Corrosion- Part I
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Lecture – 39
Understanding of mixed potential theory through the case studies and events of corrosion-I

Let us start the Lecture 39.

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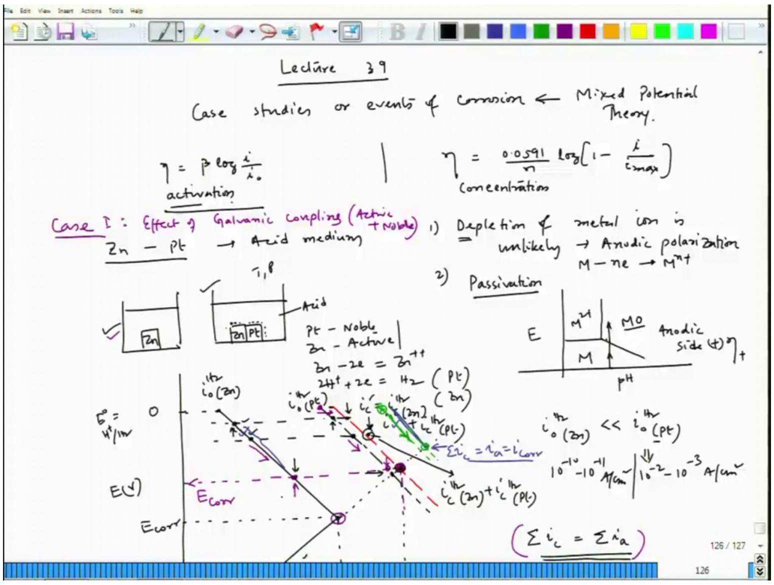

Lecture 39

Case studies or events of corrosion ← Mixed Potential Theory.

$\eta = \beta \log \frac{i}{i_0}$ activation | $\eta = \frac{0.0591}{n} \log\left[1 - \frac{i}{i_{max}}\right]$ concentration

Case I : Effect of Galvanic coupling (Active + Noble)
Zn – Pt → Acid medium

1) Depletion of metal ion is unlikely → Anodic polarization
$M - ne \rightarrow M^{n+}$

2) Passivation

Pt – Noble
Zn – Active

$Zn - 2e = Zn^{++}$
$2H^+ + 2e = H_2$ (Pt) (Zn)

$i_0^{H_2}(Zn) \ll i_0^{H_2}(Pt)$
$10^{-10} - 10^{-11}$ A/cm² | $10^{-2} - 10^{-3}$ A/cm²

$(\Sigma i_c = \Sigma i_a)$

So, we are left with two more lectures and in these two lectures remaining lectures we will consider some of the case studies or where corrosion happens in case of metallic object and we will try to understand those corrosion events with the help of mixed potential theory.

And in fact, in the last lecture we saw how this mixed potential theory can explain the corrosion event of in case of zinc in HCL. And then we try to draw Evans diagram which is basically plot between potential and log of current density.

And then we try to consider the activation polarization part only in the beginning and later on we will also see some more examples considering the concentration polarization. In this particular so that means, we will look at some of the case studies or events of corrosion considering mixed potential theory. We will try to understand through this theory; as I have mentioned that we will be concentrating on the activation polarization part initially, and try to draw events diagram, but later on also will look at concentration polarization part also.

So, we have two situations one is eta equal to beta log i by i 0, another one is eta equal to 0.0591 n log 1 minus i by i max. So, these are this is basically concentration, polarization this is activation, and in the concentration polarization we would consider cathodic polarization.

Now in this particular junction we would like to mention that we would consider cathodic polarization not the anodic polarization. Because the anodic polarization event is very uncommon there are two possible reasons one is of course, when you consider anodic polarization there should be depletion of metal ions in the interface around that interface due to corrosion event.

But since it is anodic polarization, so metal is going into iron form ah. So, there would be enough supply of metal for the formation of metal ion. So, the depletion of metal ion is unlikely so; that means, depletion is unlikely and second part is when it is during of course, during anodic polarization. Since during anodic polarization is actually going to metal ion. In the second part during anodic polarization there could be a possibility of passivation. This passivation can be explained on the basis of Pourbaix diagram.

