Corrosion – Part II
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Lecture – 28
Interaction of Anodic Polarization with an Active-Passive Metal

Let’s start lecture 28. We will continue our discussion on passivation and mixed potential theory. In the last lecture, we could see the there are 3 situations which are patterning to the interaction between cathodic polarization and anodic polarization. And here we are considering the anodic polarization to be activation Active Passive mode. So, we can have spontaneous passivity.

We can have Active Passive transition and as well as we can experience a cathodic loop which talks about the unstable passivity achievement.

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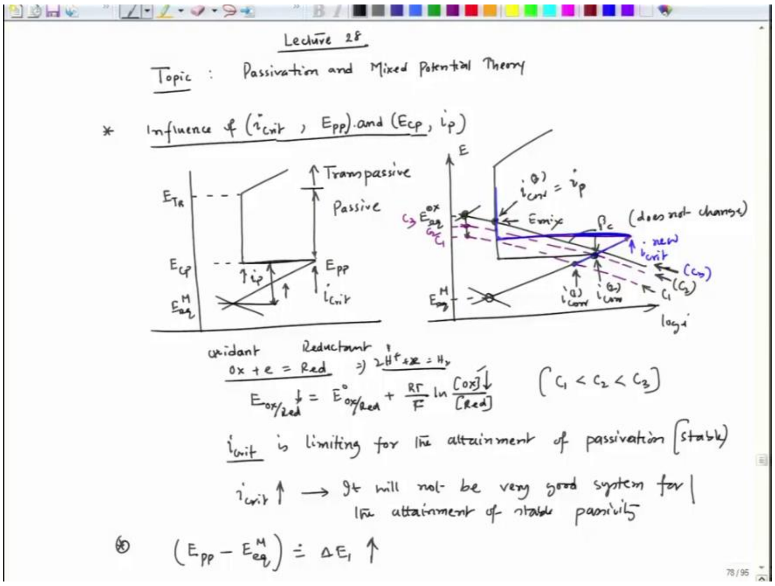

Lecture 28

Topic : Passivation and Mixed Potential Theory

* Influence of (i_{crit} , E_{pp}) and (E_{cp}, i_p)

oxidant Reductant

$Ox + e = Red \Rightarrow 2H^+ + 2e = H_2$

$$E_{Ox/Red}\downarrow = E^0_{Ox/Red} + \frac{RT}{F}\ln\frac{[Ox]\downarrow}{[Red]} \qquad (C_1 < C_2 < C_3)$$

i_{crit} is limiting for the attainment of passivation [stable]

$i_{crit}\uparrow \rightarrow$ It will not be very good system for the attainment of stable passivity

* $(E_{pp} - E^M_{eq}) \doteq \Delta E_1 \uparrow$

Now, will talk one important aspect influence of i critical as well as Epp and Ecp. So, these 3 points are very critical. Of course, when we talk about cp it is automatically coming up with because this toward in combination and Ecp and ip are in combination because if we see the passivation Active Passive plot for dissolving metal. So, these are the this is the plot and every time we are considering transpassivity.

So, this is transpassive, this particular zone is passive and this is Epp and this particular current is i critical this is i passive, this is Ecp or and this is E trans, fine. These are the points we are talking about. Now so this is complete passivation potential this is primary passivation potential. So, if we see the interaction let’s say i see an interaction like this is the plot of cathodic anodic side anodic part.

Now, if this is my cathodic line, okay. So, this is my cathodic line let’s say and then in this particular situation i will get spontaneous passivity because the system will reach to this potential which is E mix. No, if we reduce the concentration of the oxidant, so, this is E let’s say oxidant Eox and this is E of metal dissolving metal E equilibrium of the metal this is E equilibrium of ox or I can write it like this oxidant.

So, this oxidant concentration if we reduce, so, then this point will sift downwards. Why? Because if we consider ox + e = red, oxidant + e = reductant. So, my $E_{ox/red} = E^{o}_{ox/red}$ + (RT/F) ln (concentration of ox / concentration of red or reductant). This is ox basically oxidant and this is reductant. If this concentration reduces so I can have a situation like H2

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

to this particular case this is oxidant.

