Corrosion Part - II
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Lecture - 15
Galvanic Coupling between Two Active Metals

Hello everyone, let's start lecture 15.

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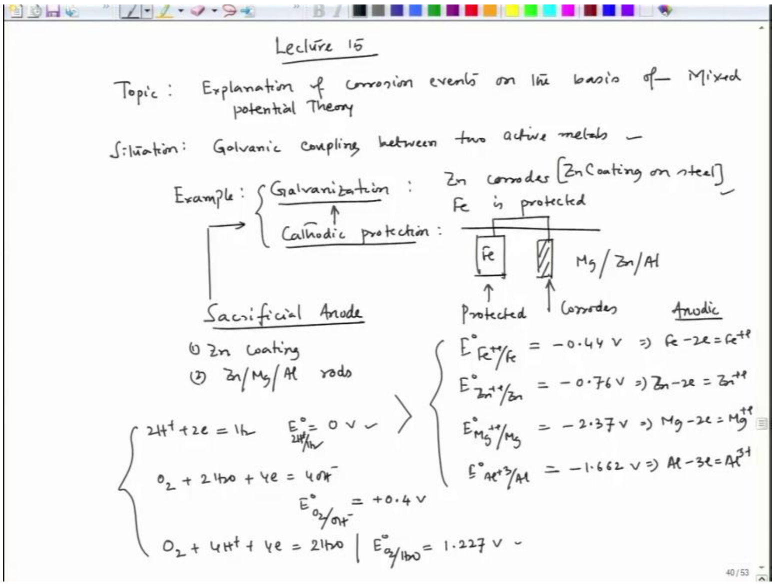

Lecture 15

Topic : Explanation of corrosion events on the basis of Mixed potential Theory

Situation: Galvanic coupling between two active metals –

Example : Galvanization : Zn corrodes [Zn Coating on steel] Fe is protected

Cathodic protection :

Sacrificial Anode

(1) Zn coating

(2) Zn/Mg/Al rods

$2H^+ + 2e = H_2 \quad E^\circ_{2H^+/H_2} = 0\ V$

$O_2 + 2H_2O + 4e = 4OH^- \quad E^\circ_{O_2/OH^-} = +0.4\ V$

$O_2 + 4H^+ + 4e = 2H_2O \mid E^\circ_{O_2/H_2O} = 1.227\ V$

Anodic

$E^\circ_{Fe^{++}/Fe} = -0.44\ V \Rightarrow Fe - 2e = Fe^{++}$

$E^\circ_{Zn^{++}/Zn} = -0.76\ V \Rightarrow Zn - 2e = Zn^{++}$

$E^\circ_{Mg^{++}/Mg} = -2.37\ V \Rightarrow Mg - 2e = Mg^{++}$

$E^\circ_{Al^{+3}/Al} = -1.662\ V \Rightarrow Al - 3e = Al^{3+}$

Today we will consider the aspect of the situation where we have galvanic coupling between two active metals and the cathodic reaction is taking place on both the metals and then we will see what happens. So our discussion the main topic remains same which is the explanation of corrosion events on the basis of mixed potential theory and today we will take situation galvanic between two active metal.

Now this particular situation is experienced in case of galvanization so where zinc coating is done on iron or steel so where zinc dissolves and iron gets protected. So this is one incident. The example, galvanization where zinc corrodes and iron is protected and where zinc is actually used as a coating on steel I would say that it is zinc coating on steel and iron is protected this is one example.

There is another example where we do experience such kind of corrosion event is nothing but cathodic protection. So in fact this galvanization is another form of cathodic protection but where zinc acts as sacrificial anode and iron is protected but there could be situations that the steel or the pipeline let’s say without having galvanic coating of zinc we can have a separate metal inserted into the soil and then we just connect these two will two metals iron or steel with that particular magnesium zinc rod.

And even we can use magnesium rod, or you can use we can use aluminium rods. These are the situations where magnesium rod zinc rod or aluminium rod decorrode and steel component is protected. So in this case is basically we have a metal steel iron which is to be protected and let’s say that is inside the soil or maybe it can be in immersed in liquid and then there could be a metal object which could be either magnesium or zinc or aluminium alloys.

