Corrosion – Part II
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology – Kanpur

Lecture – 29
Passivation and Mixed Potential theory: Case Studies

Let’s a start lecture 29.

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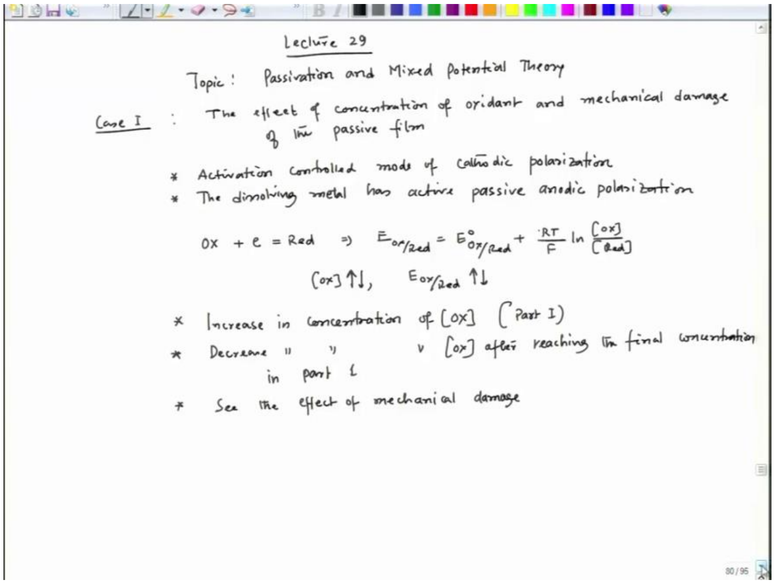

Lecture 29

Topic : Passivation and Mixed Potential Theory

Case I : The effect of concentration of oxidant and mechanical damage of the passive film

* Activation controlled mode of cathodic polarization
* The dissolving metal has active passive anodic polarization

$$ox + e = Red \Rightarrow E_{ox/Red} = E^{o}_{ox/Red} + \frac{RT}{F} \ln \frac{[ox]}{[Red]}$$

$$[ox] \uparrow\downarrow, \quad E_{ox/Red} \uparrow\downarrow$$

* Increase in concentration of [ox] (Part I)
* Decrease " " " [ox] after reaching the final concentration in part I
* See the effect of mechanical damage

And today’s discussion will be some case studies based on passivity of a metal and its interaction with cathodic polarization line and we will follow will be following mixed potential theory. So, lecture 29 is basically the topic broad topic is passivation and mixed potential theory. So, the case one the effect of concentration of oxidant and mechanical damage of the passive film or rather I would say effect of oxidant on the passivity and mechanical damage of the passive film.

So, when we try to do that and we will be considering activation control mode of cathodic polarization This is one consideration and second thing is the dissolving metal has Active Passive anodic polarization. So, when we have these two situations. Let’s see how we can get the idea of corrosion rate as well as mixed potential. When we change the concentration of oxidant.

Let’s the oxidant is ox + e = reductant and then corresponding

$$E_{ox/red} = E^{o}_{ox/red} + \frac{RT}{F} ln \frac{[ox]}{[red]}$$

Since, here we are considering one electron ln concentration of ox and concentration of red when you say this if ox concentration increases then of course, E ox red increases and similarly if it reduces this will also reduce. So, first we will try to see the increase in concentration of ox and then the second part this is the first part.

And then second part will see the decrease in concentration of ox after reaching the final concentration in part 1 and when we see the second part that time we will also see the effect of mechanical damage. Now in order to do that.

