# Corrosion – Part II
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## Lecture – 27
## Interaction of Cathodic Polarization with an Active-Passive Metal

Let’s start lecture 27. And today is topic will be passivation and mix potential theory is basically interaction of passivation and mixed potential theory. In the last lecture, we have already started this that interaction of cathodic polarization with the anodic polarization plots when the system goes into passivation mode. Now, we talk about active passive situation.

Where the active portion of cathodic polarization line intersects this activation polarization part of a cathodic polarization line intersects the anodic polarization line in the active control region.

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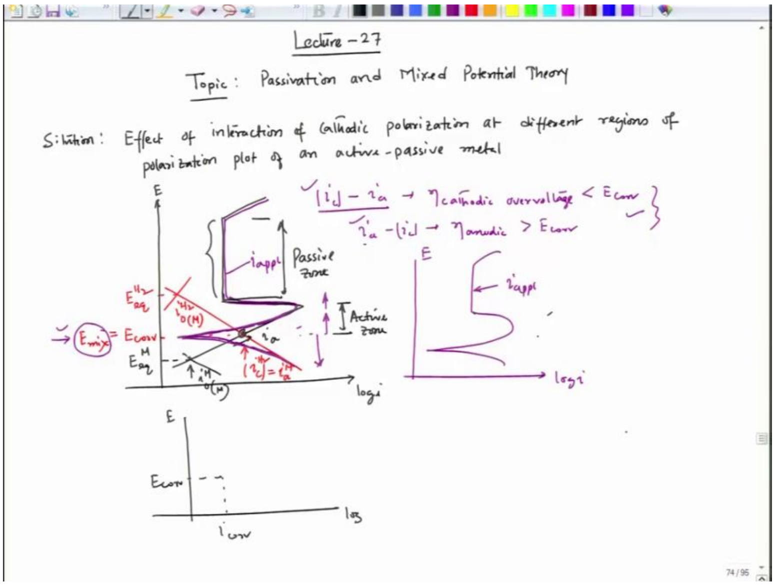

Lecture – 27

Topic: Passivation and Mixed Potential Theory

Situation: Effect of interaction of cathodic polarization at different regions of polarization plot of an active-passive metal

✓ $\underline{|i_c| - i_a} \rightarrow \eta_{cathodic\ overvoltage} < E_{corr}$

✓ $i_a - |i_c| \rightarrow \eta_{anodic} > E_{corr}$

Now, what so, our topic is passivation and mix potential theory and our sub topic for today would be effect of interaction of cathodic polarization at different sections or regions I would say of polarization plots of an active passive metal. So, this is situation we will consider. Now in the last lecture at the end, we talked about interaction of so interaction of the situation where we can have active passive transition.

So, this is my active passive that metal which gives you active passive transition where this is E equilibrium of metal this is i zero of metal over metal surface and this is nothing but ia and if the interaction happens with the cathodic polarization plot in the we are talking about activation control mode. So, that means, every interaction will be in the activation polarization part.

So, if we consider one cathodic polarization plot, so, this is my cathodic polarization plot and here we have considered this is E equilibrium of hydrogen and this is i zero hydrogen over metal surface. Now, if the interaction is in this fashion, then this becomes my E corr which is nothing but E mix at which ic which is hydrogen equal to ia which is metal dissolution at this very location at the intersection point.

And that is what we got a polarization plot like this. Now when we leave that metal in an electrolyte, let's say acidic medium, the system will achieve this particular potential because this is spontaneously achieve point were charge balance is maintained and so, when we do polarization we have to go with reference to this point and we can go downwards with reference to this point downwards or we can go upward.

Now, downside we have the plot this plot will be visible when we do polarization and the upside will have this particular polarization and this is happening as we are mentioned is a difference between two current, okay. So, this difference when it is cathodic polarization over voltage cathodic over voltage below less than E corr and this is ia - ic which is anodic over voltage greater than E corr.

Now if we keep moving upward then if we do take the difference between these two currents and that take log value of that deference will see a plot like this the plot pattern would be like this will be the plot pattern. So, this and we have seen that. Now here system with the system is left without having some external influence here the external influence we need to polarization is the basically the either you get potential or current.

But, here if you do not do anything, it is a basically open circuit mode the system will achieve this potential, but once you do polarization, the system will go downward as well as upward in the potential axis and then you get different shapes of the graph and here the shape becomes like this, this is log i and this is E and the shape would be like this, this is the kind of shape will achieve.

