Indian Institute of Technology Kanpur

NP-TEL
National Programme
On
Technology Enhanced Learning

Course Title

Environmental Degradation of Materials

Lecture – 19
Broad Subject: Passivation and Mixed potential theory

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Today we'll continue our passivation, but today we will see the passivation, the subject will be Passivation and Mixed Potential Theory. So we'll see some of the practical examples where Mixed Potential Theory as well as Passivation both will come in picture.

Now we have seen that when you have a cathodic reaction along with the anodic reaction and the metal which is showing anodic reaction or the dissolution reaction, that cathodic reaction actually takes the potential of the metal which is going under, which is basically dissolving to a potential depending on the cathodic reaction either to active region or to a passive region or it can be, you know, in the unstable passivation region. So we have already seen this example, that if you have a passive metal like this where you have started with a freshly prepared surface in an electrolyte and then in case your cathodic reaction is or cathodic polarization is going along this line where it cuts only this portion then it would attend complete passivity. And if the cathodic reaction is going along this line during the polarization this will cut the anodic polarization line at this point, and then if it cuts like this then it would be a sort of unstable passivity, and that case we have already seen that what would be the experimental curve in all those three classes, because when you do experiment that time you are taking the potential of the metal to a higher potential or you are actually doing a anodic polarization that time the actual potential curve with respect to log I would look like, in the first case this is, let's say first case, this is second case and this is third case. First case it would look like, look like this because actually you have to see the difference in currents or difference in current density between cathodic current and anodic current.

Now this is in the first case where this would be your E core. Now in the second case, this is first case, and the second case it would look like, so this would be my reference point where the system will meet to this level, if you leave it free because that time this would be your reference point for the polarization and polarization will be above this point and below this point, so this would be my new equilibrium point where the rate at which electron consumption is taking place would be equal to the rate at which electron generation is taking place, because of anodic reaction that case my curve would look like this.

And another case it would be this case where you have three reference points, so your polarization curve will look like, so I have just extending this three points, it would be like this, so this is cathodic we have seen that this part is called cathodic loop. Now during mixed potential theory we have to see that where this cathodic polarization line is crossing the anodic polarization line, and this is case 2, and this is case 3, where you are attaining this cathodic loop because of this cathodic polarization line is cutting at three positions, one at completely passive region, one at active region, and one at unstable region. But when you consider some of the examples, where you will see that top mixed potential theory and as well as passivation, and then you will see that actually this cathodic polarization line will decide whether the system can reach to this passive region or not, and from engineering point of view this point is very crucial because we have to reach to this level, so that I can attain passivity so that I can control my corrosion current or we can control, we can reduce the corrosion rate to a great extent.

Now in Titanium, intentionally palladium or platinum are added, these are very, very noble metal, highly noble metal, having highly noble characteristic and titanium is very active, initially this either this or this, they are mixed with titanium homogeneously, it's a basically alloy form. Now then we'll see the advantage of titanium and palladium and platinum on titanium and this advantage, main advantage will come from this noble metal because of attainment of passivity due to the cathodic polarization.

Now in case of titanium if you see it's polarization, anodic polarization in acid in air free acid it would go like this, it will have active, passive and passive transformation, this is E versus log I. Now when you have titanium, let's say this is my titanium and platinum, its uniform homogeneous mixture and that is an allied form. Now if you dip it in the acid, now if there is homogeneous corrosion then since platinum is noble compared to titanium there would be a sort of phenomena, that phenomena will be discussed more by Professor Chaudhuri, it's a kind of be allowing phenomena will take place. Well initially both will dissolve, but later on since platinum has higher reduction potential it will again redeposit back. So in the beginning there would be uniform corrosion, finally there will be uniform corrosion and after some time there will be platinum enriched zones, these are basically platinum enriched zones, these are all platinum enriched zone.