So, if you let us say some metal E versus log i if I consider the Pourbaix diagram let us say it looks like this. And this is metal oxide part, this is metal ion part and this is metal part. Let us say if I am operating at this p H sorry this is not log i axis this is p H axis. So, if I operate at this p H axis as I go upward; that means, if I go on the anodic side, or the positive side eta is positive. So, then initially it is in the metal part and then kindly finally, it goes to metal oxide part. So, then you have actually metal oxide forming on the metal surface and which can lead to passivation.

So, at a large over voltage or positive over voltage there could be possibility of passivation also. But the main reason is this depletion of metal line is unlikely in case of anodic polarization. And this concentration polarization happens due to depletion of concentration of ions, but in this case it is unlikely that is at anodic polarization we would not be able to consider we will see some of the examples considering cathodic polarization.

And of course, in the beginning we will consider an activation polarization. In the last lecture at the end we started talking on the effect of galvanic coupling of a metal object which is active with a noble component. And that is what we started looking at if I see the last part we started looking at combination of zinc and platinum in acid media.

So, now, you have two beaker and in one beaker you have a block of zinc, another beaker you have as block of zinc which is connected to block of platinum. And they have the same area, which are exposed to the acid medium, this is acid medium, same condition, temperature, pressure both the cases.

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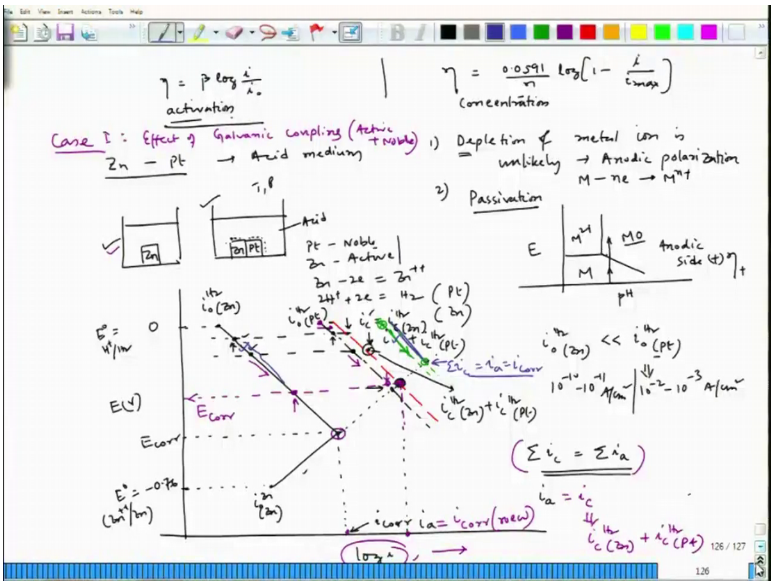

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$2H^+ + 2e = H_2$ (Pt) (Zn)

$i_0^{H_2}(Zn) << i_0^{H_2}(Pt)$

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$\Sigma i_c = i_a = i_{corr}$

$(\Sigma i_c = \Sigma i_a)$

$i_a = i_c$

$\Downarrow$

$i_c^{H_2}(Zn) + i_c^{H_2}(Pt)$

In that case we have to draw Evans diagram. And let us draw the Evans diagram, log i this is E, and we start with zinc and there because the anodic reaction is zinc dissolution and here platinum is noble, and zinc is active component. The zinc dissolution is anodic reaction, and hydrogen evolution is the cathodic reaction when we have mixed potential theory to be active.

Now, it is this is basically i 0 for H 2 gas evolution. Let us say this is on zinc surface in this case this is the case what we are considering now. This is 0 equal to and this E is equal to minus 0.76 volt. And this is for zinc plus plus zinc and this is for hydrogen H 2. And it is lying here for zinc this is i 0 for zinc on zinc surface, i 0 for zinc on zinc surface.

And then we see mix potential this is my E corr and this particular current this particular current is i corr of zinc. When there is no galvanic coupling between zinc and noble component which is platinum. Now once we have hydrogen evolution on platinum surface as we know that i 0 of hydrogen on zinc is less than equal to less than less than equal to i 0 of hydrogen evolution on platinum.

