Corrosion Part -II

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Lecture - 19

Effect of velocity on the corrosion rate of an active metal

Hello everyone let’s start lecture 19 and in lecture 18 we have started looking at some of the corrosion events where concentration polarization comes into picture and we could see that the anodic portion of the metal dissolution. If it cuts the cathodic portion which is activation control of a cathodic reaction. Then, there could be change in corrosion current density if we have change in the Tafel slope and that Tafel slope change can be possible.

If we have change in microstructure or change in composition of the metal either dissolving metal. But if the anodic polarization line with different Tafel slope that means different beta values of that anodic polarization line. If all cuts all the lines cut the concentration polarization part of that cathodic polarization section then the current density corresponding to the corrosion rate of the metals with different slopes remain same.

So those two points we have considered. Though we check that the corrosion potential do potential does change in two separate situations. But in the second case where the mixed potential appears in the concentration polarization part then corrosion rate does not change. But if the mix potential appears in the activation polarization part of that cathodic polarization line then of course.

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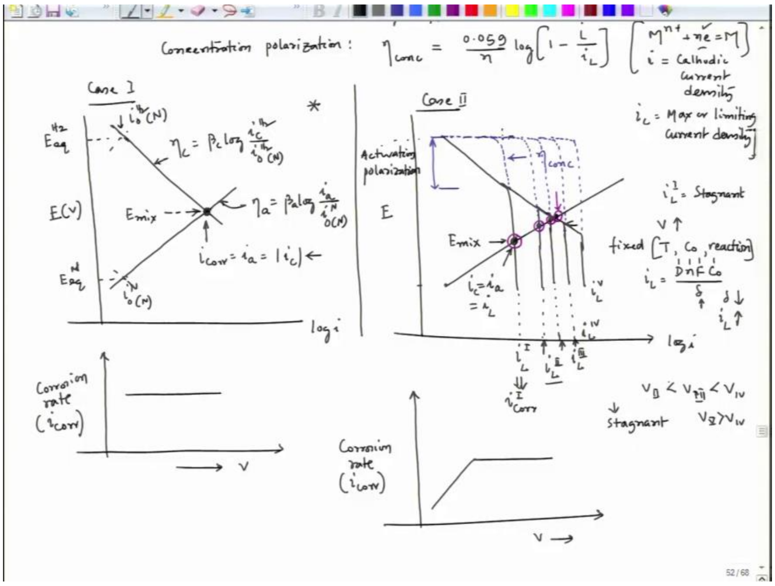

Corrosion potential change changes, at the same time corrosion rate also changes that means corrosion current density also changes. Now today we will continue our discussion of course our discussion is that lecture 19 and here topic remain Same that is the broad topic explanation of corrosion events on the basis of mixed potential theory and today we will continue our discussion and also check some of the instances.

Where we talk about the influence of concentration polarization. Now the situation what we consider here the effect of velocity. Effect of velocity on the corrosion rate, in two situation of an active metal and we will talk about two situation, case one where mix potential is under activation polarization controlled and the second instance mixed potential is under concentration polarization control.

By these two situation let's see what happens now whenever we talk about the velocity now this velocity does not have any effect on the activation polarization and in case of activation polarization the controlling equation is i zero. This is the controlling equation of course you can have anodic polarization or cathodic polarization here also anodic or cathodic and this is also anodic or cathodic.

This small a and small c these are anodic polarization and cathodic polarization and this is the major of polarization which is nothing but the over voltage. Now in case of concentration polarization the governing equation

$$\eta_{conc} = \frac{0.059}{n} log\left(1 - \frac{i}{i_L}\right)$$

Now here we know that n corresponds to this we are taking this general equation. This general cathodic equation we are considering and where i is cathodic current density and iL is max or limiting current density.

And n of course you could see that n of course is this n number of electrons participating. Now here we will take the dissolution part that means the metal dissolution polarization to be all the time activation control. But the concentration control came by part we will be considering for the cathodic polarization part that means the cathodic reaction can have either activation controlled or concentration controlled.

But anodic polarization will always be activation control. So now if we can take two instances so this is two instances this is case 1 and this is case 2. Now we can have plot between potential versus log i and if I try to plot the concentration part this is E equilibrium let's say hydrogen evolution is my cathodic reaction. Now this is i zero hydrogen over that metal surface and that metal is.

Let's say let's take some metal n we are considering that is dissolving. So we can have activation part and then metal one which is E equilibrium of N and i zero n over n it will have its own activation polarization and it is cutting at this point so this potential is E mix and this current density is i corr = ia = log of ic. And of course this line is decided by this is concentration.