If this concentration reduces. So, I will have since this is reducing so, these value will go down, so, this potential will go down. So, if this potential goes down, but the slope this is beta c if it does not change, this line will move like this it will be one and this if you further go down it will be like this, fine. So, these are the 3 situations I am considering this is the situation with a concentration C1 this is C2 and this is let’s C3.

And of course, our concentration relation would be C1 less than C2 less than C3. So, now, if we start with C1, the system will reach at this point in the free corrosion condition without having any influence of external current. Now, in case of C2 the situation system will be here, okay which is exactly so, this is i corr 1 this is i corr 2 and this becomes and once we increase the concentration from C2 to C3 my i corr moves to this point.

Which is i corr this particular situation where the concentration reaches C3 that time this particular point becomes my mixed potential point where this mix potential theory is satisfied. So, this is nothing but ip this is ip. Now interesting part is this case the metal is freshly prepared without having any oxide surface on that particular metal. So, when we have this interaction between two equilibrium potentials.

They will try to take the potential final potential in between these two extreme potentials and since it is freshly prepared, so, when the concentration is C1 that means this is C1 the corrosion rate would be here and when the concentration is C3 the corrosion would be here corrosion rate will be at this point because that becomes my next potential theory. So, it is very clear that this or this polar concentration.

This cathodic polarization line must cross this i critical. This is basically this point it must cross to get to the passive steady state passive region. So, this particular this i critical is limiting to achieve steady passive steady passivity. So, i critical is limiting for the attainment of passivation and here the passivation is stable passivation, fine. So, the concentration of that oxygen should be such that it just crosses this i critical.

So, the C2 concentration at C2 concentration this category polarization line is just crossing just touching the i critical point. So, there i will not have stable passivity. So, once it crosses that i will get a stable passivity. So, if i critical increases i would definitely it will not be a very good system for the attainment of passivity stable passivity why because if I extend this i critical point.

So, if I extend it, so, if it reaches there, so, then if I don't change the let’s do it with the blue colour. So, if I extend this i critical point and without changing the i passive region. So, now, the new i critical is this and in case of i critical in the previous instance, at least C3 composition which is this is C3 was giving me allowing that system to add some passivity, but once this i critical new has been considered.

That means, in a system where i critical is very high even with the C3 concentration. Which is pretty high concentration in this comparison to C1 it will not give me stable passivity. So, for a system to be a very good passivating metal it should have a lower i critical it should not have a very high i critical. Similarly, if I try to look at this gap, the gap between E equilibrium metal and Epp.

So, here I am just drawing this Epp as well as Ecp at the same level. So, this gap if it extends that means, if this gap increases, so, that means, if Ecp or Epp - E equilibrium metal this difference if it this is del E1 if it increases that means, this is also not good because it increases even with that with the condition of constant i critical the situation would be very different.

So, in case of i critical in terms of getting a stable passivity one should have a very low that metal should possess a very low i critical in that passivating medium and if it increases also it will lead to

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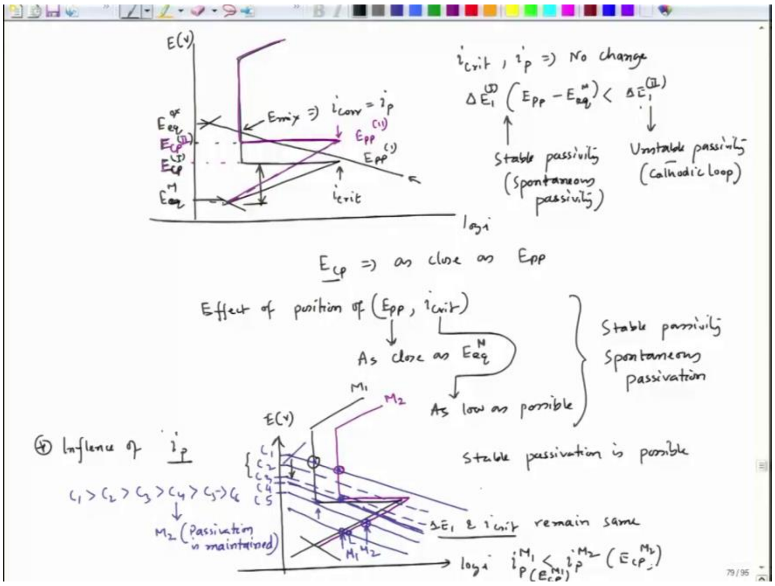