Since this value is close to 10 to the power minus 2, 10 to the power minus 3 ampere per centimeter square. And here it is 10 to the power minus 10, to 10 to the power minus 11 ampere per centimeter square, so this is the difference in their values. When we have this particular let us say this particular situation now. Now hydrogen evolution would also take place on zinc surface as well as platinum surface and since platinum is noble.

So, platinum will act as cathode and zinc will act as anode, but hydrogen evolution can take place on both the surfaces. Now if I consider hydrogen evolution on platinum surface it is exchange current density is pretty high at this point. So, this is i 0 hydrogen on platinum surface and E 0 of course, it would be same 0. Because we are considering hydrogen evolution and then it would also have it is own cathodic polarization and it is cutting here.

Now, question is would this be my new over new mix potential no because as per the mixed potential theory we see that there will be a possibility of existence of a mixed potential. Where there should not be no net current flow in this in the system. Now in order to have this second criteria to be criterion to be fulfilled. We must have summation of i c should be equal to summation of i a.

So; that means, in the scale in the system we must have to see that total cathodic current density is equal to total anodic current density. Now here we have two sets of cathodic reactions; one is on zinc surface, another is on platinum surface. And one set of anodic reaction. So, this is two sets of cathodic and one sets of anodic. Here I am considering two sets means this is happening on platinum surface, this is happening on zinc surface. But zinc is dissolving from the zinc surface only platinum would not dissolve because it is a cathodic component.

Now that case since there are two cathodic reactions in order to fulfill this criteria that total cathodic current density should be equal to total anodic current density. I should add up these two polarizations. Now in order to add up since it is a log scale. So, it will go at this point because I have to add at every potential every potential I should add this one and this one. These two current densities and get to the new current density which is this one.

Similarly, here we have to add this point as well as this point to get to the new current density, which is this point which is new ic which is ic. Let us say this is ic prime equal to ic hydrogen on zinc plus ic hydrogen on platinum and at this point it is basically ic hydrogen on zinc plus ic hydrogen on platinum. So, like that we have to add up all the cathodic reactions. Now if we add up then if we connect them then we will see that the added part would follow the red line.

And now if I look at this point this point here I have i a which is this one and if I try to see the total ic. So, this is these are the two points where I could see that at this point the circle point i c i c equal to ia and this ic has two parts, one is this ic another one is this ic. So, ic on hydrogen evolution on zinc surface plus ic hydrogen evolution on platinum surface. Then I could see that at this point at this point, I have two hypothesis of mixed potential theory are met first one is it is reaching to a mixed potential.

And then at that potential I could see that this condition is fulfilled; that means, when this condition is fulfilled. So, since ic and ia they are flowing opposite directions and of equal magnitude there will not be no net current density. So, now this particular potential would be new E corr and corresponding current density which is i a is basically i corr new. Now when there were no platinum connection between zinc there. There was no connection between zinc and platinum only this case I had current density for the corrosion is this one this particular current density was the corrosion current density.

But as we have connected to platinum which is a noble component I could see that the current density for the corrosion has gone up enormously. Because you remember this is a log scale and also one more thing since it is a log scale value. So, when you add this particular polarization with this particular polarization that the current densities for the cathodic reactions it will not shift log wider distance.

Because the scale has to be maintained that is what if there is a small increase on the right side of this point. So, that small increase is coming because of this log scale nature of this x axis.

Now you could see that this case one when we have connection of an active component with a noble component. The corrosion rate of the active component goes up enormously this is the explanation why it goes up with the help of Evans diagram. Now let us look at a second case this is case one I would say this is case one. Case one is effect of galvanic coupling and with active plus noble this is the galvanic coupling considering.

But remember when we have seen this galvanic coupling we have said that that they have the similar same area which is exposed to the acid medium. The area is not changing, the galvanic that active component has got the some area let us say one centimeter square then platinum would also have the same area.

