchange current density of hydrogen evolution on platinum and zinc surface. And then how the zinc corrosion rate increases many fold and also the E mix or the new corrosion potential moves up as compared to the situation where zinc is not galvanically connected to platinum.

Then we have solved one numerical problem now in this case we will see a situation where let's say one active component is connected to a galvanically connected to a noble component in a practical situation. And like copper and iron where iron rivet loses its strength if that rivet is used to join two copper plates and there one situation is of course the exchange current density over that cathodic opponent of that cathodic reaction could be high.

And at the same time area of the cathode in a situation where let's say the example what we have mentioned before that copper plate and iron rivet. The cathodic component area is much higher than the area of the anodic component when both are exposed to corrosive, so we need to discuss that part and will also try to solve one numerical problem and try to see how the corrosion rate has way less corrosion potential change. Now we have already seen this example let's draw this.

This example we have seen this is E in volt and of course we are talking about with reference to SHE. It is Standard Hydrogen Electrode. Now if platinum and zinc, we have considered now is not in the last class where this is the couple and we are talking about passive medium acid medium of certain pH depending on the pH, I can have equilibrium hydrogen and we have already seen that the corrosion rate, so now this is, so this is the combination.

So this is i zero hydrogen over zinc this is i zero hydrogen over platinum and this is nothing but i zero total = i zero hydrogen over zinc and + i zero hydrogen over platinum and this point is i zero zinc over zinc surface. And this is E equilibrium zinc. Now when we extend it so this becomes my new E mix and this was the corrosion rate earlier this is E corr when platinum not connected this is platinum connected.

When the corrosion rate also changes this is i corr = ia when platinum not there and this is i corr = ia equal when platinum is connected. So these are the differences we have seen this but both the cases this area was one centimeter square this was also one centimeter square that means the zinc this is for zinc this is for platinum, so that means equal area were galvanically connected. Now if area of the platinum increases in comparison to zinc so that means A platinum is more than A zinc.

So then what would happen. So let's say that we take 100 centimeter square of platinum and one centimeter square of zinc. Now this green line is for one centimeter square galvanic couple. So this particular line indicates platinum and zinc both at one centimeter square. So now we need to see what happens if we increase the platinum area hundred times as compared to zinc so this is the log i scale this is the log i and which is ampere per centimeter square.

Now if the Platinum surface is not changed it remains same the solution remains same all the conditions remain same, only change is the area of the platinum. So area of the Platinum increases so do we think that the exchange current density of hydrogen evolutions on the Platinum will change no it will not change it will remain same. So if it remains same, so then whether it is a 100 centimeter square area or 1 centimeter Square area, i zero would be always at the same point.

Always would be at this point that means the exchange current density, I am talking about density with the unit is ampere per centimeter square that will be same whether it is a one centimeter square. So i zero hydrogen over Platinum would remain same. So then if we try to see the effect of that area change over this E verses i plot that means the current density plot will not be able to express it properly or will not be able to do it.

So, then what would we like to do or would I what should we do, now let's see what happens if we consider the tafel equation i zero i by i zero this is valid for a or c and this is a or c and this i zero is corresponding a or c. a means anodic and c means cathodic. So I consider this to be a generalized equation i zero. We are saying that this i zero does not change and in fact if i zero does not change with the area then if the area we consider that line would also follow this particular track.

Because we are always considering current density. And then always will come across this point. So this particular that that means the addition of those i zero's also will be following this particular green track. So we will always come across this particular E mix and i corr which is current density remember this plot is about current density. You know how we attack this, so now if we try to modify this equation by considering the area so let's say I consider some area A.

So if I multiply area on both sides denominator as well as numerator so both side if I multiply so then equation this particular equation will turn out to be capital I by I zero so because we are multiplying the same area for both the current densities. So this equation would each should be equally valid. Now if we try to plot instead of log small i so that means if we try to plot log capital I instead of log small i, we will be able to understand that this particular corrosion event of the active component because of the increase of area of the cathodic part.

So in that case what happens the I zero so this and I zero hydrogen over platinum this is a capital I zero and small i zero they will be different because in case of, let's say i zero hydrogen over platinum if it is 10^{-5} ampere per centimeter square, so then I zero hydrogen over platinum of 1 centimeter square would be 10^{-5} ampere but, I zero hydrogen over platinum surface if it is 100 centimeter square it will be 10^{-3} ampere.

So then I could see that this particular point if this plot becomes instead of small i if it is capital I this shifts to the right and interestingly that will explain the rapid corrosion of the active component when we connect active metal with a noble metal and the noble metal area is higher than the active component. So let's stop here we will continue our discussion on this particular issue in our next lecture, thank you very much.