Corrosion Part - II
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Lecture - 11
Effect of Exchange Current Density on Corrosion Rate of an Active Metal

Hello everyone.

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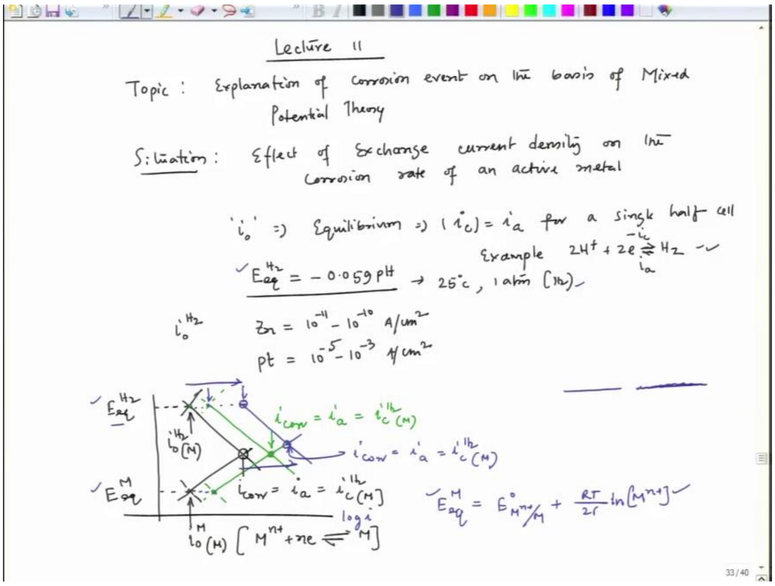

Lecture 11

Topic : Explanation of corrosion event on the basis of Mixed Potential Theory

Situation : Effect of Exchange current density on the corrosion rate of an active metal

'i_0' ⇒ Equilibrium ⇒ $(i_c) = i_a$ for a single half cell

Example $2H^+ + 2e \underset{i_a}{\overset{i_c}{\rightleftharpoons}} H_2$

$E_{eq}^{H_2} = -0.059\,pH$ → 25°C, 1 atm (H_2)

$i_0^{H_2}$ $Zn = 10^{-11} - 10^{-10}\ A/cm^2$

$pt = 10^{-5} - 10^{-3}\ A/cm^2$

$E_{eq}^{M} = E^{0}_{M^{n+}/M} + \frac{RT}{nF}\ln[M^{n+}]$

Let’s start lecture 11 and topic we will continue explanation of corrosion event on the basis of mixed potential. Our theory in the last lecture we thought that we will be able to complete two situations. One was effect of when a electrochemical process that means corrosion of zinc is taking place in HCl rather impure HCl with dissolved oxygen. So, that case we can have 3 catalytic reaction and 1 anodic reaction.

And we could see different situations different effects on the basis of mix potential theory. So here, so we will consider effect of exchange current density on the corrosion rate of an active metal. Now, we know that this exchange current density is the measure of equilibrium. Since ic equal to ia for our single half cell. For example, H2 or rather

$$2H^+ + 2e = H_2$$

So this is for a single half cell process.

So this is my ic and this is my ia opposite reaction. And then we have E equilibrium of hydrogen, which is nothing but 0.059 pH. And here we consider 25 degrees Celsius, 1 atmosphere pressure for hydrogen gas. So, this is when hydrogen gas is at one atmosphere pressure. Now, this i zero if we consider for hydrogen evolution reaction on different metals let's say, we consider zinc and we consider platinum.

Generally, here the value is around 10^{-11} to 10^{-10} ampere per centimetres square. And here its 10^{-4} to 10^{-3} ampere per centimetre square. So, this values or maybe it might go to minus 5 levels. So the next class I will show some tables and its also available in internet you can just look through, what are the values of exchange current density of hydrogen evolution on different surfaces, metal surfaces in acid medium.

So, similarly other catholic reactions or anodic reactions or any half cell reactions i zero can have different values. Now, for example, if I consider a situation like metal some metal it has some extreme current density see if the situation is like this. Let's say this is i zero of metal over metal surface. And here

$$M^{n+} + ne = M$$

and this reaction is considered and this is my E equilibrium of that metal.

And similarly, if I consider E equilibrium of hydrogen if I can see the hydrogen evolution reaction on that metal surface, so, I will have i zero hydrogen over metal surface and that time we are considering hydrogen evolution reaction or the half cell reaction is

$$2H^{+} + 2e = H_2$$

and the corrosion rate is here. So, this is i corr equal to ia equal to ic hydrogen over metal. Now, there could be in a different acid.