This cathodic polarization line over voltage cathodic over voltage which is

$$\eta_c = -\beta_c log\frac{i_c^{H_2}}{i_{o,N}^{H_2}}$$

and this is hydrogen evolution and this particular line is

$$\eta_a = \beta_a log\frac{i_a}{i_{o,N}^{N}}$$

So this is the mixed point mixed potential point where I could see the charge balance is maintained and the concept of mixed potential is maintained so now if we change the velocity in this particular case.

So I could see that the velocity does not have any effect you we make it stagnant and we also steer it if steering we are actually increasing the velocity in these two situations I will not have any influence on it on the corrosion rate of the metal N, because all the time the corrosion current density will remain here. Now if I try to plot the corrosion current, the rate of that means if I plot corrosion rate.

Which is nothing but i corr will be and let's say this is velocity in the direction velocity is increasing. So I will have a parallel line with reference to the velocity axis. Now in case of concentration polarization part let's say we go to a very high current density and once we go to high current density will experience concentration polarization and now if I try to see the situation in case of concentration polarization side.

This is also log i and this is potential. Now corresponding line if I try to see this is this is parallely drawn so that means by the side by side. If I try to see now if the situation appears like this. This is activation part now if this current density is relatively very high current density. We can appear we can see that there is a concentration polarization appearing.

Then if we increase the velocity what would happen? Now actual corrosion actual concentration polarization part is this one so this line is concentration which is nothing but the over voltage. And up to this segment it is activation polarization, and beyond this and concentration polarization is making an influence from this and then the polarization is going down rapidly. Because at this point ic is reaching to iL

And here also we could see that when we try to understand this region we could say that since the current density until it reaches close to the limiting current density the concentration polarization or the concentration over voltage has got a minuscule change. We will also see with reference to a problem solving there we could see that yes until unless it reaches this current density.

Reaches close to the limiting current density, we will have very minimal influence on the concentration polarization over voltage. Now once we see this let's say if the cathodic polarization anodic polarization line let me remove all those thing, so now if I have a situation like this, if this line goes like this. Now in this particular situation let's say this is in a stagnant condition.

This is iL1, and iL1 is stagnant solution. Now when it is stagnant solution and if the anodic polarization line cuts the cathodic polarization line at this particular potential so this becomes my E mix, and now corrosion current density is nothing but i corr one because at this particular point ic = ia = i limiting okay. So at this point I have we are satisfied the mixed potential theory. Now if we change the velocity let's say stagnant solution.

If we change the velocity that is velocity increases in that electrolyte, then what will be the change. We are not changing temperature we are not changing concentration that the initial concentration which is C 0 so these two factor and we are not changing the reaction so these three we are not changing fixed, okay if they are fixed. So, now if I look at the equation for iL = DnF = C 0 by Delta so Delta is the basically boundary layer thickness.

D is the diffusivity of that ionic species. And here it is H+ ion and F is 1 Faraday, n is the number of electrons participating in that cathodic reaction and of course here n is 1 because it is a hydrogen evolution reaction and C0 is the initial concentration and Delta is the boundary layer thickness. Now if you fix temperature initial concentration as well as reaction then this quantity this quantity this is constant and this all four quantities are not changing.

The only change will take place because the velocity is this one. Now if we increase velocity this boundary layer thickness will reduce. If this Delta reduces so what would happen to iL increases so that means if we increase the velocity then Delta reduces iL increases then activation controlled polarization part will extend because I am getting iL at this point, at this point so which is iL II so if that is the appearance.

So now I should get concentration polarization part here so now if we try to see the effect so I will extend this I will extend this is the point. So I will get this. Now I have to extend this segment and then I will join there, so this will be the new appearance. Now if I increase it further so if I increase it to this place, so that means this is iL 3 so now it will further go down, so now activation control part will extend.

And then if I increase it further so if it goes here, so which is corresponding to iL 4. So that means the velocity if I consider corresponding velocity V 1 less than V 2 less than V 3 and of course less than V 4 and V 1 is nothing but stagnant condition or I could say that this is to be a step that means there is that and in fact we should not mention that because I cannot have any velocity over there because it is stagnant solution.

Now if I extend this, it will come here. So now the cutting point when velocity is changed from stagnant to some speed in the in the electrolyte. When we are appearing when you are getting iL 2 that case I am cutting the, we are seeing the situation that the mix potential is appearing in the concentration polarization part of that cathodic polarization and when we take i 3 it is still cutting in the concentration polarization section.