Now, interestingly if we have another metal let us say if it is connected to another component in let us say instead of platinum we add platinized platinum that case the corrosion rate would further increase. In that time what happens? This particular current density would shift to switch to some other current density let us say at this point.

Because current density exchange current density for hydrogen evolution on platinized platina is higher than that on say plane platinum surface. So, again further if I follow the same way what we have done in case of platinum this one would be the new mix potential and we could see that the corrosion current density has gone up where this line indicates the addition of this current density.

The current density following this particular polarization of hydrogen evolution on zinc surface and hydrogen evolution on platinized platina following this particular arrowhead. If I see the green arrow head this particular polarization so that this particular line this blue line is nothing, but the addition of this one and this one. So, then only at this point I could see i c summation equal to i a is equal to i corr. So, that way we have discussion or the explanation of increase in corrosion rate when we combine an active component with a noble component.

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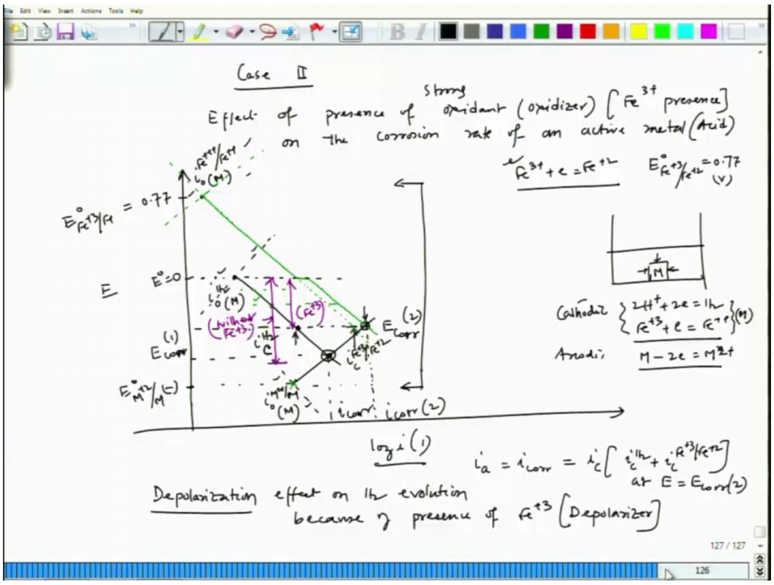

Case II

Effect of presence of strong oxidant (oxidizer) [Fe^{3+} presence] on the corrosion rate of an active metal (Acid)

$Fe^{3+} + e = Fe^{+2}$ $E^{\circ}_{Fe^{+3}/Fe^{+2}} = 0.77$ (V)

Cathodic $\left\{ \begin{array}{l} 2H^{+} + 2e = H_2 \\ Fe^{+3} + e = Fe^{+2} \end{array} \right\}$ (M)

Anodic $M - 2e = M^{2+}$

$i_a = i_{corr} = i_c\left[i_c^{H_2} + i_c^{Fe^{+3}/Fe^{+2}} \right]$ at $E = E_{corr}(2)$

Depolarization effect on H_2 evolution because of presence of Fe^{+3} [Depolarizer]

Now, let us consider the second case study case two where we consider the effect of presence of oxidant or we call it oxidizer. And that should be strong oxidizer for example F e 3 plus presence on the corrosion rate of active metal. Now again let us draw Evans diagram.

Now whenever we have let us say this is an acid medium. So, if it is an acid medium we have hydrogen evolution reaction E equal to E 0 equal to 0 here. And let us say this is my E 0 of this some value. Let the sum this value is in the minus direction now they will have their own mix potential, this is my mix potential. Now F e plus 3 plus e equal to F e plus 2 this has got a very large E 0 this is almost about close to 0.77 volt if I remember correctly.

Now, if I try to see this is positive 0.77 equal to E 0 F e plus 3 F e. So, let us say it is position is here this is i 0 F e plus 3, F e plus plus on metal surface. Because this is in the ionic form in the solution, so you have a system like this, this is a acid this is the metal. And on top of it I have hydrogen cathodic reaction as well as this reduction reaction.