Now initially the cathodic reaction that is taking place is hydrogen evolution on the titanium surface since it's an acid medium so that case situation like this where this is my hydrogen evolution on titanium surface (titanium) and my corrosion rate would be this one corresponding to IA = - IC = I Corr, corrosion current density. Now once you have this situation where after some resolution you have re-deposition of platinum on the titanium surface, now you will have that effect of higher exchange current density of hydrogen on platinum surface, the hydrogen I0 of hydrogen evolution on platinum surface is very, very large compared to I0 on platinum, so what would happen this point will slip to this point this is 0 let's say 0V.

Now from there my polarization line will start, but since you have this reaction also going on parallelly on the titanium surface so the finally you have to see what would be my total cathodic reaction rate. My total cathodic reaction rate would be this is my cathodic reaction on platinum and you have to add this thing so after adding you have to see where would be my total cathodic reaction, fine, now total cathodic reaction is given by this red line, let's say this is my IC on titanium surface and this is my IC on platinum surface for this hydrogen evolution reaction, and the red one is this is IC Ti + IC Pt. Now you see initially when there was this reaction only it was cutting in the active zone, now once you have this platinum enriched zone because of de-alloying and re-deposition of platinum your equilibrium point has shifted to this. So now you see initially you are in active region now because of this platinum enrichment on the surface your corrosion current is now this one, so this one is my new corrosion current IA = -IC, I would say total since this red curve line is basically the total of IC on Ti and IC on Pt = I Corr, and this is in log scale, so once you have this platinum enrichment your I corrosion is going to the level of passive region, so you are attaining stable passivity, so your corrosion rate of titanium will reduce to a great extent, this is one example.

And here we are using the mixed potential theory because we are following the two postulates of mixed potential theory, one is there could be n number of cathodic or anodic reactions and at the same time there should be equilibrium or the equal rates for electron consumption and electron generation, so this is that point. This is and that's what if you add this platinum or platinum the palladium effect also will be same because hydrogen exchange current density on palladium is also very large compared to the hydrogen exchange current density on titanium, so you are attaining stable passivity. So this is a sort of advantage of adding noble metal in titanium, but there could be, so this cannot be straightforward that every metal if you add titanium or add platinum or palladium you will get the same effect that means you can achieve the passivity but it may not be. For example in the case two, where I have iron and there I am adding a noble metal platinum, then it's a homogeneous mixture of iron and platinum, now if it is exposed to air free acid then your cathodic reaction would be hydrogen evolution and the same thing will follow, you will have, in case of titanium again you will have platinum enriched zones on the iron surface.

So you have the situation again, this is now iron and on the surface you have platinum enriched zones. Now again in case of iron you have also this kind of situation, this kind of situation it's also an active passive metal, this is E this is log I, but in that case initially the hydrogen evolution reaction is taking place on iron over the entire alloy so that case my hydrogen evolution reaction this is 0V and the I0 position is here. This is iron platinum alloy, I0 position is this one so I'll get the polarization we have to see the polarization cathodic as well as anodic polarization and this is my line where I get I Corr = IA = - IC, but once you have this situation then IH 1/2 H2 on Fe Pt less than, less than I0, this is I0 exchange current density for H on Ti I'm sorry on Pt, so very, very large. So this point would shift to this point, but voltage will not change because we are considering the same reaction, and then accordingly we have to also see that what would be the total cathodic reaction rate, so this is my cathodic reaction rate on platinum, this is my I0 H 1/2 H2 on Pt surface, and this line, this line gives me the idea, if the cathodic reaction rate on platinum, so what would be my total cathodic reaction, because here also this reaction is still going on. So my total cathodic reaction would be you have to just add this two, so this is my total cathodic reaction the red one. Total cathodic reaction rate rather because this is the relation between E and small I, which is the current density. And current density is nothing but the reaction rate.

