Corrosion - Part II
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Lecture - 32
Anodic Protection of an Active-Passive Metal and an Introduction of Linear Polarization

Hello everyone. Let's start lecture 32.

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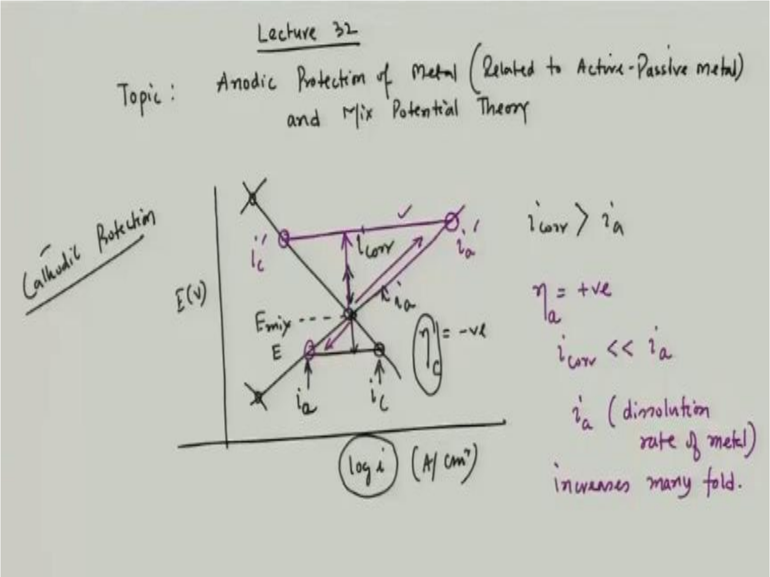

Lecture 32

Topic: Anodic Protection of Metal (Related to Active-Passive metal) and Mix Potential Theory

$i_{corr} > i_a$

$\eta_a = +ve$

$i_{corr} << i_a$

i_a (dissolution rate of metal) increases many fold.

Now, in this case, the topic will be anodic protection of metal which is related to active-passive metal and its analysis. And I would say, and a mixed potential theory. Actually, we will be, we will try to have reasons on the basis of mixed potential theory, why active-passive metal can be anodically protected. Now, as we have seen in case of cathodic protection, the theory says the mix potential theory says, if you see the cathodic protection.

So, this is E volt. And then, this is log i ampere per centimeter square. Now, that case, we have interacting active metal interaction and with cathodic reaction. So, this is my ia, this is ic. And this becomes i corr. So, respective points; we know what are those points. Now, the theory says in case of cathodic protection; once you get a stable E mix corresponding to i corr; if you reduce that potential, okay; so, if you go downwards, that means, we are going, our this becomes negative or over voltage becomes negative.

So, that becomes, that is what this becomes cathodic over voltage. So, when you, let’s say from this is the stabilized potential. And then, if you go downward, then you will see, that if you keep the potential at this location, you could see that your cathodic reaction on the metal surface increases, because ic would be here; but corresponding ia would be at this location. Now, if we compare i corr and ia, we see that i corr is > ia.

Or I would say ia is lower than i corr, that means the corrosion rate or the dissolution rate as indicated by the anodic current density decreases drastically since this is in log scale. So, this is the cathodic protection. But if I go positive direction, that time situation becomes different. If I go positive direction from the stabilized E corr or E mix, I could see that, if I go this way, I could see that this line I have to extend.

And now, let’s say, I have reached this particular potential. And interestingly, i see that the ic on this particular metal surface would be here. That means the ic decreases. But if we see ia prime or ic prime, i in this particular case where neeta equal to positive or it becomes anodic over voltage; then i corr would be much lower than ia. So, that means, ia or dissolution rate of the metal increases many fold, fine.

So, that means, in case of this active metal, if I go positive side, that means anodic polarization. Then I would always increase the corrosion rate or the dissolution rate of the metal. So, no way I can protect that metal. But if I go downwards, if I go cathodic polarization; that is what the cathodic protection name comes in. So, I could see the corrosion rate can reduce from this to this.

But if I go positive side, corrosion rate increases from this to this. So, if we follow anodic polarization in case of active metal, I will never be able to protect the metal. Rather, I would always increase the corrosion rate. But this situation would be different if we follow active-passive metal. So, in case of active-passive metal, if we draw the active-passive metal anodic polarization part.

