Corrosion Part - II

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Lecture - 18
Corrosion of metals when cathodic protection is concentration controlled

Hello everyone let's begin lecture 18 the topic of course the explanation of corrosion events on the basis of mixed potential theory. We have talked about cathodic protection and We have tried to contact I compared the mixed potential theory of two separate modes of cathodic protection one is impressed current cathodic protection as well as sacrificial anode. There are lot more into the cathodic protection.

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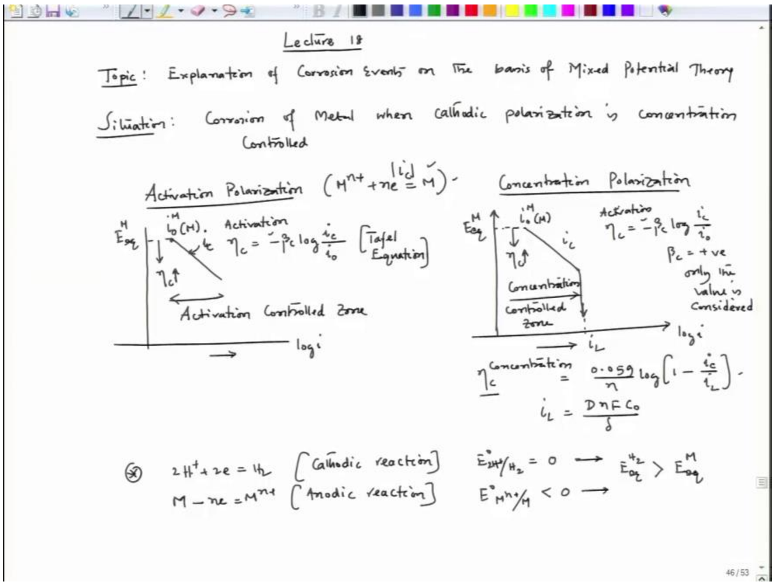

Lecture 18

Topic: Explanation of Corrosion Events on The basis of Mixed Potential Theory

Situation: Corrosion of Metal when cathodic polarization is concentration Controlled

Activation Polarization $\left(M^{n+} + ne \overset{i_c}{=} M\right)$.

Activation $\eta_c = -\beta_c \log \frac{i_c}{i_0}$ [Tafel Equation]

Concentration Polarization

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

β_c = +ve only the value is considered

$$\eta_c^{\text{Concentration}} = \frac{0.059}{n} \log\left[1 - \frac{i_c}{i_L}\right].$$

$$i_L = \frac{DnFC_0}{\delta}$$

⊗ $2H^+ + 2e = H_2$ [Cathodic reaction] $E^\circ_{2H^+/H_2} = 0 \longrightarrow E^{H_2}_{eq} > E^M_{eq}$

$M - ne = M^{n+}$ [Anodic reaction] $E^\circ_{M^{n+}/M} < 0 \longrightarrow$

But will not talk at this particular junction because we are our main interest is to see the mixed potential theory to analyse the corrosion events. Now today we will start another will take another situation, the situation where we consider cathode, concentration polarization and then let's see how the concentration polarization effects corrosion rate of metals. So the situation corrosion of metal when cathodic polarization is concentration controlled.

We have already discussed in part 1 corrosion as well as in the beginning of short review on two types of polarization one is activation polarization and the concentration polarization. In case of activation polarization if we try to see the, for example for a cathodic reaction let's say

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

If we try to see ic variation this is E equilibrium of cathodic reaction this is i zero of cathodic reaction on metal surface so here we are considering the cathodic reaction.

The same cathodic reaction so this is I could say that instead of c, i can write M now if this is the point I can have activation polarization which is decided by i zero. So this equation which is the Tafel equation. This is the controlling factor so we and this axis is log i. So the potential drops due to cathodic polarization we are talking about cathodic polarization and this line is nothing but variation of ic.

Now when it is concentration polarization so that time I will have the effect of concentration polarization at a higher current density this is also log scale and in this case again all the factors are same equilibrium M. This is i zero M over M surface. Now if I try to see the polarization so initially it will be cathodic polarized cathodic polarization is activation controlled and then at a higher potential higher cathodic over voltage as well as higher cathodic current density.

Because I could see that the current density is in increasing this way and also over voltage is gradually increasing in both the situation. So this is neeta c increasing that means further and further it is going downwards in the potential axis. Now as we go from a low current density to higher current density I am talking about ic, my governing equation initially it will be of course

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

Even I can at that time since I am putting - sign so that time beta c is taken as a little mode value so that means only the slope value i am considering there i am not taking negative sign so this negative if I put negative sign here that suggests that beta c is positive. So only the value is considered. Now after that we could see we have already observed that neeta c when it is concentration controlled the governing equation becomes

$$\eta_c = \frac{0.059}{n} log\left(1 - \frac{i_c}{i_L}\right)$$

So I could say ic by iL.