Now once we go to iL 4, I could see that because my polarization activation polarization will extend and here it will start the concentration effect. So in this case when the velocity changes to V 4 so that case we are getting a mixed potential just like to activation controlled polarization line cutting across. So now if I try to see the concentration this corrosion rates in case of iL 1 the corrosion rate point is here.

iL 2 corrosion rate point is here, iL 3 corrosion rate point is here and iL 4 the corrosion rate is here. Now after iL 4 if we increase the velocity then I will get let's say the velocity is changed to V 5 which is higher than V 4 then I would get concentration polarization line like this and then activation control polarization line will extend like this and I will get the graph like this.

So if I try to see V 5 condition this is let's say iL 5 and corresponding to V 5 which is V 5 so that case which is greater than of course V 4 so my corrosion current density as per the mixed potential theory is same as the corrosion current density corresponding to V 4 because every time I will get a cut at this point beyond V 4 so now if I try to see the corrosion rate the corrosion rate as a function of velocity the plot will be interesting plot.

So this is corrosion rate which is nothing but i corr. Up to V 3 i corr is same as the limiting current density add that those corresponding cathodic polarization part and once we go to i4 at V 4, I am getting mixed potential in the activation part and then onwards every time the corrosion rate will be in the activation part and will not have any influence of velocity on the corrosion rate so initially it will increase this is velocity so initially it will increase.

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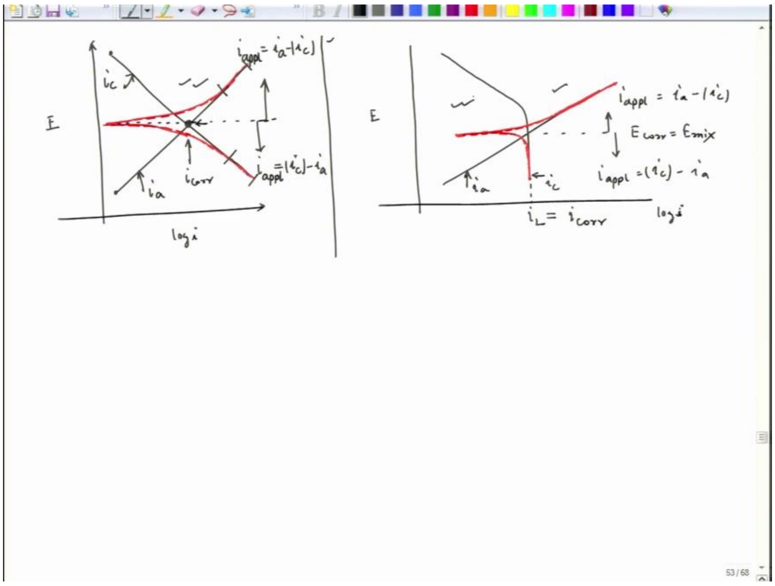

And then it will remain constant. So this is the variation of corrosion rate with velocity in this two cases case 1 and case 2. Now another interesting thing we have to consider in case of case 1 and case 2 so if I try to see the polarization plot dynamic polarization plot as we have understood in case of in we have talked this in corrosion part 1 where if this is E this is log i now these are the two individual lines.

And I am not putting all those indications that means i zero, E equilibrium all those values implied here. Now this is my point where I will meet the mixed potential theory. Now if I try to see the plot experimental plot, the plot experimental plot will be as we have understood before in this segment i or i experimental or i measured or i applied = ic - ia and in this part in this part it is

$$i_{applied} = i_a - i_c$$

Because this particular line is this is the ia plot this is ic plot separately. Now if I try to draw the experimental plot would be so experimental plot would be the red line. So this is clear that in order to get the corrosion current density which corresponds to this i corr. I have to take the straight line part that means this straight line part and here also the straight line part take a tangent.

And then that straight line if I extend wherever it cuts that means here it will cut that cut point corresponds to the corrosion current density and corrosion potential. But if I take another situation where we have concentration controlled so if it is E and this is log I so if the intersection is like this and it is like this so it is simply the same principle will operate because this is E corr or E mix below this I applied = ic - ia.

And this is nothing but ic this is ia and beyond above this which is activation which is the anodic polarization here I applied = ia - ic. Here we are taking mode because ic has got a negative connotation. So now if I try to plot try to see the difference the plot nature would be, okay, so the plot nature would be like this. Now when the plot nature becomes like this in order to get corrosion current density, iL this is because it is so the corrosion current density is nothing but there we cannot draw those Tafel slopes.

We have to just extend the straight line part in case of concentration polarization control corrosion effect will be i corr but the plot would be like this in this case and in this case it will be like this. So this is the experimental way to decide which cases concentration control which case is cathode activation control in case of activation control the plot nature the Tafel plots will be like this in case of concentration control it will be like this. So let’s stop here. We will continue our discussion in our next lecture, thank you.