Corrosion – Part II
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Lecture – 22
Theory of Passivation: I

Let’s start lecture 22.

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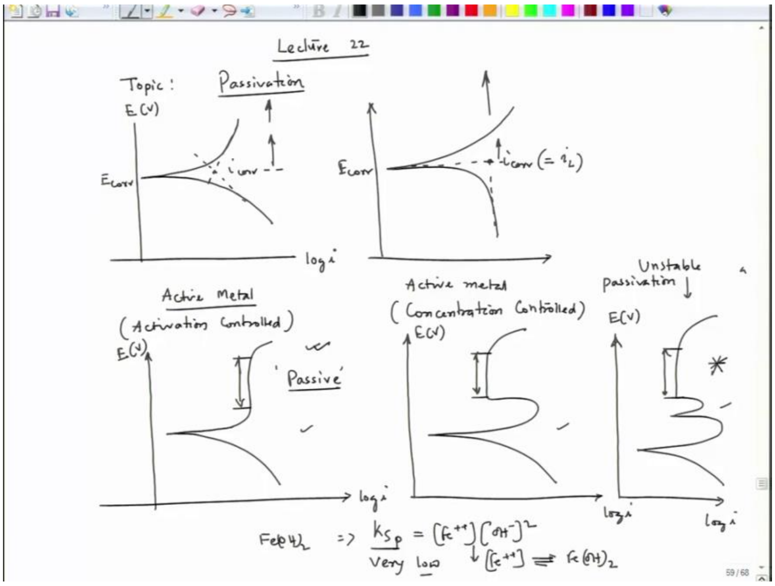

And our discussion for today's lecture is Passivation. We started our discussion on passivation, the later part of the last lecture.

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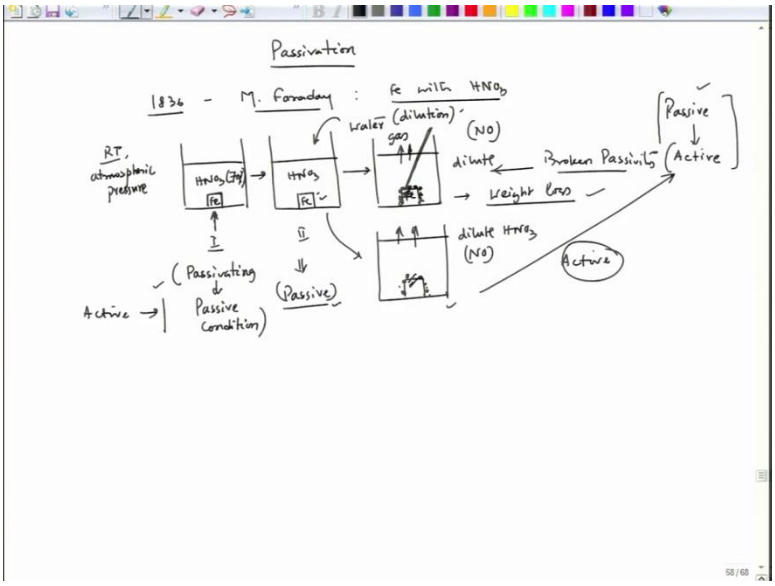

And, where we discussed about the very experiment what the great Faraday. That means, Iron with a HNO3 solution. You can have a strong solution and dilute solution and then we could see that there is a transition from active to passive as well as passive to active because of some actions taken on that. So, we could introduce the passivity. Now, while we talk about passivation.

We have already talked about the stainless steel where it passivates even Iron also does passivate, the experiment what Faraday did, is talking about the passivation of iron. There are other metals like titanium, chromium, aluminium, they are nickel, copper, molybdenum they are very strong passive metals. And if they even silicon is a very passive matter if they are present in Iron. They can lead to passivation, okay.

So, that means corrosion rate reduces greatly in certain electrolyte containing those elements. And if we perform polarization test that means if the metal is forcefully taken to a positive potential that means, if we forcefully take the potential to the anodic side and that indicates that if we do anodic polarization, we can see several forms of the polarization graph. In case of active metals.

The polarization graph if we understand the polarization graphs looks like log i E volt, the polarization graph looks like this. This is the kind of polarization we experience for active metal, where this point is E corr and then you can draw a straight line and then get i corr, fine. So, this is the polarization plot you get for the active metals this is for active metal.

And in case of active metal one type of polarization graph could be like this. Like this one can see. So, this is activation control and this is for also active metal and there the corrosion rate is this is E corr and this point is i corr = iL and this is concentration controller, fine. So, these are the plots we could see.

But in some certain metals if we extend the positive part, so, if we try to see this part, this segment if I extend it further, what some interesting patterns or noticed. The one pattern could be log i E volt, one pattern could be like this, another pattern could be like this. Now, there is one more pattern, which we will discuss later, but just I am just drawing it for your understanding and for your reference.