Which and then they are connected by a conductor or wire, so that time this is protected and this corrodes. Similar to the situation where we have this zinc corrodes and iron is protected but that case zinc is coated on the steel but in this case it is not coated rather that rod of zinc or magnesium or aluminium, they are separately used as in the form of rod or different other shapes are possible. So now this kind of situation we call it this particular cathodic protection this is also a form of cathodic protection.

When one electrode corrodes and the other electrode is protected this is the kind of cathodic protection where we use sacrificial anode. And in this case the first case zinc coating is the sacrificial anode. And second case zinc, magnesium or aluminium are basically rods or some other shapes. So these are the examples where we do experience a corrosion event which is the galvanic coupling between two active metals why because iron is also active, zinc is also active, magnesium, zinc, aluminium iron all are active.

Because if I consider their potential values. Okay, so for example iron E zero iron = 44 volt. Then E zero of zinc = 0.76 volt. E zero = + 2.37 volt. E zero aluminium + 3 aluminium = E zero of aluminium + 3 to aluminium is + 1.662 volt. We could see that if iron or zinc or magnesium or aluminium they are exposed to the environment.

Where cathodic reaction is let’s say we expose them in acid where cathodic reaction

$$2H^+ + 2e = H_2$$

This becomes my cathodic reaction where E zero = 0 volt. So now this particular potential is always greater than all four metals. Then if they are exposed to the atmosphere in case of neutral solution and if we have dissolve oxygen then the reduction reaction would be and where E zero O2 going to OH + is = 0.4 volt.

So we could see that if these two reactions are cathodic reactions then all the metals here whatever we have mentioned here aluminium, magnesium zinc or iron they are all active that means they would all dissolve they would all corrode. And if we have dissolve oxygen in acid, so that case E zero O2 H2O = 1.227 volt. So this also these all three reactions are cathodic to all the reaction like Fe++ + 2 e.

So if we have if we expose iron into this environment where these reactions are possible these cathodic reactions are possible. Then iron will dissolve in this fashion, 3 +. So these anodic reactions, anodic reactions would happen so that means with the environments of acidic or neutral or basic any media we consider where either we have hydrogen evolution reaction or oxygen reduction those are acting as a cathodic reaction with reference to those metals and they are active.

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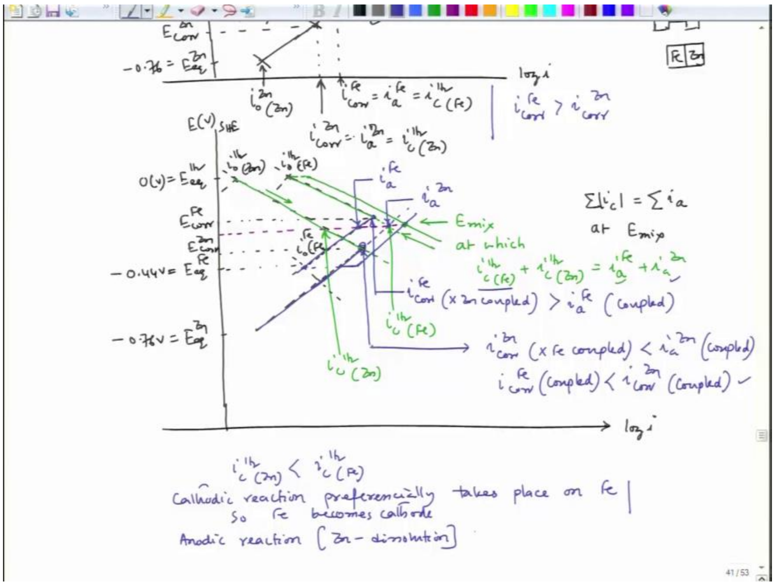

$i^{Fe}_{corr} = i^{Fe}_{a} = i^{H}_{c(Fe)}$

$i^{Zn}_{corr} = i^{Zn}_{a} = i^{H}_{c(Zn)}$

$i^{Fe}_{corr} > i^{Zn}_{corr}$

$\Sigma|i_c| = \Sigma i_a$ at E_{mix}

E_{mix} at which $i^{H}_{c(Fe)} + i^{H}_{c(Zn)} = i^{Fe}_{a} + i^{Zn}_{a}$

i^{Fe}_{corr} (x Zn coupled) $>$ i^{Fe}_{a} (coupled)

i^{Zn}_{corr} (x Fe coupled) $<$ i^{Zn}_{a} (coupled)

i^{Fe}_{corr} (Coupled) $<$ i^{Zn}_{corr} (Coupled) ✓

$i^{H}_{c(Zn)} < i^{H}_{c(Fe)}$

Cathodic reaction preferencially takes place on Fe |
So Fe becomes cathode
Anodic reaction [Zn – dissolution]