What would be my new equilibrium point where we have IA = IC? This is my new equilibrium point where this is my I Corr = IA = - IC total, and here you see this is much higher than this. So here though you are getting positive effect because of an addition of noble metal that is platinum in titanium in case of iron it gives the, it gives a negative effect because if you add platinum, because the position of this point with respect to the anodic polarization plot for iron in the air free acid, so here after this situation the allowing and platinum enriched zones on the iron surface, my corrosion rate of iron or that alloy increases very much, increases to a great extent because this is in log scale. So here it gives a negative effect, this is case two. So that means depending on the position of this cathodic polarization start point and the polarization curve for the active passive metal, noble metal addition can be advantageous it can be disadvantages, so in case of iron you should not add platinum because if we add platinum we are going to increase the corrosion rate.

Now this is one, now case three let us also have two more examples. Now one example is, case three, now if you recall that we see that the effect of velocity on the corrosion rate of active metal if it is totally activation control let's say in case of zinc that case my corrosion rate, and this is velocity, as you increase the velocity of the solution or as you increase the turbulence in the solution in case of active metal like zinc it is a flat kind of thing, it remained constant, it remains constant, corrosion rate remains constant if it is activation controlled only, but if it is concentration polarization control for the cathodic reaction then that case my situation would be like this where as you go higher and higher velocity your corrosion rate would initially increase but after some time it will become flat and if you see the mixed potential theory corresponding to this two curves then one situation your curve will meet like this, this is E versus log I and this is anodic polarization, this is cathodic polarization and it is meeting here, so this is my corrosion current.

And second case where we have concentration polarization controlled, this is activation polarization that's why we call it activation control and if you see this, if it is concentration polarization control that time I will have this situation so 1, 2, 3, 4, 4 velocities as we increase the velocity you are going to decrease the delta which is the boundary layer thickness, if you decrease the boundary layer thickness you are going to increase the IL, and IL is nothing but this at different velocities and V4, V3, V2, V1 and V4 greater than V3, greater than V2, greater than V1, and accordingly IL4 greater than IL3, greater than IL2, greater than IL1, now if you see that up to level 3 that means if you increase the velocity to velocity V2 up to 3, third velocity region you see that gradually it's increasing corrosion rate, because corrosion rate is nothing but the point where cathodic as well as anodic polarization lines are cutting, but once you cross V4 it will always cut in the active region and now after that you keep increasing velocity and keep increasing IL or the limiting current density you are not going to have any effect on the corrosion rate. So corrosion rate will be flat, so up to this, this is up to V3 and after that V4, V5 you are going to have constant corrosion rate, because that time always this anodic polarization line will cut the cathodic polarization line in the active zone in the flat zone, this zone.

So now we have this situation, there we saw one type of metal it can show this kind of variation let's say this is my corrosion rate there I can have this situation initially it will increase and then after reaching some value critical value or some value of velocity it will suddenly drop and then after that you will see that it's almost constant, so what could possibly be the reason for this phenomena where this is my velocity, in order to understand this that time I mention that we need to understand the passivation basically this curve relates to two phenomena, one is concentration polarization for cathodic reaction + passivation. So these two things will combine together and then give you this sort of corrosion rate.

How would we do that? Let us see that example, let me draw it on top of this again this potential versus log I, now I know the position of anodic polarization line of that metal, that metal let's say particular metal M its situation is like this, fine, this is my active passive metal. Now I have the cathodic reaction let say my cathodic reaction is starting from here, and I have this is my activation part of that polarization for that cathodic reaction, and then I will see that once I reach to a value, i value where if I find that cathodic concentration polarization is starting so my, I will reach to the level of IL at that velocity, so this is my IL1. So what would be my corrosion rate? Corrosion rate would be this one, so let me go there and start plotting that, that case my corrosion rate would be let's say this, let me put it in red color just on the side of this, this is my corrosion rate corresponds to this.

Now I increase the velocity, as I increase the velocity IL would increase so I can reach to the last level, so that case this is IL2 this is my corrosion rate because that point I have IL I Corr = IA = - IC, so this I would further increase the corrosion rate because I see that there is increase in current density from here to there. Now I can further increase the velocity or the turbulence in the system so I can reach to this level. Now the point is I am cutting this active polarization curve, anodic polarization curve at three position, one position is this, this another position is this, another position is this, so it can either remain here, it can either go there, or it can either go there, so it is cutting in the passive region, in the active region and also in the unstable region.