Now, as we are seeing that, in this particular case, if we leave it in the open circuit mode, the system will be at E corr in the potential log axis and the current value would be i corr which is this particular very point. Now, this is also similar to polarization between two active sites of cathode and anodic polarized polarization as we have seen in the previous when we have talked about interaction of active zones up to polarization plots that is cathodic anodic.

But the situation would be different if we have a kind of intersection, when we have a situation like this.

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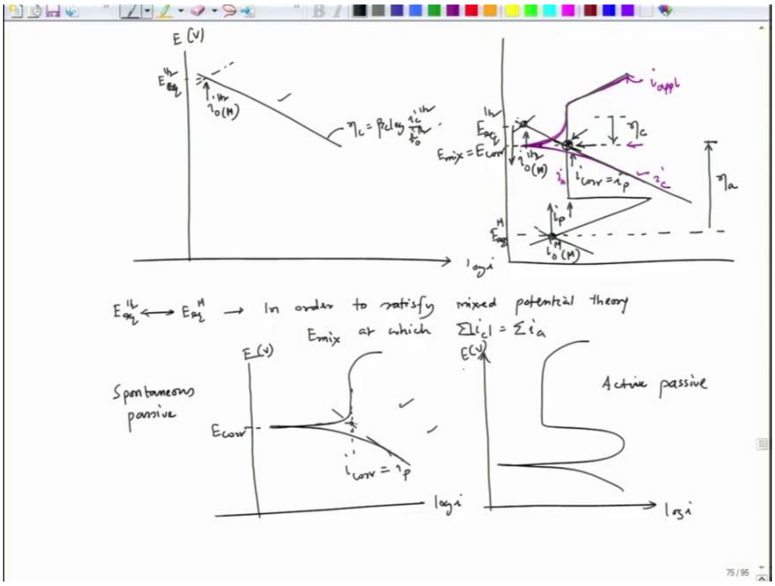

$E_{eq}^{H_2} \longleftrightarrow E_{eq}^{M} \rightarrow$ In order to satisfy mixed potential theory $E_{mix}$ at which $\Sigma|i_c| = \Sigma i_a$

If we have a situation like this that said this is log i, and this is E volt and if the cathodic polarization line moves like this. This is let’s say hydrogen evolution here I am considering as my cathodic polarization hydrogen E equilibrium. This is i zero hydrogen of metal surface this is its activation polarization which is

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

And this is hydrogen. So, this particular line has this equation this one.

Now, if I try to see the anodic polarization plot, so, this is going to be my anodic polarization plot. If this is my anodic polarization plot which is E equilibrium of metal i zero metal over the metal surface. Now, we have to see the interactions between these two. One way that this line can cut here another way that this line can cut here. Now, when this line cuts here, we have already seen how the graph appears if we do polarization.

But, if this line cuts at this position in the passive stable passive region, the steady state passive condition where the rate of growth of oxide film is equal to the rate of dissolution, which is nothing but ip the current density related to the passive zone. So, then what will be the shape of the curve. Now, in this case, we are not initially if the position relative position of this particular polarization.

Cathodic polarization plot is such that it is cutting like this instead of this if it cuts here, so, this is the polarization plot this is E equilibrium hydrogen. This is i zero hydrogen over that metal surface if it cuts there. Now in the free on when that open circuit condition this two potential this is the potential and this is the potential these two potential that means, E equilibrium and E equilibrium M and E equilibrium hydrogen.

These two potential would try to take the potential to this location in order to satisfy mix potential theory which suggests that it should be E mix at which ic = ia. Now if you see this that means, these particular potential will drag this potential upward at the same time this potential will drag the potential downwards and it will come over there. So, up till this we will have cathodic polarization or cathodic over voltage.

And from this if we compare, we will have anodic over voltage from the equilibrium or reversible potential. So, if we have this very situation then in the open circuit condition the system would try will reach to this point which corresponds to what corresponds to steady passive region. So, that means, the E corr would be this would become my E corr and or it is nothing but E mix and this particular corrosion current will be equal to ip.

So, now, what will be the plot what will be the polarization plot as we have understood that the polarization will be done with reference to E corr. So, if we try to draw the polarization graph with reference to E corr and then we have to see the difference between two currents that means, current density rather one is ic and one is ia as per this principle and then this is the principle we have to add up.