Affect the passivity in a negative fashion. Why? let’s see that particular influence this becomes my log i and E volt. One case I get plot like this. So, this is my Eox and this is or E equilibrium ox and this is E equilibrium metal. So, this becomes my E mix when I will have this particular very situation on where it just crosses i critical this is i critical. So, in this case I will have stable passivity.

So, here correspondingly i could not get i corr which is nothing but i passive. Now, if this particular difference increases keeping the i critical constant as well as ip constant. The ip and i critical they do not change. So, what will be the situation so, i change that particular so if it is coming here and then if the pattern is this. So that means I am not changing i critical remains same.

So, in this two plots i critical remain same ip same or I would say no change i critical ip no change only changes in Del E1. Which is the difference between Epp - E equilibrium m, so, this point belongs to Epp and here it is Epp this is case 1 case 2 or this is case 1 this is case 2, fine. So, in this case if we consider case 1 is less than Del E1 case 2 so, in that situation when we go to this I get stable passivity and here i get unstable passivity.

Since, in this situation i will get cathodic loop, fine, but here i will get spontaneous passivity, okay. So, that means, it is very clear and also correspondingly i could see the Ecp effect. So, this is Ecp this is Ecp2 and in this case it is Ecp Ecp1. So, i could also correspondingly see the effect of Ecp also Ecp. So, Ecp should be as close as Epp so, that will help us to get to stable passivity also.

Now, these are the two influences that means the effect of position of Epp and i critical. So, this should be as close as E equilibrium metal which is reversible potential this potential at the same time i critical if I try to see the i critical condition it should be as low as possible. So, these two situations i would get stable passivity and under this circumstance because the polarization plot for the cathodic side is cutting across the anodic part in the passive region.

So, i would get spontaneous passivity or spontaneous passivation is possible. Now, let's look at the influence of ip, okay. So, influence of ip. So, the influence of ip is very clear. For example, if we get up mixed potential theory log i and this is E volt. So, if I try to plot if I try to see these two plots. One case it is and both the cases this point is maintaining. So, these 2 different colours are indicating let's say this is metal 1 and this is metal 2.

And if the cathodic polarization line is like this. This is the cathodic polarization line, okay. So, I could see the both the cases I would get. So, in this particular situation the stable passivity will get for both the cases. So, this is for metal 1 this is for metal 2. So, stable passivation is achievable for both the cases is possible, okay. So, if we do not have any change in the i critical or i critical as well as this gap maintain same.

So, that Del E1 as well as i critical remains same. So, that case i could achieve stable passivation in both the metals. But the major problem appears when we start decreasing the concentration of the oxidant. So, this particular potential will start going down. So, when it goes down, it will go like this. So, if I try to look at within, so, this will go down like this, let's say and in this case, another solid line I'm drawing.

So, when the concentration goes down like this, so, that means this is 1, this is 2, this is 3, this is 4, this is 5. So, all those corresponding to C1, C2, C3, C4, C5 so, these are the concentration and the relation is C1 greater than C2 greater than C3 greater than C4 and greater than C5. Interestingly if I look at when we achieve this particular passivation point, once we achieve this passive particular passivation point, then if we reduce the concentration.

Okay, so that is passive layer now has formed. So, if we no Do not disturb the passive layer in the form of scratching or let's say increasing the turbulence in the medium, so, that oxide layer gets dislodge from the surface that this passive layer is dislodged. So, if we do not do all those things, until unless we cross this particular point for metal 2 and this particular point for metal 1. I would keep the passivation the passivation will be maintained, okay.