Now the point is we have started with freshly prepared alloy, or some metal, if it is freshly prepared metal then the anodic polarization will happen on the basis of the cathodic polarization. Now the cathodic polarization is cutting the line first at this position because now it's already in active state, there is no surface layer if there is no surface layer until unless the material reaches here, the metal reaches here it cannot form any passive layer, it cannot have any passive layer on this metal, so it will still remain active, so that case if you start with a fresh metal then my corrosion rate would be this point and other two points will not be considered, so my corrosion rate again I am increasing, so my corrosion rate would be this. Now as I keep increasing, keep increasing I see that this lines, this cathodic polarization line is cutting at three different, four different positions. Let's say this point see again I am increasing because current density is increasing, this point current density is increasing, this point current density is increasing, now at this point now I see you please this point is very critical, because this point IL = IC, I is critical, not C it's a critical, I critical that means this is also corresponding to I critical off that cathodic current density, so this is a very, very crucial point because at this point I further increase it to this, so if I add it up I am seeing that corrosion rate is increasing with the progress in velocity, and at this point I have this point correspond to this because that point only gives you the rate of electron production generation would be equal to the rate of electron consumption, because of the cathodic reaction.

Now see if I increase the velocity little bit, increase the velocity little bit, so I am changing this plot little increase the velocity little bit, I see that this cathodic polarization line is cutting this anodic polarization line at this point, so if it is cutting at this point and it's not cutting any where this curve let me put it the red one, this is my critical and this is my, this red one is the velocity which is, this velocity let's say this velocity is 1, 2, 3, 4, 5, 6, 7, 8, velocity 2 is greater than velocity critical, this is basically correspond to velocity 8.

Once this velocity is attained, I see that this cathodic polarization line is cutting the anodic polarization line in the passive zone, this zone and it's not cutting anywhere and since we have started with the freshly prepared surface without any surface oxide layer or the surface film initially it will keep increasing but once we have this situation we will suddenly go to the passive zone. So once we go to the passive zone what would happen, my corrosion rate here it was this correspond to I critical, now once we increase the velocity from V critical to V8 I will come to this point. Now if you compare this two points, it's having a very, very low corrosion current, so I'll reach to the level, this is my new corrosion current I Corr and I am putting P here because this corresponds to the passive zone, and this would lie between second point and third point. So the second and third point, this is my third point and this is my second point, so it will immediately drop to this point, and this point corresponds to I Corr P, and after that you keep increasing the velocity, what will happen? This will always cut at this point, so my corrosion current will always remain constant so the corrosion current, corrosion rate would be constant after that.

So this is actually what is happening, if you have both this combination, and accordingly we can explain the other graph what we have, what we could not discuss, we could not explain at that moment, so this is the explanation for this to happen, and the mixed potential theory actually explains this. Thank you.

Let me give one more example, Case 4, let's say you have a metal which is active passive metal where you have your polarization plot, if you do anodic polarization for that E versus log I and that case my polarization plot would be like this. Now this active passive metal you have in that particular aqueous medium or electrolyte now along with that you are adding, in that case you have cathodic reaction which is coming from some oxidizer, and let's say you keep adding the oxidizer into the solution that means we are basically increasing the concentration of oxidizer in the solution, so that case I can have this relation which is ox/red the Nernst equation E0 ox/red + RT nF Ln ox/red, now if you increase this concentration of oxidant or oxidizer in the solution you are going to increase this one, if it is at 1, no problem reduction potential would be equal to the reduction potential at standard state, but if you keep increasing the oxidizer and let's say if you have started the concentration of oxidizer in the solution at much lower value, and if you keep increasing this, this potential will keep moving up, so initially I have started with this some concentration where my potential, this potential is basically nothing but, why I start with this at some particular concentration, and I'll have to see where my cathodic polarization line is cutting the anodic polarization line, so accordingly this would be my I Corr.