This is in one acid and a different acid or the if we change the surface nature of that metal, we can have a situation like this, here the exchange current density can go to this and the exchange current density of hydrogen can remain here or it can change here, let's say if changes here. And if we maintain the tafel flow for about the reactions same, then it will go like this.

So, this becomes my i corr equal to ia of the metal equal to ic hydrogen over that metal. Now, it may happen that the influence of that metal surface on the hydrogen evolution reaction could be such that this one comes here, but this one stays here. So, that time I will extend this line.

So, my corrosion rate will be here. i corr equal to ia equal to ic hydrogen over metal surface. Now, these all three or three independent effects.

So, here all the time, this equilibrium potential remains fixed. And here also equilibrium potential of the metal remains fixed, because we are considering the same amount of metal ion and as well as same amount of or the same pH value. So, here it can only remain like this provided H2 is maintained at one atmosphere, temperature is 25 degrees Celsius and everywhere the pH is same all the acids, then this E equilibrium value will not change.

Because this equation says that these value cannot change and here also the metal ion concentration remains fixed. So, this this particular equilibrium of that metal will not change because here

$$E_{eq}^{M} = E_{M^{ne}/M}^{o} + \frac{RT}{nF} ln\,[M^{n+}]$$

and so this is the concentration of metal ion because M is nothing but the pure metal. So, that time if this remain same for both all the cases, this will also remain same,

But since we are changing the exchange current density so, here we have changed here we have changed the same hydrogen evolution reaction is taking place on the metal surface of different texture or nature. But the same metal we can change the texture of that particular metal surface. That means I am talking about the physical texture. So, or the, for example of a metal surfaces is like this we can have a small perturbation on the metal surface like this.

So, we can have a different i zero. So, like that way we can have change in the corrosion rate. So, you could see that if the exchange current density of hydrogen evolution reaction increases like this. So the corrosion rate also increases like this. And remember, this is in log i scale. So it’s an order of magnitude increase of the corrosion rate. Now, this is on the same metal.

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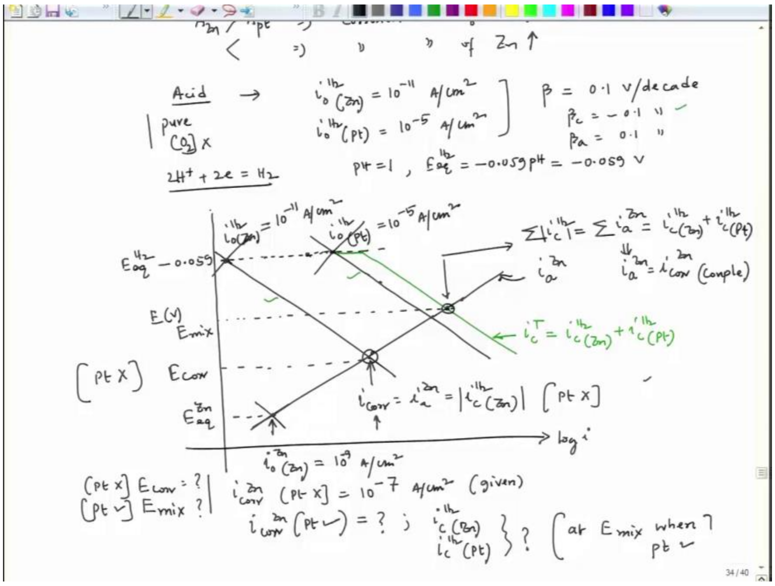

But many times we can have a situation for example, we can have a couple between this particular galvanic coupling where both have same area. So this is extremely important. Will feel it around that if the area of the this galvanic area of the individual component of that galvanic couple are different, the corrosion rate of the zinc of zinc or the active component will change. We will see that if the area of the Platinum.

This area let's say a platinum and this area is a zinc in case this is greater than this that case corrosion rate of zinc decreases. If a platinum or if it's this corrosion rate of zinc increases. So, we will see that effect. So that's what we are initially considering a situation where both have same area so that is cathodic as well as anodic reactions are finding a anodic reaction that is taking place on zinc.

So area effect we are not considering here. So, now, if they are dipped in acid. Okay. And if we assume that i zero hydrogen evolution reaction on zinc surface is tends to the power minus 11 ampere per centimetre square and i zero of hydrogen evolution reaction on platinum is equal 10^{-5} ampere per centimetre square. So, these are some arbitrary values I am considering. These are though arbitrarily taken but at least we know that the hydrogen evolution reaction on zinc surface in acid is much lower than the hydrogen evolution reaction.