One more pattern could be like this. So these are the kind of patterns you will experience when you change potential and then see the current response. In all the three cases, I could see that between these two points current value does not change. And these two these segments, where the current values are not changing, these are the typical regions for passivity.

So, these are the region these segments are called passive regions. Where the current density does not change with the change in potential. So, if we analyze those segments carefully, we will see that some layers are forming on top of it and the layer formation layers could be, layers in the form of some complex forming with the reaction of the metals reaction of the with the electrolyte or it is forming due to the influence of the pourbaix diagram.

For example, lead forming lead sulphate H_2SO_4 where the lead sulphate is the product because of the reaction between lead at H_2SO_4. But when we have iron in H_2O without having any other radicals or ions except H_2O there is nothing. And if you start with pH seven, we could also see the passivation mode the constant current zone with the variation in potential. So, there also passivation happens.

But, that happens because of formation of complex oxides hydrated oxide or oxides or hydroxide and that is basically having relation with the pourbaix diagram of iron and pourbaix diagram is nothing but the real the potential pH diagram for a system where metal and H_2 are present that means, the influence of H + iron on the metal for the formation of different oxides hydroxide.

And those oxides and hydroxide if they form on the surface and the surface is then protected from further dissolution, because, for the dissolution, you need freshly exposed surface for the ions to come out from the surface to the electrolyte and once oxide form this oxides have very low solubility and that means the dissolution will be decided by the solubility product of those oxides.

Or, the complexes what are forming on the surface. So, that solubility product will decide how much of metal ion will dissolve into the metal. Just to extend our discussion on solubility product for example, we have if FeOH whole 2. So, the solubility product which is KSP is decided by product of a Fe + + and product of OH - square. So, the concentration Fe + + and OH double - that is the solubility product.

And, if it is very low so, that means the concentration of Fe + + in equilibrium with FeOH doubles 2 that is Fe-Hydroxide iron hydroxide will be extremely low. So, that means the amount of Iron which is going into the solution will be extremely low too. So, that means the dissolution rate with time the dissolution amount with time that means the rate of dissolution will be decided by the solubility product.

So, that condition we say that the metal is passivating, okay. So now, when you talk about passivation. So, we always refer this kind of graphs. And of course, this particular graph is our typical graph which confuses us that way that the metal is attaining impassivity or not. So, when we experience this graph this has a origin we will talk about that origin.

Why these graphs happen appears we call it unstable passivation this particular segment is called unstable passivation and this is these two are forming stable passive state this is spontaneously passivating this particular segment is spontaneously passivating. So, when we get to the passive segments.

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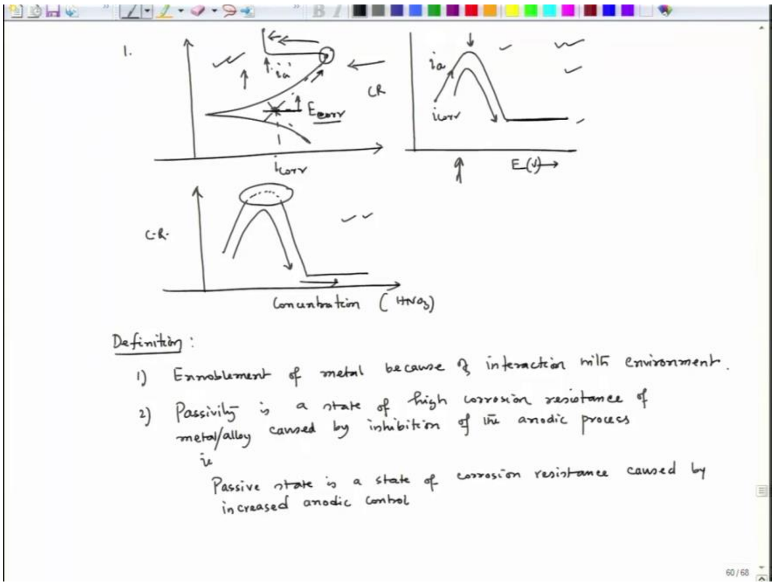

Definition :

1) Ennoblement of metal because of interaction with environment.
2) Passivity is a state of high corrosion resistance of metal/alloy caused by inhibition of the anodic process
ie
Passive state is a state of corrosion resistance caused by increased anodic control

We could see that some of the statements related to the passivation. Let's point those they said it has mentioned those statements. The first statement is the corrosion rate, if we try to draw corrosion rate. So, when we try to see the corrosion rate if it is active passive, if it is active metal, so, corrosion rate will be here, fine. So, that means the reduction in corrosion rate is happening, because we have we are taking it to the anodic side, okay.

So, we have if we try to see the corrosion rate so, that means we need to anodic polarization. So, that means, this was the E corr. Now, in the free corrosion condition, the potential would be maintained at this level. Now, when you take it forcefully to the positive side anodic side the corrosion rate with corrosion rate changes it will be here. And as we are going this way the corrosion rate is increasing and reaching to a maximum level.