This becomes my equation and I could see that when ic reaches iL, neeta c which is the concentration over voltage becomes infinite. So I can say that this is activation controlled and this is also activation but once we go to a very high current density it will take a flat depth. So this point becomes iL and iL = iL can be expressed as which is diffusivity of the ionic species in this in that electrolyte, n is number of electrons participating in this reaction, F is 1 Faraday and c zero is the composition bulk composition of that metal ion.

And delta is the boundary layer thickness or the diffusion layer thickness. Now there could be a situation that the cathodic reaction is in the activation control zone and there could be situation that cathodic reaction could be concentration control zone. So one case the cathodic polarization within this zone that is always in activation control zone and another case the cathodic polarization can reach to this which is concentration controlled job.

So these two cases the corrosion pattern of an active metal or other active metal compared to that cathodic reaction can be different. So that is the situation we are talking about corrosion of metal when cathodic polarization is concentration control. So till now whatever situations we have considered all are within this activation control zone and we could see that if all the situations that cathodic reaction as well as anodic reactions are following Tafel equations that means both are activation control.

Now if we try to see the concentration control defect that concentration polarization effect on the corrosion of metal the situation could be very different. Now let's talk about some metal an arbitrary metal let's say M we consider a situation like hydrogen evolution with so this is going to be my cathodic reaction and some metal M which is active compared to hydrogen evolution I will say that I will talk about that part

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

This becomes my anodic reaction.

And here E zero of H2 = zero. So E node rather E node of M^{n+}/M is less than zero and of course in the solution and electrolyte I can have a situation where E equilibrium depending on the pH value of that solution, hydrogen evolution can be greater than E equilibrium of metal. In that situation of course hydrogen evolution will be the cathodic reaction and metal dissolution will be the anodic reaction. So let's see what would happen there.

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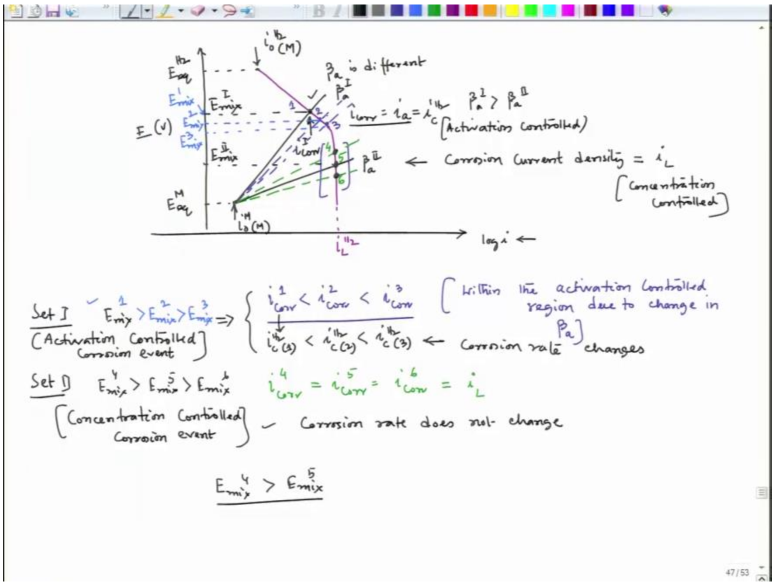

$i_{corr} = i_a = i_c^{H_2}$ $\beta_a^{I} > \beta_a^{II}$ [Activation controlled)

← Corrosion current density $= i_L$ [Concentration controlled]

Set I $E_{mix}^{1} > E_{mix}^{2} > E_{mix}^{3} \Rightarrow \left\{ \begin{array}{l} i_{corr}^{1} < i_{corr}^{2} < i_{corr}^{3} \\ i_{c(1)}^{H_2} < i_{c(2)}^{H_2} < i_{c(3)}^{H_2} \end{array} \right.$ [Within the activation controlled region due to change in β_a]

[Activation Controlled Corrosion event]

← Corrosion rate changes

Set II $E_{mix}^{4} > E_{mix}^{5} > E_{mix}^{6}$ $i_{corr}^{4} = i_{corr}^{5} = i_{corr}^{6} = i_L$

[Concentration Controlled Corrosion event] ✓ Corrosion rate does not change

$E_{mix}^{4} > E_{mix}^{5}$

Now if I try to plot mix potential theory. Again this is E volt and this is log i. Depending on the pH value this is E equilibrium of hydrogen and let's say this is i zero of hydrogen over that metal surface. And this particular point is E equilibrium of that metal and this is i zero of metal on metal surface. There could be two situations. Let's see first draw both cathodic polarization that means one is activation control another one is concentration controlled.