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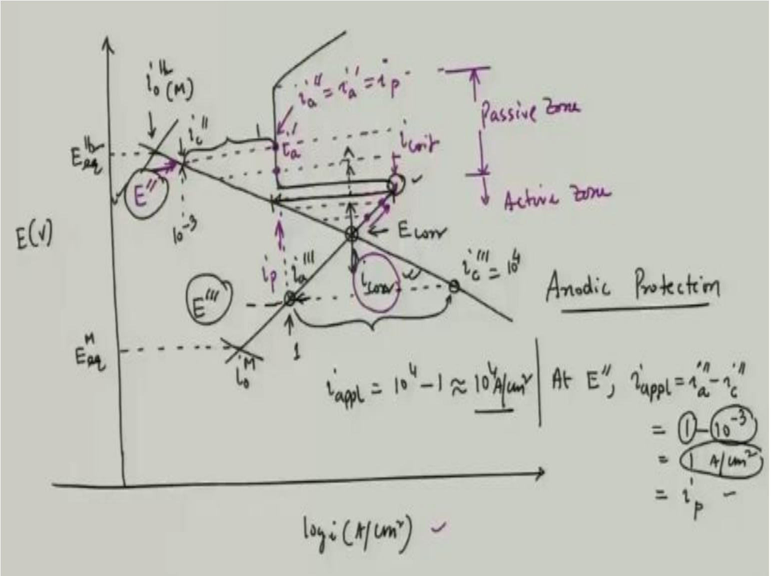

So, let me draw that. So, let's say there, this is the anodic polarization part. Let's say this becomes my E equilibrium of that metal. This is i zero of that metal in the solution. And let's say hydrogen evolution is the my cathodic reaction, okay. So, somewhere we have the hydrogen evolution reaction happening at this location, let's say. This is the location, okay. So, this, let's say this is the location, okay.

So now, if I see the, if I try to see this location. So, now if I draw the cathodic polarization plot; so, this becomes my cathodic polarization plot. And let's say this becomes my E equilibrium hydrogen. And this is i zero hydrogen on that metal surface. And this is of course potential. And this is log i ampere per centimeter square. Let me extend it little more. Now, my natural or steady state corrosion potential is this.

And current density corresponding to corrosion rate of that particular metal, active-passive metal is at this location. I can go down for cathodic protection. But if I go up from that E corr. That means, if I go anodically, if we follow anodic polarization. Let's say I am going this way, okay. And gradually, I am moving upward, okay. If I increase the potential from that E corr, that is the steady state potential.

So, I see that, if I follow that, I see that gradually I am increasing the corrosion rate, because ia is gradually moving this way. So, finally it reaches to i critical which is the maximum current density that is possible in this particular situation. And then, once I cross this i critical, let's say potential comes to this location, fine. Now, that time, my ia is; let's say this is my ia prime, is located in the passive region.

And similarly, if I follow that anodic polarization further, I could see that ia is still, this is ia prime, double prime, which is equal to ia prime equal to i passive. So, that means, I could see that the corrosion rate is not changing; which is indicated by the anodic current density. Because, once I take the potential to this particular location, I always have the current density corresponding to the metal dissolution situating in the passive region.

Since, this particular zone is the passive zone as per this particular drawing. And below this, it is basically active zone. Now, if I can keep the potential at this location, okay. So, if I can keep the potential at this location, that is say, let's say this is E prime, double E Prime; if I keep E double prime, let's say corresponding to i double prime. So then, I could see that the corrosion rate of the metal would always be as same as the i passive.

Now interestingly, if you see that, initially when I go for anodic polarization, corrosion rate increases, reaches maximum at i critical. And if we increase the polarization further, that means anodic polarization, I could see that the corrosion rate becomes i passive. That means, the corrosion rate, what it was in the steady condition which is i corr, it has gone to the i passive, okay.

So, the corrosion rate has decreased to a great extent, since this is the log scale current density axis. So, this is the very concept of anodic protection. Now, even if we do anodic polarization, instead of increase in corrosion rate, as we have seen in case of active metal which is this incident. Here we can experience reduction in corrosion rate. And that is what this is called activation or cathodic anodic protection. Anodic protection.