So, now in case of metal 2, I could maintain the passivation till concentration C4, okay till concentration C4 that is in this concentration for metal 2 passivation is maintained, but once this concentration goes to C5 that was the concentration reduces that oxygen concentration reduces the line become C5 that case that C5 cuts the polarization anodic part of the m2 in the active zone. So, this is the cutting point.

So, the passivation will be lost and then metal will metal 2 will dissolve in the active fashion. But, if we consider M1 this M1 for the metal 1 till it reaches C5 that means it is just touching the corner point this corner point till that C5 it will maintain its passivity, but once we cross C5 let's say the C5 is crossed that means C6 if I consider another consider C6. So, C6 points let's say here.

So, we will have a polarization plot like this, where it will cut here in case of metal 1 and the metal 2 also this is the point so, which is for metal 2. So, both the cases now passivity will be lost, but interestingly metal 1 if I compare the passivity metal 1 ip of metal 1 is lower than ip of metal 2. So, when we reduce after achieving the passivity stable passivity if we reduce the oxidant concentration.

Then until unless that cathodic polarization line crosses the ip point, which is basically the cp ip point Ecp. So, this point corresponding to Ecp M2 this point corresponding to Ecp M1, so that point until unless that cathodic polarization line crosses will not be able to break the passive layer provided of course, in case of in between C1 and C3 for M1, M2, for M2 in between C1 and this range.

If we do not disturb it, if we disturbed the situation will be different we will talk in the next lecture, but if we do not disturb the passive layer in case of M2 C3 is the critical concentration corresponding to ip of that M2 and C5 is the critical concentration for metal 1 corresponding to ip metal 1 or corresponding to Ecp of metal 1 and this is in this M2 case this is Ecp metal 2.

So, it is very clear that if ip is less and other things are same so, that particular metal would have a better possibility of getting to a stable passivity and maintenance of stable passivity, okay. So, this is one critical aspect. So, that means,

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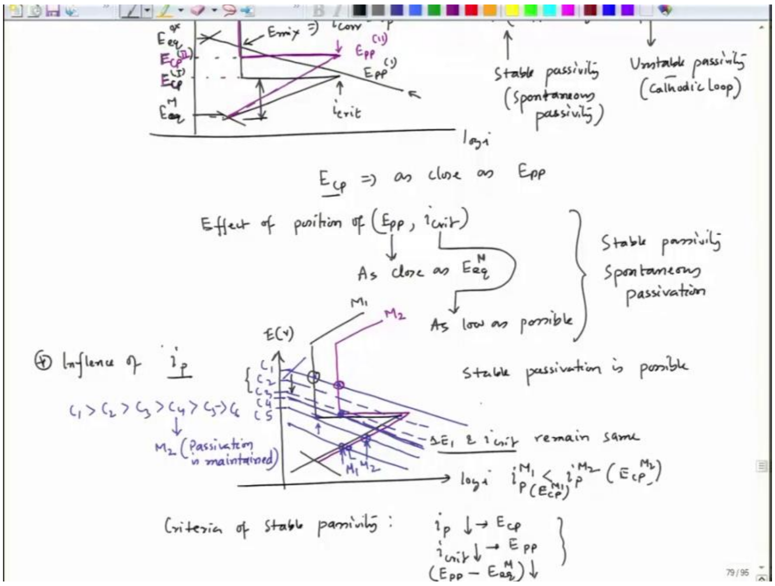

In order to have our criteria for passivity ip should be as low as possible and correspondingly. So, that means, if we combine all the other situations. So, ip should be low i critical should be low as well as Epp - E equilibrium this gap should be low also. So, those situations I could achieve passivation very easily provided the cathodic polarization line is positioned same fashion in all the cases.

So, this is the criteria for stable passivity and when we talk about ip, I am discussing also I am taking part of Ecp when I am talking about i critical am taking consideration of Epp also. So, let’s stop here. We will continue our discussion in our next lecture on this very aspect of passivation. And its interaction with the cathodic polarization line this anodic polarization and catholic polarization line.

In the passive zone as well as if we go away from the passive zone. So, thank you very much. We will continue in our next lecture.