Exchange current sorry exchange current density of hydrogen evolution reaction on zinc surface is much lower than the exchange current density of hydrogen evolution reaction on platinum. So, we are maintaining that difference by assuming these two values. Now, what would happen and if we assume that beta is always 0.1 volt per decade of current density decade of course, beta c would be negative 0.1 volt per decade and beta a would be 0.1 volt per decade.

And these values are all the time they are similar in all the reactions that are possible and this acid is pure as well as no dissolved oxygen. So, that case only one cathodic reaction which is

$$2H^{+} + 2e = H_2$$

This is possible. Now, we have to see the effect of that galvanic coupling as well as the effect of that exchange current density. Now, let’s draw E versus log i okay will have zinc E equilibrium.

And i zero, zinc over zinc surface, I assume it to be 10 to the power let assume it to be 10^{-9} ampere per centimetre square. And if we consider pH to be one, if we consider pH equal to 1. So, E equilibrium hydrogen is equal to minus 0.059 pH equal to minus 0.059 volt. So, this is minus 0.059 equilibrium hydrogen. Now the hydrogen evolution reaction on the let me shift this particular axis a bit. Okay.

So, this point will lie left to this point. So, this is i zero hydrogen over zinc equal to 10^{-11} ampere per centimetre square and on the platinum surface also it will have this hydrogen evolution reaction will take place. So, potential will not change because pH is maintained same for both this pH of the solution is always one. So, now its hydrogen evolution reaction on Platinum surface.

So, this point or I can draw further right. We have to maintain that log scale, log scale ratios. So, this is i zero hydrogen over platinum equal to 10^{-5} ampere centimetre square. Now, it will go like this. Now, I will just change the slope little bit. So, this is for a situation where there is only one zinc is dissolved or zinc is dipped in the acid, but when this couple is dipped in the acid. So, hydrogen evolution reaction also takes place on platinum surface.

Now, these two reactions this one this one and this one both have beta to be 10 to the power 0.1 volt per decade that means the cathodic tafel slope and they are parallel and since there are these two catalytic reactions are taking so same cathodic reactions are taking place over the over zinc as well as Platinum surface. And as for the mix potential theory we have to add them and then take a log.

So, we will find that this new line which is the additional line. Let me draw it to the green colour, so that will be we just added up and then the parallel line will go like this. So the green line is ic total equal to ic hydrogen evolution over zinc + ic hydrogen over Platinum equal to ia zinc. Sorry, this line is this and this particular line belongs to ia zinc. Now I could see that as per the mixed potential this point is the E mix.

Now and here we maintain ic hydrogen equal to ia zinc equal to ic hydrogen over zinc surface + ic hydrogen over Platinum surface. Now, we could see that if Platinum is not there only zinc is present. So, that case this will be my i corr equal to ia zinc equal to ic hydrogen over zinc surface of course, this is the mode because that negative sign is nothing but the current this ic is flowing opposite to ia.

And this would have been my E corr and the condition is when Platinum is not present and this is the condition when Platinum is not present. Now, we could see that since the exchange current density of hydrogen evolution on Platinum surface is much higher than the hydrogen evolution of hydrogen evolution exchange current density on zinc surface, I could see that the corrosion rate has gone up from this value to which is ia zinc equal to icorr zinc for couple situation other galvanic couple situation.

So, it’s very clear that if we connect to if we connect any structural component to a noble component and the exchange current density of the noble component of that cathodic reaction that is taking place in that particular equilibrium in that particular electro chemical system. I will have much higher corrosion rate of that active component. So, this particular diagram explains the corrosion event taking place.

When exchange current density over the noble component in a galvanic couple is much higher in the condition of course. So, let’s solve this particular problem with the following data. So, these are the data that are available. So, whether we can get the value of, so our solution would be what we need E mix we need to find out E corr when Platinum not present, when Platinum present.

Now, if and the value i corr is given zinc when Platinum is not present is equal to 10^{-7} ampere per centimetre square, this is arbitrarily chosen value. Now can we get this is the value given.

So, these two we have to calculate. Another thing we have to calculate is i corr zinc, when Platinum is present. This is we have to find out and individually we have to find out ic hydrogen over zinc surface as well as ic hydrogen over Platinum surface.

We have to find out at E mix when Platinum is present, so, we have to solve this. So, in order to solve this we have to go step by step.