That means all those metals whatever we are considering here are active with reference to those individual those cathodic reactions now that is what we are saying that galvanic coupling between two active metals so this zinc individually is active iron individually is active. So when we combine them what would happen? That is the main discussion point for today's lecture. So in order to do that let's see how individually they are behaving. Let's say if we expose a metal M1 or let's say iron and zinc exposed separately in acid medium.

And where this acid is pure acid and also there is no dissolve oxygen. So now if we plot them separately so this is log i axis this is E volt with reference to SHE that means standard hydrogen electrode and let's say the pH is decided some pH X which is same for both the Solution temperature is same the pressure of hydrogen is one atmosphere. So all those are matching and let's say temperature is at 25 degree Celsius. So if pH, T temperature pressure of hydrogen all are matching.

Even if we assume that that iron ion concentration and zinc ion concentration both the medium are similar level. So if we consider that, then this is my E equilibrium hydrogen the same level E equilibrium hydrogen then we have E equilibrium of iron this is E equilibrium of zinc. Now for the sake of our understanding we can take them as the standard reduction potential which is zero here which is + 0.44 volt and here it is zero and here it is + 0.76 volt.

Now if we see them then their mixed potential theory as per the mixed potential theory we achieve the corrosion rate like this. So here also I can have a situation like this. This is i zero hydrogen over zinc surface, and this is i zero zinc over zinc surface, this is i zero iron over iron surface, this is i zero hydrogen over iron surface. Now we could see that now this is i corr = ia iron = ic hydrogen over iron surface. This particular point and this point is i corr = i corr.

This is iron this is zinc = ia of zinc = ic of hydrogen over zinc surface. So this could be one typical situation when iron and zinc both are immersed in acid medium. Now we could see that in this particular drawing that iron has got a little higher corrosion rate than the zinc. And here since we are considering + 0.76 and + 0.44 which are basically the standard reduction potential so we are considering that iron and zinc both are in pure state. So that case iron might have higher corrosion rate than zinc.

But when we combine them the situation becomes different and that is the point of discussion of combining two active metals and here individually, you could see that iron is dissolving here individually zinc is also dissolving. So zinc and iron both are active in acid medium. Now when you combined them we are to make use of mix potential theory. So if we combine them let's combine them. Now this E equilibrium hydrogen which is zero volt does not change for both the metals.

Now what we are doing individually this case in this case in this particular situation iron and zinc both are separately exposed in that acid medium. But here now what we are doing if this is my iron piece and this is my zinc piece both are now connected galvanically. So we have a situation like this, so this is iron this is zinc. So that case what would happen. Now as per this diagram we could see that hydrogen evolution reaction that exchange current density on iron is little higher, higher than the exchange current density of hydrogen over zinc surface.

So if we follow that relative positions of their respective points I can put them like this. This is the one position which is for iron and then for zinc is this is the position. Now E equilibrium iron is + = 0.44 volt +. So the relative position this will be here okay. Now they will have their own plots. Now this is the point and this is i zero iron over iron, now there will be one more point which is E equilibrium zinc = + 0.76 volt.

So this is lying at this point so it will if this drawing is bit tricky so you have to practice a lot just to have a relative position. So this is, this becomes those two points this is basically and if I consider these values this is E corr zinc this is E corr iron. And corresponding to this I could see that, this becomes E corr iron and this point is E corr zinc. Now what would happen once we connected them one.

So now we have to make use of mixed potential theory that means we have to have this particular concept ic should be = ia, fine, at E mix. So we have to find out the new E mix position. How do we find that, so now these are the two anodic lines the anodic lines let me plot with a blue one this is one anodic line, this is another anodic line so now they have to be connected at this point. So now we connect them now we take the new anodic line like this, and the cathodic line let me put it in blue, green colour.