And let me plot that at this point, this is let say corrosion rate Corr rate as a function of concentration, as a function of concentration of the oxidizer. So this is my I Corr and corr rate is nothing but the current density, I can also have because I Corr proportional to corrosion rate, we have already proved that and there is some time, there will be a constant term, constant term with this.

So now that point let's say it's coming here, let's say this is my point corresponds to this let me put it as 1, this is my 1, now as I increase the concentration of oxidizer, my potential is gradually lifting and then from that point and I0, let us assume that I0 is changing I0 will remain same at this level because we are not changing the metal, now it will also have its parallel polarization, activation polarization for the cathodic reaction, so this is point number 1, this is point number 2, so I see that concentration corrosion is using, so this would be my point number 2.

Now I can have a situation where I increase the concentration of oxidizer in such a manner so pressure line is cutting, cutting this anodic polarization curve at this point, where I attained which is the current corresponds to I passive and it's just crossing, it's the kind of tangent to this curve at this point. So this case -- I will see because I have started with a freshly prepared surface, so it cannot reach there rather it will remain here, because I don't have the formation a passive layer, so my corrosion rate let's say this is my point corresponds to 3, my corrosion rate would be let's say 3. Again, I – further so at this line at three different positions 1, 2, 3,one is passive zone, one is unstable passive zone, and one is – zone and since we have started with the freshly prepared surface it will remain here because it cannot remain here because either it can go there or there because this is unstable zone, but since we have started with the passive active, since we have started with a freshly prepared surface where do not have any existence of oxide layer so it will remain here, so my corrosion rate again further increase, so this is the point corresponds to 4, so this is my 4 point.

Now I raise this concentration in such a manner I cut this point, cut this anodic polarization line in the critical zone, so that time I will have this point as well as this point but since we have started with freshly prepared surface at this point I have that equilibrium between the rate at which oxide layer is forming and the rate at which metal dissolution is taking place, so this point is still unstable, so I can have, still this I cannot reach there because since its unstable zone I will reach here because we have started with freshly prepared surface, again my corrosion rate increases so this is my 5th point which corresponds to 5th which corresponds to I critical.

Now beyond that if I increase the condition little bit, I can bypass this point, once I bypass this point I see that the cathodic polarization line is cutting the anodic polarization line curve at this point which is the stable passive zone. So now see here it was the earlier case, it was 8 which corresponds to 5, now once we reached to this level of concentration and seeing that the corrosion current or the rate of corrosion is in the passive zone and this is my I passive = I Corr = - IC. And I see that from here to there, there will be huge drop in the current density corresponding to the corrosion current density. So my corrosion rate would come down, it would come down to a large extent, it will be here because it will, this value is much lower than this value so it will drop here.

And after that if we increase the polarization concentration I'll cut this line at these points, so this is my point number 6, 7, 8, so up to 8 I see that it's cutting the anodic polarization in the passive zone, so from 6 to 8 I will have a constant current density for corrosion, so I am not changing the current, because it's on the vertical line with respect to the log IX, so this is my 6 point, this is my 7 point, this is my 8 point, so I'll connect this all those points and I see that my corrosion rate is raring like this, if you have started with freshly prepared surface.

Now if you increase it further, now you'll see from this to this let's say this is my 9th point where it cuts the cathodic polarization line cuts the anodic polarization I see that there is increase in corrosion rate, so my corrosion rate point, this is my 9th point see that from here to there my corrosion rate is increasing from this to this, so my corrosion rate would increase. Now if I increase the concentration further cutting I'll cut line this is the point, this is my 10th point so I have, this is the variation of corrosion rate.

Now let say I will get back, now initially I increase the concentration now let me decrease the concentration from this point onwards. If I decrease the concentration as the way we have increased the -- of the oxidizer it will also follow the same track, now let's say I is the concentration in such a way the line cathodic polarization line is following this track, then I will get back to 9 position which is corresponding to the corrosion rate. Now if I get back to 8th, I'll come to this, if I get back to 7 by decreasing the corrosion rate, because in the oxidizer concentration of oxidizer, I'll get back to this like this I will go up to 6th, up to 6th let me go back.