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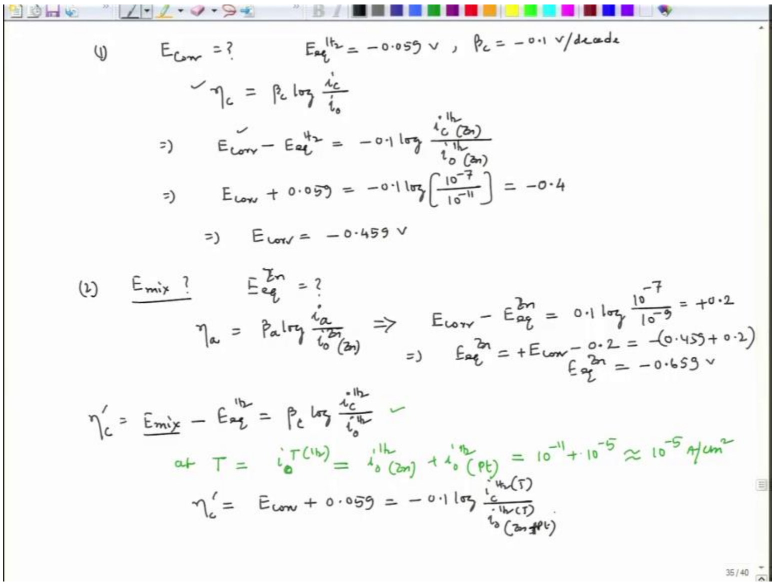

(1) $E_{corr} = ?$ $E_{eq}^{H_2} = -0.059\ V$, $\beta_c = -0.1\ V/decade$

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

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

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

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

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

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

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

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

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

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

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

First let’s find out E corr. So, in this case we know that E equilibrium hydrogen equal to 0.059 volt, since its pH 1, beta c equal to minus 0.1 volt per decade. So

$$\eta_c = \beta_c log \frac{i_c^{H_2}}{i_o^{H_2}}$$

So here neeta c is nothing but E corr minus equilibrium hydrogen equal to 0.1 log ic hydrogen over zinc surface divided by i zero hydrogen zinc surface.

Now, we know all those values except this. So, let’s put them E corr + 0.059 equal to 0.1 log 10^{-7} divided by 10^{-11}. Since at this point ic hydrogen evolution over zinc surfaces is equal to i corr. So, if the over voltage is this much, so this over voltage is calculated here. So equal to, this becomes 0.4. So, E corr equal to minus 459 volt. Now, we can calculate in order to calculate E mix. This is stage 1, 1, 2. we have to calculate E mix.

For that we need to calculate first E equilibrium zinc. Let’s calculate this is also easy, because we have to consider over voltage this neeta a. So, this over voltage is beta a log of ia i zero zinc over zinc surface. So, then it becomes E corr minus E equilibrium zinc equal to 0.1 log 10^{-7} divided by 10^{-9} equal to minus 0.2, so, then equilibrium zinc equal to E corr minus 0.2 okay. So this would be like this. So sorry this would be plus.

So this becomes 0.459 + 0.2 equal to 0.659. But now interestingly we have to find out this point that means E mix where to find out. So if we see E mix let's say some value. So E mix minus E equilibrium hydrogen. Let's say equilibrium hydrogen equal to I can write this equation equal to neeta c prime equal to beta c log ic hydrogen over i zero hydrogen. Now, if I say this I am now considering over voltage in the blue colour is green colour.

I am considering this over voltage. Now, can I find out this point? So, here this is the condition neeta c. And since this is a pair of this green line is a parallel line for this So, that means slope for the green line is same as a slow for the black line that the cathodic polarization line for hydrogen evolution. So, I can find out this particular point, which is let's say the T point if I try to find out the T point. So, the T at T, I see that ic hydrogen or ic total if I put i zero total for hydrogen reaction equal to i zero hydrogen over zinc + i zero hydrogen over platinum.

So equal to 10^{-11} + 10^{-5} which we can consider as 10^{-5} ampere centimetre square. So, once we know this, I can put it up here so this

$$\eta_c = E_{corr} + 0.059 = \beta_c log\ (10^{-5})$$

Some ic hydrogen total divided by i zero hydrogen total over zinc as well as Platinum surface. So I am just adding + sign here does to indicate that this is the total value of exchange current initiatives.

At this point I am talking about. So, the point is nothing but ic hydrogen or the way we are notifying i zero hydrogen. T means total. So, this let's stop here. So, you try to solve this problem. Once you know this, then you have to consider another equation which is nothing but this over voltage with this a prime and try to solve these two equations we are generating and try to see whether you get E mix. However, we will continue this problem and solve completely in our next lecture. Let's stop here. Thank you very much.