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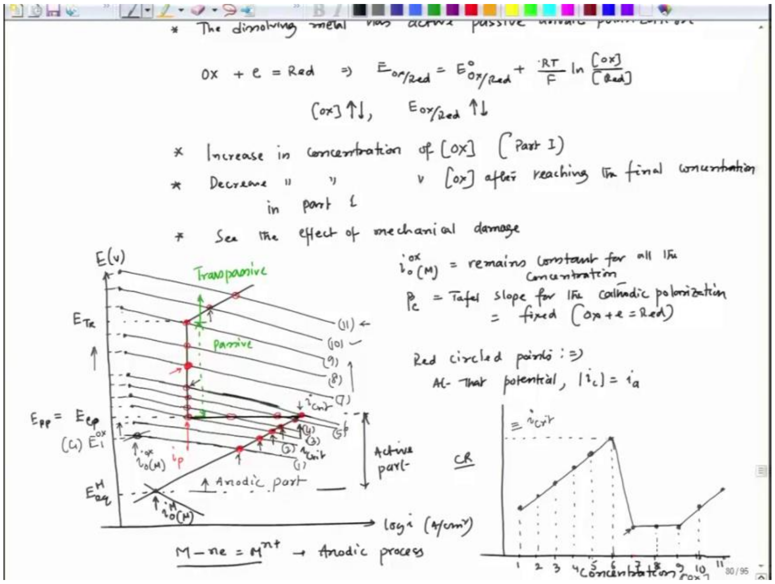

* The dissolving metal has active passive

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$i_0^{ox}(M)$ = remains constant for all the concentration

β_c = Tafel slope for the cathodic polarization = fixed (ox + e = Red)

Red circled points :⇒ At that potential, $|i_c| = i_a$

$M - ne = M^{n+}$ → Anodic process

We have to draw mixed potential theory. So, let's say this is going to be my E versus log i plot this is ampere per centimeter square this is in volt now, let me first draw the anodic part of the passive Active Passive metal and here we are considering E transpassive Ecp and that means, here we could see that Ecp as well as Epp are at a same position these are at the same position as per this particular diagram this is i zero of M over M.

This is E equilibrium of M. Now, this is the diagram this is the anodic part where I can have M - ne =M^{n+}. So, this particular process is the anodic process and this particular line indicates the anodic line this is i critical, okay. So, now, when we have this situation let's try to draw the diagram for cathodic line cathodic polarization part. So, this is anodic polarization part because this way anodic part.

Now if we go let’s start with concentration C1 so the concentration let’s say the C1 and that time this is the anodic. This is the polarization part. So, this is E1 corresponding to concentration C1 of the oxidant and this is i zero of ox over metal surface. Now here we are considering here considering i zero ox over metal surface remains constant for all the concentration beta c which is the activation the tafel slope for the cathodic polarization.

This is fixed for ox + e = red this reaction. So, if we keep changing the concentration let’s say concentration first increases though this particular point will sift upward. So, it will sift like this. So, this is the second composition this is the third composition, this is fourth, this is fifth, this is sixth, and which is let’s say just crossing i critical. This is the way it is moving this is the seventh, this is eighth let’s say this is nine and this is 10 and this is 11.

So, we have taken 11 compositions. So, 1,2,3,4,5,6,7,8,9,10,11 compositions we have taken so correspondingly we have this point is shifting this point will safe but there will be no change in the i zero that was the assumption we have taken and E equilibrium value E ox equilibrium of course this is E ox that will keep on increasing because we are increasing the concentration and that value is increasing that value is increasing and beta remain same.

So, that is what every lines are parallel, but they will have interactions according to at the way they are cutting across the anodic polarization part of the dissolving metal. So, what are those points, so, this is 1 point second, third, fourth, fifth, sixth, and then we have other connections also this is 1,2,3,4,5 So, these are the connections or the crossing points, red colored circles. Now, if we try to see the corrosion rate.

So, those red points are those points where I could see that mixed potential theory is maintained. So, the red circled points, I could see that at that potential ic = ia but as we have said our initial condition was a metal was freshly prepared and it does not have any oxide layer to start with. So, it will only see the circle point when the concentration of oxidant is increasing. And those circle points should remain should be considered.