One is cathodic concentration control if we cathode if we see activation control it starts with activation control. So this is my activation control and then at a very high cathodic current density I will reach iL. So I will have this line which is nothing but iL of hydrogen depending on the pH of the solution. Now this metal is guided by activation controlled so there could be two situations.

One situation is this one, another situation could be this one. Now when can we have this two situation this two situations can be possible if beta a is different so in this case beta a1 and this is beta a2 which are basically the Tafel slope and beta a1 > beta a2 the Tafel slope of the anodic reaction. Now in one case it is cutting in the activation zone the another case it is cutting in the concentration control job now when it is cutting in the concentration control zone the corrosion rate in this situation the corrosion current density is nothing but iL.

But here the corrosion current density so this becomes my i corr 1, so here this is E mix 1 and this is E mix 2. One and two these are two situations. When beta a are different in those two situations in this case i corr = ia okay. So I can denote those of course it will be same as ic hydrogen but in this case ic hydrogen is activation controlled and in this case ic is nothing but concentration controlled.

So i could get two different situations but when you see this particular incident now let’s say if i follow this one let’s say okay if i change the beta A little bit by doing something some metal surface modification or something. I can change this line. I can change the slope to this or this okay so i could see that the corrosion current density is gradually increasing so if i consider this is point1 this is point2 this is point3.

So i corr 1 is less than i corr 2 less than i corr 3. So this situation I am getting within the activation region due to change in beta a. However, if beta a is changed within this segment. If we change the beta a let’s say beta is changed like this. This is one change there could be little increase in the change so here I could have situation like 4, 5, 6. Now in this situation if I try to see there corrosion rate of that metal this is 4 = i corr 5 = i corr 6, since all are = I limited.

Now and in all cases corresponding ic 1 hydrogen 1 is less than ic hydrogen 2 less than ic hydrogen 3. So the same situation because we have to follow the mixed potential theory where at some mixed potential the rate of cathodic current density the cathodic reaction is = the rate of anodic reaction. But in this situation i could see that E mix is changing so that E mix values if i try to see the corresponding E mix value this is E mix 2, E mix 3.

So this is E mix 2 this is E mix 3. So I could see that E mix and if I point this one as E mix1 so E mix 1 is greater than E mix 2 greater than E mix 3, fine. So this is the situation of E mix we are seeing but when we get to the concentration polarization side. If i try to see the E mix 4 then E mix 5 E mix 6 that means we are talking about this 3 points so those are the mixed potential potential points

Their relation I could see that this is greater than this is greater than this is greater than this. So that means the if we change their position that means if i change Tafel slope which can be done by changing the composition of that particular metal and if those situations are guided by concentration polarization or activation polarization of that cathodic reaction. Then i could have two different situations one is set one another one is set two so these two situation will come across.

And in one situation even if we change the concentration composition of the metal thinking that we can reduce the corrosion rate by changing the beta value that means the slope value but if they intersect with the concentration polarization line or the concentration controlled polarization segment of that cathodic reaction will not have almost no change in their corrosion rates but if they intersect by changing the composition or the surface condition if we change the beta value that the slope value.

And if they intersect the cathodic reaction in that activation control zone. We can have change in their corrosion rates. So the set one is I could say activation controlled corrosion event and set two is concentration controlled corrosion event. And in this case corrosion rate does not change but in this situation corrosion rate changes considerably, considering the fact that this axis is in the log scale so there will be order of magnitude change.

But here everything is cutting the concentration polarization part which is basically the iL and that is what the corrosion rate does not it. But remember we could see the change in the corrosion potential and now in this concentration side we could see that though in case of 4 in case of 4 Situation 4 and if we consider the situation 5 though E mix 4 is greater than E mix 5. So I could see I could think that that situation 4 I could ennoble the metal compared to the situation 5. But even if we ennoble it still I could say that the corrosion rate does not change the corrosion it still remains at iL.

So that suggests that ennobling of metal does not mean that every time it will have decrease in corrosion rate of course in the set 1 place one and two and three if we compare if we compare one and two the one has got a higher corrosion potential than the two so that time if since I won as higher corrosion potential and at the same time. It is cutting that metal polarization line is cutting the hydrogen polarization line at a lower corrosion rate.

So here in ennoblement is taking place at the same time in ennoblement leads to decrease in corrosion rate of that metal. But in the set two even if I know in ennoblement takes place corrosion rate does not change. So we have to be very careful while considering corrosion events and that is what we have to understand the graph polarization graph very carefully so we will talk about polarization curve in the next lecture. So let’s stop our discussion here, thank you very much.