And then again decreasing and then maintaining a flat portion. So, this is corrosion rate width I could say that with potential, okay. So with potential I am having a change in corrosion rate like this. So, initially the corrosion rate is i corr and this is basically i corr and this is the variation of ia and ia is reaching to the maximum and then it is dropping and then maintaining a constant segments with potential the potential is changing constantly.

So, this is one nature one could recognize the other nature is, if we can have, let's say change in concentration. So the corrosion rate CR is a corrosion rate with concentration. If we see, so, initially the corrosion rate , for example, the very experiment what Faraday did, if we put iron block in dilute HNO3, the corrosion rate would be high as we are increasing the concentration will keep having increasing corrosion rate.

But, at some critical level we will see the corrosion rate suddenly drops. Now, this particular segment where we could see that we could have see dotted portion, this dotted portion can be analysed when we talk about mix potential theory and relate this mix potential theory are the attainment of passivity at that time we will be able to understand this dotted portion because that portion is very difficult to experimentally achieve.

Now, another portion this is basically the concentration effect that means HNO3 I can take and then there I could have similar situation where as the HNO3 concentration is reaching to a critical level, the potential the corrosion rate reduces to a great extent after taking to a peak and then it maintains a constant level to a certain concentration zone. This is one part and then so, that means, this is one and this is one, one is concentration effect one is potential effect.

And this particular graph could be different for different metals for example lead though, in case of lead, if we have lead sulphate forms in so we could see that variation of corrosion rate with potential with reference to this graph. At the same time there could be variation of corrosion rate with concentration HNO3. Where once it reaches to a certain level of corrosion rate suddenly reduces our maintenance at a very low value.

This is related to Faraday's experiment. Now, there could be a variations of this graph. For example, in case of lead, lead is a very interesting example, lead the container it can reserve it can hold HNO3 acid and the dilute HNO3 acid sorry it is a H2SO4 acid and in H2SO4 acid. So, the lead sulphate form and it keeps on depositing on the surface and it gives production. But if sulfuric acid concentration increases.

If it is a strong sulfuric acid, then the lead sulphate dissolves, and then it exposes fresh lead surface. So that time corrosion rate increases, increases greatly and the lead loses its ability to hold H2SO4 and at the lead tank fails. So it is not always that the concentration increases means the system will attain passivity there could be reverse trend where concentration can lead to a breakdown of passivity.

That means the passive portion will passive tendency will be destroyed. So when we see this kind of graph, then we can define our passivity. So, the definition the very definition of passivity it can be expressed in the form of in a form of statements. The one definition is in ennoblement of metal because of interaction with environment. Why, because Ennoblement means what we understand is the material achieves a nobility.

That means there is a reduction in corrosion rate the metal will be protected. So, that is what Ennoblement is happening, because when we see this particular graph, the corrosion rate is reduces and then it maintains at a constant level at a low corrosion rate position. So, that means, enablement is taking place, but if we compare, if you see this graph, the corrosion rate is decreasing and this decrease in corrosion rate is because of increase in potential.

So, that means potential has gone up. So, we have seen that, if we have two metal connectors two metal joining portion, the metal which is cathode has got a higher potential than the metal, which is anode that means, and here remember the cathode does not mean that the only that particular reaction related to the metallic portion, metallic part of that particular cathode. For example, if Platinum is acting as a cathode.

It does not mean that the Platinum is depositing because the cathodic reaction is taking place that does not mean the Platinum is depositing there could be cathodic reactions other than Platinum dissolution. So, in that case, that cathodic reaction has got a higher potential. So it is a noble potential as compared to the active metal which has lower potential. So, here we could see that the potential is increasing.

That when if we are saying that this ennoblement of metal because of interaction with the environment, so the second statement, what we have here, passivity is a state of high corrosion resistance of metal and alloy caused by inhibition of the anodic process. Or we can say that passive state is a state of corrosion resistance caused by increased anodic control. So, if we see this graph as well as if we compare this graph.

We could see that this decrease in corrosion rate is taking place because of anodic polarization. So, we are getting into the anodic control, we are not on the cathodic side rather on the anodic side of the metal where our expectation is the dissolution would increase, but rather instead of increase in the dissolution, it decreases of course, after reaching to a maximum, okay.

So, here also you could see that it reaches maximum and then reduces with the increase in potential. So, the passivity is a state of high corrosion resistance so, we could see that the corrosion resistance is decreasing. So, this is ia which is nothing but the dissolution rate of the metal, okay and because of the inhibition of the anodic process. So, because here we have reached the maximum anodic dissolution.

And because of something anodic dissolution is innovated and it reaches to this level, okay. So let’s stop here. We will continue our discussion in our subsequent lectures and we will talk about interaction of mixed potential theory and passivity of metal. Thank you very much.