So, and dissolution reaction is 2 plus, this is my anodic reaction and these two are cathodic reaction. So, now you could see that this entire corrosion process is divided into a one anodic reaction and two cathodic reactions. And both these cathodic reactions are taking place on metal surface. So, that is what we are considering i 0 for F e plus 3 to F e plus 2 on the metal surface. So, it would have it is own activation polarization cathodic as well as anodic.

Now, since this particular point which is i 0 M 2 plus M on metal surface and hydrogen this is i 0 hydrogen on metal surface. Since these two potentials are lying below this potential, so then everything will be coming between these two extreme.

But mixed potential would come in between these two extreme, depending on the situation where I have the (Refer Time: 22:38) cathodic current density is equal to the net anodic current density. So, that particular point we have to find out. So, now without this F e plus 3 presence; I would have gotten this particular point to be my new mixed potential and corresponding corrosion current density. This is i corr, this is E corr 1, let us say this is 1.

Now once we have this presence of F e plus 3 it is a strong oxidant, that means, it will have a very large very high tendency to get reduced and there would be strong cathodic polarization. Because it is in very strong cathodic reaction and remember all this individual redox reactions, or half cell reactions would have their own anodic as well as cathodic polarization.

So, this is anodic polarization for hydrogen evolution, this is cathodic polarization for methyl and this is the cathodic as well as anodic polarization for F e plus 3 to F e plus 2. So, now it would come like this and once it reaches to this particular plane immediately it is seeing that there is another cathodic reactions which is hydrogen evolution reactions.

So, now as per our concept in the previous example we have add up the total cathodic current densities. So, now we have to add up that total current densities, so had it gone through the actual path it should have been like this.

But since there is one more cathodic reaction which is hydrogen evolution it would add up. Since this is in log scale, so this adding will not go very far. So, it will be small increment as per the value at different potentials. So, then we add up and we get to this and then if we extend it we could see that at this point which is new E corr let us say condition 2 where this is my i corr case 2. And then if we extend this particular line I have 2 current densities cathodic current densities these two.

So, now let us say this is i H 2 on metal surface, or rather I say i H 2 cap i c of H 2 and this is i c F e plus 3 F e plus 2 and at this point I could see that i a equal to i corr equal to i c, and this i c is basically addition of i c H 2 plus i c F e plus 3 F e plus 2 at E equal to E corr to the condition 2.

So, then we could see that again the corrosion rate of the metal is going up and since it is a log scale. So, this corrosion rate increment of that metal is very very high. And interestingly one more thing if you look at this carefully had there been no F e plus 3, the corrosion rate would have been here. And this should have been my the rate of hydrogen evolution on metal surface.

But once we have F e plus 3 the corrosion rate is increasing, but the rate of hydrogen evolution on zinc surface is decreasing as compared to the rate what it should have been there without F e plus 3 presences in the solution. So, then you could see that the metal ion on the metal hydrogen bubbling rate bubble formation is reduced somewhat.

And this reduction is coming because of depolarization effect what is depolarization? Depolarization means what should have been the polarization. Now that polarization amount or the over voltage has reduced had it been only M and hydrogen reductions metal riddle dissolution and hydrogen evolution reactions my over voltage would have been this much.

Now with the presence of F e plus 3 the over voltage for hydrogen evolution is this much. So, this is when F e plus 3 is presents and this is without F e plus 3. So, we could see that the over voltage for hydrogen evolution reaction has gone down or decrease due to the presence of F e plus 3, that particular effect we call it depolarization effect on hydrogen evolution because of presence of F e plus 3.

So that is what F e plus 3 is called depolarizer. And in fact, the same effect was seen in this case also you could see that when platinum when the platinum is connected hydrogen evolution rate on the zinc surface is reducing.

So, platinum is also acting as a depolarization for hydrogen evolution on zinc surface. So, now we have seen two examples case 1 when we connect active component with a noble component. And the second case when we have a presence of strong oxidizer and both the cases I could see that the corrosion rate of no active metal is increasing to a great extent. So, let us stop here we will continue our discussion considering few more case studies.

Thank you very much.