And then, we have to take log and then plot that particular log value with over voltage or absolute potential. Now, if we try to do that the plot nature because this is my ic and this becomes my ia. So, now, it is the basically difference between these two currents and since it is a log scale, so, the plot would become like this. This will be the plot in this particular situation. Now, in this particular situation in the free corrosion condition.

This will be the potential but once we in have a forceful polarization that times have applied this line is basically i applied line in this case, this line is basically i applied line or this is i applied line and that i applied is basically the difference between these two currents and taking long here also it happens like this. So, what will be the nature of the plot. Nature of the plot would be nature a plot would be like this.

Now, when we do have this particular when we have this particular situation my corrosion rate would be they should be my corrosion rate or ip and that time we should not do like this particular operation. So, even if we do this, then we draw this and then extend this flat line. And that becomes my i corr, okay and then E corr would be this would be my E corr. So, this will be the very plot nature.

Now in the, if we compare the plot what we have seen in the last this particular situation. So, if we compare these two plots, one case the plot becomes like this and that is plot become like this, now, in this case, we are having the mix potential in the active zone of the in the active zone after dissolving metal. Because this is my active zone, fine and if we go by for polarization.

Then we can see this graph. So, here until unless we go in to the polarization and reach in this zone we cannot achieve passivity. So, we have to forcefully take it to this region for attaining passivity. Because this zone is this zone is the passive zone. So, that is what it is called Active Passive transition. But, if we try to see this one, in this case, without having any polarization I can reach to this particular location which is the passive location.

So, that is what it is called spontaneous passivity. But here it is Active Passive passivity. So, this is Active Passive graph and this is spontaneous passive graph. So, this is the difference between these two situation, fine.

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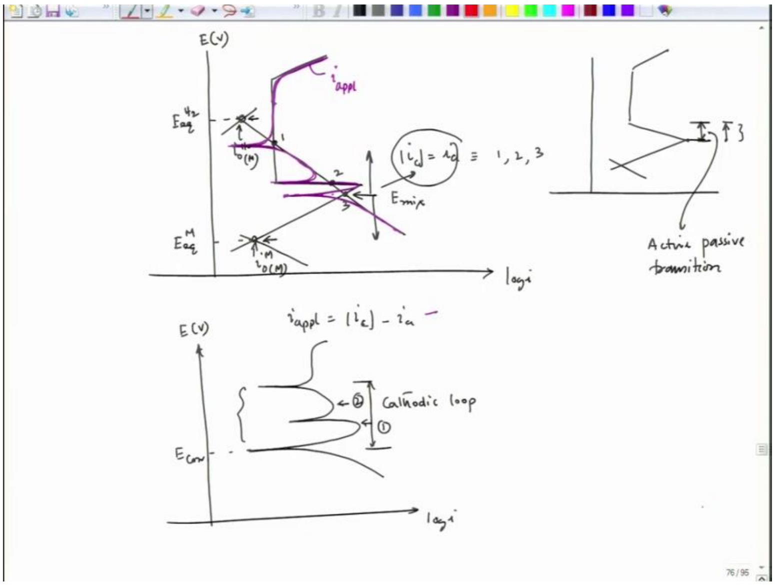

Now, we can have another situation this situation is basically between in between these two positions. Now, if the interaction with the anodic polarization plot and cathodic polarization plot is in this fashion, let’s draw that. So, if this is my anodic polarization plot this is E equilibrium of metal this is i zero over metal surface of that metal and if the interaction is like this. So, this is my is i zero hydrogen over that metal surface.

And this is E equilibrium hydrogen. In this case, now, where I could see 3 points, this is 1 point, this is another point and this is another point this is 1, 2, 3 points, I can have all three points, I can have 1, 2 as well as 3 all 3 points I can have this particular condition meeting. So, that means, now, where should I go, okay where in the free corrosion condition where would it stay.

Now, this is a tricky situation and this particular condition is actually can explain that why this zone is called unstable zone. So, when we see the anodic polarization plot we have seen that this particular region is basically unstable zone or this zone can be written as active passive transition or passive active transition. So, this zone the influence of that zone will be coming into picture. In this zone actually we are not getting a stable passivity.