Now once we have this, let's say I have come back to the constant corresponding to this line, now there is an important phenomena that is going on. When you are coming back from this to this, I'm getting back to the passive region, so if I am in the passive region and it's all completely covered then it will, in this case it will remain here, it will not reach there because already we have the passive zone, passive film so it cannot break like this, so here it cannot break, so the passive zone will remain or passive layer would remain and the corrosion rate would be at this point, because it cannot reach there, because we have already have the passive layer.

While we have started from here then as we move gradually so up to this point we didn't have any passive layer, but when we are starting from top we are up to this point we are having, at this point also we are having the passive layer so it will remain, here the corrosion rate will remain here. So five situation in case of five also it will remain there, what would happen to the 4? So forth also, it is cutting at three regions, now since we are cutting at passive zone either go there or there but since we have started we have already existence of passive layer it will remain here, my corrosion rate that case will come correspond to the 4 position it will come here.

Now gradually if I go to the 3rd level it will still remain here because I am here its, I passive is just touching so I can still remain there. My corrosion kind while, while going it's following this track, while coming this is following this track, this track. Now once we come to this level we see that only this zone an active zone, so that case the passive layer will break and it will get back to this point. And then if you again decrease it will follow this track, so while going it is following this track while coming this is falling like this, but at this point we are still having the passive layer it will remain passive and when we are reaching to the second level the concentration corresponding to this line we have, thus have passive layer is broken and I have the corrosion rate which would reach to the second level and accordingly if I go back to this concentration which corresponds to this line then it will come back there, okay. So that means depending on your situation where from you are starting, if you are starting with a freshly prepared surface you have to see where we are attaining the complete passivity, and if you are starting with passive layer, already passive layer, then we have to see where we completely where we completely remove the situation where we do not have any cross linking or cross crossing of this cathodic polarization line with the anodic polarization line in the passive zone, fine, there we will go back to this point.

Now this exactly happens in a Faraday's situation, Faraday's experiment, what he did initially you have concentrated HNO3, you have a put iron surface in that case it is attaining passivity and that thing you are taking it there and you are putting it in concentrated in dilute HNO3 it does not have any reaction, so what is happening? Actually you have reached to this level and now whether you decrease concentration of oxidizer it doesn't matter because you are already having the passive layer. But now whatever let me give one small note here at position 5, at position 5 this corresponds to this corrosion rate, let's say let me put it as 5 dust, this is 5 dust so while coming back it will remain here, but at this point let me put us, let me give a scratch on the metal, if I give a sketch if I put a scratch on the metal what would happen? Now we have exposed the passive layer, and we have exposed the fresh surface of the metal, so that case it will no longer remain in passive region, it will go back to this, so if it is scratched it will go back to this that it'll form 5 dust to 5 it will reach. Let say in case of this level of concentration if I put a scratch then from here it will move to this place, so that case it will move this level, so like that the scratch effect also is coming in the Faraday's experiment where if you second case same dilute HNO3 you put the sample iron passivated iron piece with some scratch, with some scratch you will see that vigorous bubbling is forming because now you are no longer remaining in the passive zone, rather you are going to that active zone, so this is the effect of oxidizer on the corrosion rate of active passive metal.

Acknowledgement
Ministry of Human Resource and Development

Prof. Phalguni Gupta
Co-ordinator, NPTEL IIT Kanpur

Prof. Satyaki Roy
Co Co-ordinator, NPTEL IIT Kanpur

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Jai Singh
Sweety Kanaujia
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Sweta
Preeti Sachan
Ashutosh Gairola
Dilip Katiyar
Ashutosh Kumar

Light & Sound
Sharwan
Hari Ram

Production Crew
Bhadra Rao
Puneet Kumar Bajpai
Priyanka Singh

Office
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari
Saurabh Shukla

Direction
Sanjay Pal

Production Manager
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an IIT Kanpur Production