Those points should be considered which are basically the connection between the active parts of the anodic polarization portion so this is the active part So, this particular region is the active part and of course, these two region so, the passive part, so, this is the passive part and beyond this, we have transpassive, fine. So, as we are using the fresh metal. So, we have to consider this point because it will only consider the cross-section points of the active regions.

So, the corrosion rate if we try to plot corrosion rate plot would be with concentration if we try to plot. So, this is corrosion rates CR means corrosion rate. So, when we have C1 this is 1,2,3,4,5,6,7,8,9,10 and this is 11. So, now, if we consider this, so, the corrosion rate is at this point that say this is 1 point. This is the let's say to start with this is the point now, as were going with a higher and higher concentration.

I will see that the concentration is increasing at the same time corrosion rate is increasing because I could see that the corrosion rate was here and then when the concentration has changed from C1 to C2 corrosion rate has gone to this like that way the corrosion rate is increasing. So, 2 let's say this is the point 3, this is the point this 1,2,3,4,5 all though are concentration of oxidant concentration.

So, then 4, I will have this point so 4, is if I try to see the 4 is this one then 5 is this one. So, 5 is still further increasing it has gone to this now 6 when the concentration has been to C6 which is this particular line, we are considering that is just crossing the c critical i critical it just crossing i critical. So, since it is the fresh metal to start with the corrosion would be red would be here not at this location because we are starting with the fresh metal to begin with.

So, now at six the corrosion rate would be equal to is equivalent to i critical, okay, fine. Now, once we cross 6 once we go to 7, I could see that mixed potential is located at this particular location, fine. So, now corrosion rate suddenly drops and that drop-in corrosion rate. So, this is corresponding to i passive ip. So, it will be similar to ip so, if I try to C7, so, 7 the corrosion rate has move to ip.

So now, if I again start increasing my and then it at this particular location, it will achieve stable passivity because only one location it is plotting across that anodic portion. And now, if I increasing increase the concentration for this if I go to 8 and then 9, so, 9 is basically the location where the transpassivity still just starting. So, if it is just starting so, till 9 it will maintain the same corrosion rate.

And then once we go to 10 this the corrosion rate will be the mixed potentially satisfied in the transpassive zone and I could see that the corrosion rate is increasing again. So, corrosion rate would be here because i small i nothing but the rate of dissolution. So, this is the location I could achieve and 11 it is still further increases it is increasing so, it will be here. So, what will be the plot nature.

So, the plot nature as we increase the concentration from C1 to C11 the plot nature would be this will be the plot nature. Now, once we do this after that.

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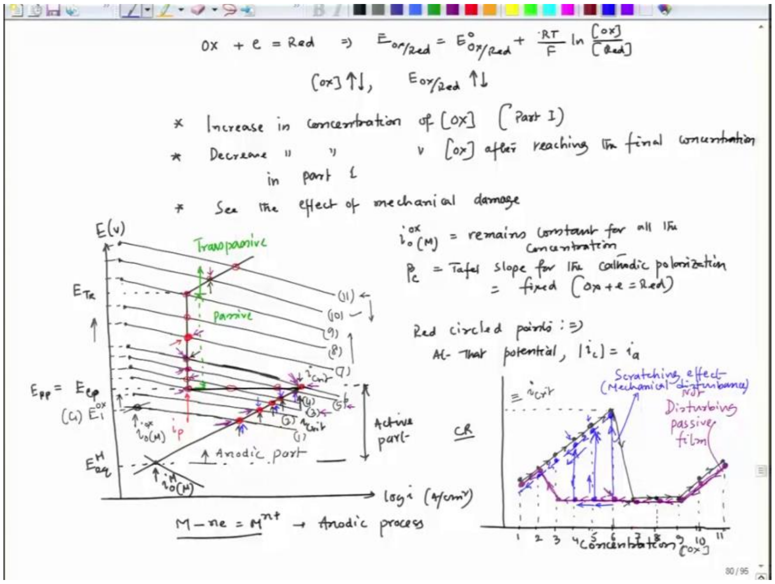

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If we decrease the concentration from 11 till 1, okay. If I try to do that, what will be the situation? Now, if I go to 11 to 1, if I draw with a different color, let’s say I draw it with a blue color. So, in that case 11 the point would I am just drawing by the side of by just below this particular line. So, this is 11 so, it will be here if I do it with this color this will be here and then 10 it will be similar to this will be here when I go to 9.