Now, interestingly, if I try to see the current requirement at this particular location when the potential is E double prime. I can also find out that; let's say this particular current is almost about, let's say about 10 to the power minus 3 let's say, okay, ampere per centimeter square. Now, at this location, let's say the current density is 1, okay. So, that means, it is 10 to the power zero.

So, that means, this is 1 ampere per centimeter square. Let's say this is 1 ampere per centimeter square. So, that means, the current requirement when the at E prime, double prime, i applied would be equal to ia double prime minus ic. Let's say this particular current density is ic double prime. ic double prime becomes 1 minus 10 to the power minus 3 equal to 1 ampere per centimeter square, okay.

So, this is the current amount. You need to pass through that particular circuit, in order to have the potential maintained at E double prime. And that time, corrosion rate would be same as this becomes i passive too. Because, these particular cathodic current density is very low compared to the anodic current density. So, it will be least felt. Now, if I try to achieve the same current density corresponding to if I follow cathodic protection; so, that means, from the steady state E corr, if we go down, I can reach to this potential, okay.

So, this is let’s say E triple prime potential where I have reached, if I follow cathodic polarization. So, then I would see that, that case, my ic triple prime is this one. Let’s say this value becomes 10 to the power, let’s say, it becomes 4, okay. And this particular current density, of course this is equal to ip, which is 1 ampere per centimeter square. So now, that case, what would be the i applied.

In that case, the i applied was this much. But in this case, i applied would be this much, which is, would be equal to 10 to the power 4 minus 1; would be equal to 10 to the power 4 ampere per centimeter square. Now, when if we follow cathodic polarization, I can reach to this E triple prime potential. That time, the corrosion rate would be equal to the ia triple prime, which is at this particular location.

And that would be the dissolution rate of that particular metal. But if we see the total current requirement for that circuit is 10 to the power 4 ampere per centimeter square, which is a very, very large current requirement. But here, if we follow anodic polarization and if I reach E double prime potential, I see that the current requirement which is i applied would be only 1 ampere per centimeter square.

So, that means, in case of active-passive metal anodic protection becomes beneficial economically, because I need a lesser, much lesser current flow in the circuit, for getting the same degree of protection. So, there it helps. So, this is the very concept of anodic protection. And this particular anodic protection is always applied for active-passive metal. And here if you see that, if we allow that particular metal to be in open circuit condition, the corrosion rate of course will be this, okay.

So, that means, here you have to forcefully take the potential to E double prime, so that I could experience the reduction in corrosion rate, because of the very interaction of that potential line, potential region, potential plane with the passive zone of that particular active-passive metal. Now, if I try to see this, of course, in the beginning of the polarization, I have to go through this i critical, that is the maximum current density.

So, in the beginning of the process of anodic polarization, I do need a very high current flow. Because, if I see i critical, the total current density requirement would be this much, which is very large current density requirement, which becomes my i applied. So, in the beginning, it will be very large current environment; but once we cross that particular barrier of high, large current, then I will be needing a very, very small current in the circuit, for getting a very, very good protection of that particular metal.

And that happens because of the passive film formation on that particular metal, at that potential which is E double prime. So, this is the concept of anodic protection and as well as the comparison with the cathodic protection. So, in case of active-passive metal, it is always better to have anodic protection, if of course we have a very cheap source of electricity. But if we try to follow the same protection in case of cathodic, by doing cathodic protection in active-passive metal, we will be needing supplying all the time very large current density.

So, that way, the cathodic protection becomes disadvantageous in case of active-passive metal. So, this is about active-passive metal, passivation and mixed potential theory interaction. So, we will not go further. But there could be many other things that can be talked about. For example, we have talked about that passive film or the passive region. We see a transpassive zone. But there could be possibility that sometimes in the polarization graph, you might find some hatches, some;