So these are the two cathodic line so now we have to also add them so along this so this is added this is added. So now this becomes my new position where I could see that this becomes my E mix at which ic hydrogen over iron surface + ic hydrogen over zinc surface = ia iron + ia zinc. Now how do I find these quantities if I draw a line like this, Fine, now if I continue this line, and this line also and then the blue line, Okay.

As per this diagram its meeting like basically here it is meeting this is as for this diagram but you can have a different diagram you will see that they will not meet. Now this quantity if I try to find out this is the hydrogen evolution on iron surface. So let’s see hydrogen evolution on iron surface what is that line this is this line. So this is i so this point is ic hydrogen iron and then we have to find out ic hydrogen over zinc so hydrogen ic hydrogen over zinc is this line.

And this point this particularly E mix horizontal line to the current axis is this so this is ic hydrogen over zinc and we have to find out this line so the anodic, this particular thing we have to see where this particular E mix is cutting across the anodic point. So this is my anodic point, this is ia iron and zinc we have to find out this, so this is this point ia zinc. Now interestingly we see that after coupling iron dissolution rate has gone down.

From this is i corr iron, not connected or I would simply mention like this, no zinc coupled, fine. So now you could see that the corrosion rate of iron when it was individually exposed to the acid is higher than the corrosion rate apparent when it is galvanically coupled to zinc. That suggests that the corrosion rate of iron actually goes down but what happens to the zinc corrosion the zinc corrosion rate was at this point and that has gone up to this point.

So that means the zinc corrosion rate has increased so the corrosion rate of zinc was individually when it was not connected to iron was this is i corr zinc not iron and a coupled but this is less than ia zinc and this is more than ia iron when coupled and this is coupled. So now interestingly we could see that the corrosion rate of iron goes down when we couple it with zinc and the zinc corrosion rate goes up when we couple it with iron.

But when they are individually connected I could see that the iron corrosion rate is higher than and this so that means when individually connected that time i corr iron is greater than i corr zinc. But after coupling i corr after coupling I could see that i corr iron coupled is less than i corr zinc coupled, so that means when we connect two active metals the active metal which has lower reduction potential would have a higher corrosion rate than the active metal which has higher reduction potential.

So this is the situation what we typically experience when we have galvanic coupling between zinc and iron and zinc corrodes in zinc dissolution rate increases and the iron corrosion rate decreases, so iron is in fact protected. Now remember that the cathodic reaction on both the surfaces are the same reactions but the cathodic reaction over the surface where the corrosion rate decreases that means iron that cathodic reaction rate is more than the cathodic reaction rate of that particular on the on that active metal which is which whose corrosion rate is increased.

For example, here if I consider this if we consider this the ic hydrogen over zinc surface has in is more than sorry it is less than ic hydrogen over iron surface. So that means I can have a statement like this cathodic reaction preferentially takes place on iron, so iron becomes cathode but that does not mean that the iron dissolution rate is not taking resolution is not taking place.

But it is taking place at a much lower rate than had it been exposed to that particular environment without having zinc layer on it. So this is the basic principle of this particular condition what we have started with that is, when what happens when galvanic coupling between two active metals in a corrosive medium and here we have considered the example of zinc and iron coupling in acid medium.

And there we have seen that the cathodic reaction preferentially takes place on iron and so iron becomes cathode and of course anodic reaction which is nothing but zinc dissolution so like here what we have seen this particular case, are zinc dissolution rate increases or ia zinc is more than ia of iron when they are coupled, preferentially it takes place on zinc surface, so zinc becomes anode. So it is a basically preferential anode it does not mean that cathodic reactions are not taking place on both the surfaces.

But the metal which has higher reduction potential when it is coupled to a reduction with a metal which has a lower reduction potential would get protected due to the higher dissolution rate of the metal which is a lower reduction potential. In comparison to the first one but the cathodic reaction would preferentially take place on the metal which is a higher reduction potential but remember this situation is for both of when both the metals are active in that particular medium when they are individually exposed.

So, let’s stop here we will continue our discussion on this and try to link it with cathodic protection that means the other instance where iron object is protected by zinc or iron plates zinc or magnesium or aluminium plates or rods. So let’s stop here, thank you.