I could see is it just crossing the transpassive, passive to transpassive zone, the corrosion will be same as that particular current density of that anodic portion, 8 I could see that again that passivity is achieving. So, 8 I will be the corrosion rate this. 7 the corrosion rate would be here because it is at this location. Now, when I go to 6, what will be the situation if I go to 6 that mean at this location as well as this location.

2 points that particular polarization plot for the cathodic polarization is crossing the anodic portions, but since the passive layer has already formed, if the passive layer has already formed, if we do not disturb the passive layer, this passivity will maintain So, it will not reach to the i critical rather it will try to stay at i passive because we are not disturbing the passive layer. So, if it does not disturb, so, then in case of concentration C6 the current density would be at this location.

So, current density would be same as this one, okay. So, now 6 if I go to 5, so 5, I could see the 3 points it is crossing that this particular concentration, but since we are not disturbing the passive layer, the current density will remain here at this location. Similarly, it will be 4 in this case it will be there and 5 if I consider the concentration 3. I could see that it is just at the i passive to active condition zone.

But, still it is having a cut point at the i passive section and it is not disturbed. So it will still remain 5 also it will be here and 4 also it will be here in the closed in the i passive zone and 3 also, if I see 3, this will also stay here, but once we cross 3, i go to 2, then I could see that the Active Passive at this mixed potential theory is maintained at this location. So, the corrosion rate should increase in case of when a go from 3 to 2.

So, the corrosion rate would be at this location and then if i go to 1, the corrosion rate would be at this location. So, the corrosion would be here. So, now what will be the plot the plot nature would be if I go if I see the reverse trend, when I change the concentration, it will follow this track and then it will move like this and then go down. So, the plot nature would be like this. So, in the forward scan going to increase the concentration.

The movement would be like this and the reverse scan, when we change the concentration after reaching that C11 the path the plot pattern will be like this. So, in this case, I am not disturbing the surface not disturbing the passive film. Now, if we disturb what would happen let's say after reaching 6 that means 6, we have this point which is basically the corrosion rate when we return from C11 to C6.

At C6 initially the point is here without disturbing condition disturb condition, but if we now disturb let's say scratch it, the surface is scratched, okay. So, once the surface is scratched, I am breaking open the passive film. So, once we break open the passive film the system would try to achieve the corrosion mixed potential corrosion rate at this location, fine. So, instead of remaining here the C6 the concert the point would reach to this point.

So, the movement would be this once we scratch the surface after reaching 6 C6 concentration and then once it is passive layer is broken, then after that, if you decrease the concentration, it will all is follow this track, fine. So, then it will follow this track it will follow remember these points and this point both are the same location, but just to give you an indication that how the movement happens that for I have drawn it little away from the black spear black point black circle, okay.

So, the location would be so, the movement would be this way. Now, instead of 6, if I scratch it at after reaching C5. So then the concentration then the movement would be this way. So, it will follow this and this and this and after reaching C4 if we scratch it again it will till C4 it there will be nothing there will be passivity with a maintenance of passivity, but at C4 concentration I'm scratching it the moment would be this way.

So, the corrosion rate will move to this location, fine. So, like that way, this is the effect of scratching. So, the blue color is basically the scratching effect or we can say this the mechanical effect mechanical disturbance of the passive film. So, this is the way it should operate in case of Active Passive metal when we change the oxidant concentration from low concentration to high as well as high concentration to low concentration.

So, let me stop here. We will continue our discussion on this very aspect. And will take up two more instances where or case studies where we could see the influence of Active Passive metal and when we have when we consider mixed potential theory. So, let’s stop here. Thank you.