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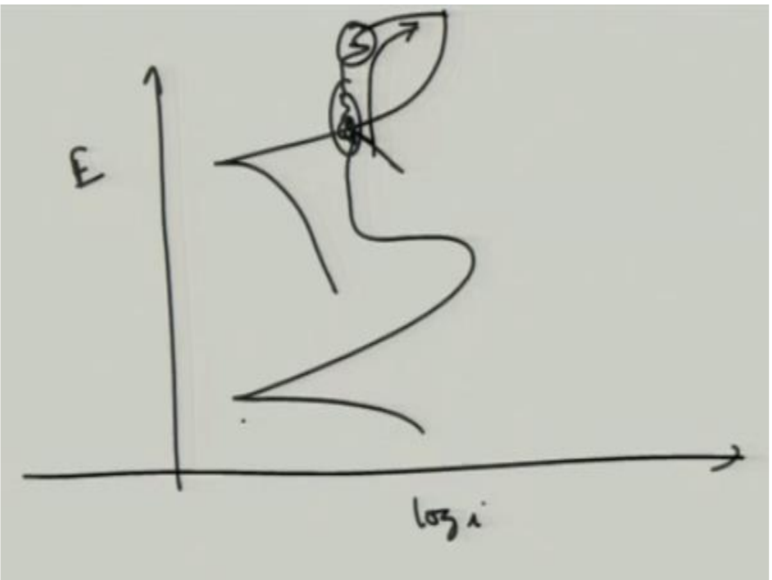

If I try to see the polarization graph, the experimental peroration where E versus log i is plotted; you might find a plot like this. So, those particular noises, they could be indicative of metastable pit formation, okay. So now, those metastable pit might, one of those metastable pit can grow and form a stable pit. And then, that stable pit keeps on increasing with the increasing potential.

So, in there are techniques called potentiostatic technique; there are techniques called potentiodynamic cyclic potentiodynamic test, where you can sense where is that particular potential where I can start getting those metastable pit. Now, if I try to see this particular graph, the pit has growing, pit has growing. And then finally, it is failing. That for particular metal, passivation is breaking.

And that is what you have a transpassive zone. There could be cyclic polarization. A cyclic polarization graph could be like this. So, that time, this could be the point which is basically indicative of the repassivation potential. So, we are not getting into those complications. So, let’s confine our discussion on the active-passive metal and its interaction; and how with different cathodic reactions; and then, whether we can analyze those data with the help of mixed potential theory.

So, we have discussed a corrosion events on the basis of mixed potential theory. And for that, we have considered 2 aspects. One case is when the metal is active throughout. Another case is when metal is active-passive. And there are situations like the corrosion is controlled by activation processes at the metal surface. That means cathodic as well as anodic processes are all in the activation mode.

That means, that can be explained by Tafel equation. And in another situation where we have considered active metal; and the cathodic process will be concentration controlled. And that we have seen in case of a metal corrosion when the velocity is changing. Then in case of active-passive mode, we have considered in active-passive as well as active metal, we have considered effect of galvanic coupling with a noble metal.

And when we have galvanic coupling with a noble metal, the active metal corrosion increases as the i zero, that means exchange current density of the cathodic reaction increases on the noble metal surface. But, in case of active-passive metal, there could be situation where, because of the galvanic coupling with a noble metal, the metal can reach passivity. And that could be a case where we have considering case of titanium-platinum alloy, where titanium passivates because of galvanic coupling of titanium with platinum.

But, it may not be the same for a situation where iron is galvanically coupled to platinum, in a situation where iron also shows active-passive transformation. But, if it is coupled with platinum, that time, the corrosion process will be all the time activation controlled, but it will not reach the passive region. So, those are the typical considerations we had. And also, we have understood from the active-passive, this mixed potential theory, the concept of cathodic as well as anodic protections.

In case of cathodic protection, we have to go for these particular type of protection in 2 ways. One is impressed current cathodic protection. Another one is sacrificial anode. But both the cases will be applicable to an active metal. But, anodic protection, that means, the metal can get protected if the polarization happens in anodic site. That time, that kind of protection can be possible if the metal shows active-passive transformation.

Otherwise, it will not be possible to protect any metal anodically. Now, once we understand these things, only one small consideration we will have. That is called linear polarization. And in case of linear polarization; we will talk about linear polarization.