Rather steady state passivity is not opting in this particular active passive zone, rather we are if we go from lower potential to higher potential, if we start from here, if we go there, then we will achieve stable passivity or if we go. So in this particular zone, I am getting kind of transition to steady state passivity. Now, when we are dipping that active passive metal into an acid medium.

That time and if it is a freshly prepared metal without having any oxide surface on that particular metal or hydroxide surface on that particular metal the metal will be that potential. So, these potential and this potential these 2 potential will try to drag those potentials downwards and upwards to reach to that mix potential position and it is a freshly prepared fresh sample.

So, freshly prepared sample, so, where we do not have any pre-existing oxide layer. So, that case the system will try to find the first location where mixed potential theory is satisfying. So, that time the first location where mix potential theory satisfied is this location where this becomes my E mix and correspondingly I will get a situation like this were charged balance is maintained. Now, if this is my E mix.

So, accordingly the system will try to reach there and then it will become steady over there and then if we try to understand its polarization behaviour, so, I have to go downwards and then upwards from this location that E mix location and see the plot to behaviour. So, in this case, again we have to do the same principle that means, i applied = ic - ia and then taking log of i applied with respect to the potential.

So, the plot would become so, this will be the plot. So, this will go like this and then final come like this. So, the plot will be like this. So, how the plot looks like so, this will be the plot. Now this plot is appearing because this is i applied, which is the difference between these two currents and if we follow that principle it will get to this particular very polarization graph.

So, the polarization graph so, if we see the plot. So, if this becomes my E corr. So, I will have a plot like this. The plot becomes like this. So, that time this segment we call it cathodic loop this segment. So you have to I would say a peak in this particular graph, I will get so, this is the two loop again this is one loop this is second loop I get, Now, what will be the now, if we see the.

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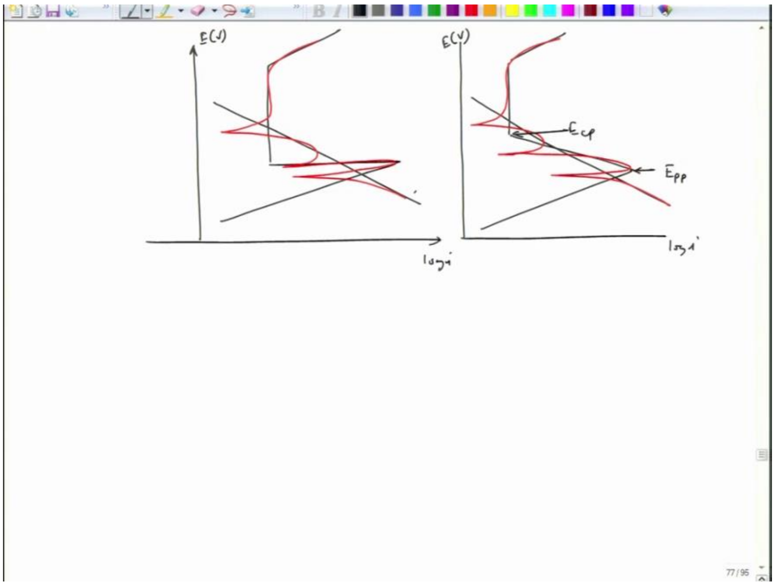

The influence of this active passive transition zone. Let's say in one case, the intersection is like this. And another case the intersection like this. So, both the case if we consider this to be the slopes are saying so, this is the slope. So, I could see that cathodic loop appearance in both the situation would be one like this, another case would be like this. So, I could see there could be variation in the cathodic loop.

So, this red ink plot is basically the cathodic blue and in both cases this is Ev log i, this is log i and this potential. So, I could see that the cathodic loop pattern can change and that gives us a kind of idea that how is basically the position between ip and this Epp this point belongs to Epp and this point belongs to Ecp. So, we can have an idea that how close they are situated. So, let's stop here.

And we will continue our discussion in our next lecture. So, we could see three situations, when we have interaction between cathodic portion cathodic polarization and anodic polarization of an active passive metal. In one case, we get spontaneous passivity and other case we get active passive transition another and in another situation where the polarization plot of the cathodic portion cuts the anodic polarization plot in three locations.

We get cathodic loop. And in case of cathodic loop we do not get proper passivity. Because the system if we start with a freshly prepared metal surface, it will stay in the active zone as we have seen, but if we have a kind of previously passivated sample, we could have a different situation. We will talk about those cases in our next lecture. Let's stop here. Thank you very much.