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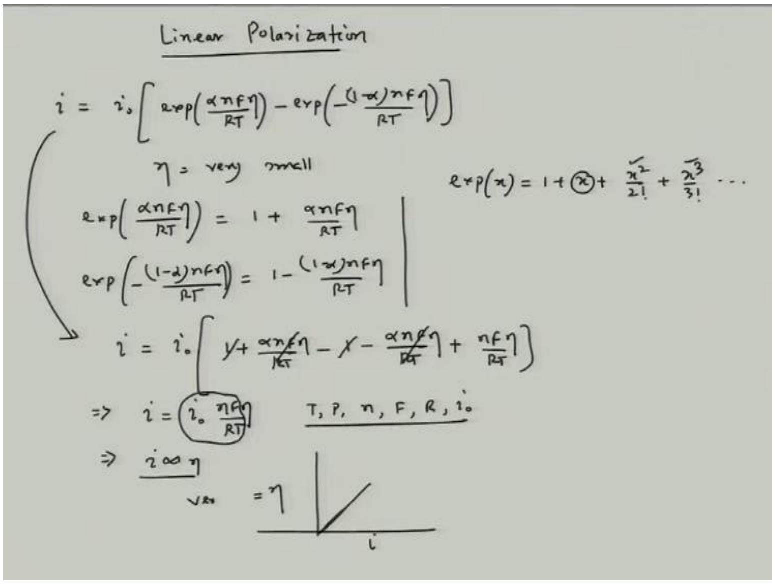

Linear Polarization

$$i = i_0\left[\exp\left(\frac{\alpha nF}{RT}\eta\right) - \exp\left(-\frac{(1-\alpha)nF}{RT}\eta\right)\right]$$

η = very small

$$\exp(x) = 1 + \textcircled{x} + \frac{x^2}{2!} + \frac{x^3}{3!} \cdots$$

$$\exp\left(\frac{\alpha nF}{RT}\eta\right) = 1 + \frac{\alpha nF}{RT}\eta$$

$$\exp\left(-\frac{(1-\alpha)nF}{RT}\eta\right) = 1 - \frac{(1-\alpha)nF}{RT}\eta$$

$$i = i_0\left[\cancel{1} + \frac{\alpha n\cancel{F}}{\cancel{RT}}\eta - \cancel{1} - \frac{\alpha n\cancel{F}}{\cancel{RT}}\eta + \frac{nF}{RT}\eta\right]$$

$$\Rightarrow i = \boxed{i_0\frac{nF}{RT}}\eta \qquad \underline{T, P, n, F, R, i_0}$$

$$\Rightarrow \underline{i \propto \eta}$$

And once we consider this, then we will close our discussion on this corrosion. And then we will catch up with the high temperature oxidation. So, in case of linear polarization, if I see the Butler-Volmer equation which is

$$i = \ i_o[exp\ exp\ \left(\frac{\alpha nF\eta}{RT}\right) - exp\ exp\ \left(\frac{(1-\alpha)nF\eta}{RT}\right)]$$

If we see this equation, where of course alpha is a symmetry factor; n is the number of electrons involved in that reduction or oxidation process; F is 1 faraday; R is universal gas constant; T is temperature; and neeta is basically the over voltage.

Now, if neeta is very small, that case, I can expand

$$exp\ exp\ \left(\frac{\alpha nF\eta}{RT}\right) = \ 1 + \ \frac{\alpha nF\eta}{RT}$$

Whereas,

$$exp\ exp\ \left(- \ \frac{(1-\alpha)nF\eta}{RT}\right) \ = \ 1 - \ \frac{(1-\alpha)nF\eta}{RT}$$

In, this is basically expansion, we know that exponential x can be written as

$$exp\ exp\ (x) \ = \ 1 + x + \frac{x^2}{2|} + \frac{x^3}{3|} \dots \dots \dots$$

So, if we follow this and if this x is very small, we can neglect, ignore the higher order term. And then we get these, only the first 2 terms if we take. And then, if we do approximation; then, we will see that, it will become

$$\left[1 + \ \frac{\alpha nF\eta}{RT}\right] - \ \left[1 - \ \frac{(1-\alpha)nF\eta}{RT}\right]$$

So, all the term cancelled. So, finally I get this

$$i = i_o \frac{nF\eta}{RT}$$

So now, this term, if we consider a fixed temperature pressure in F, R, even i zero; all are constant for a particular process.

Then, I could see, this i proportional to neeta. And that means, if I try to plot i versus neeta, then I will get a straight line plot. So, this is possible if this is very small, fine. So, this is the concept we will be using in order to explain or in order to get the relative corrosion tendency of 2 metals in a particular solution. So, we will take it up in our next lecture, this linear polarization part.

And then try to understand the relative corrosion tendency of metal in an electrolyte. And in fact, we will be trying to understand the polarization resistance. So, let’s stop here. We will continue our discussion on this linear polarization in our next lecture. Thank you.