

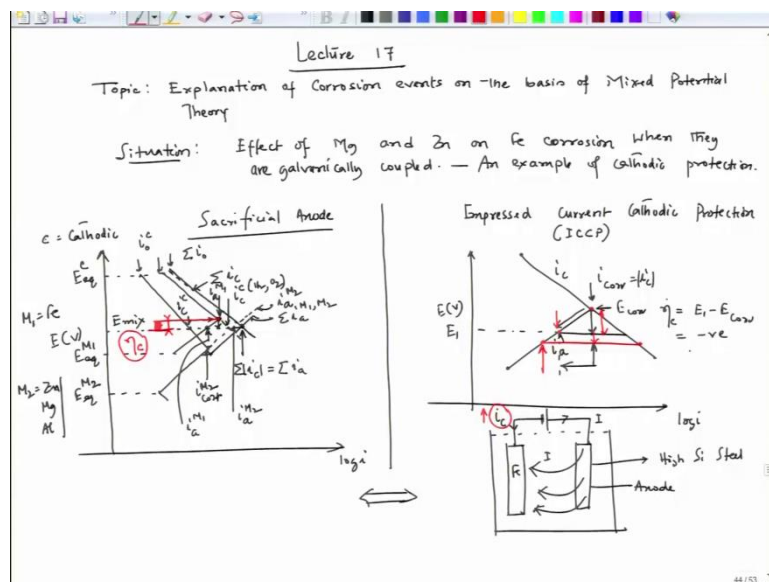
Corrosion Part-II
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Lecture -1 7

Effect of two active metals on Fe – Corrosion when they are Galvanically Coupled

Hello everyone today we will start our lecture 17 and it is the same topic will be continuing explanation of corrosion events on the basis of mixed potential theory. And we have discussed several situations and in the last 15 and 16 lecture we talked about galvanic coupling between two active metals. And then we could see that one active metal corrodes heavily, the another active metal is protected. An example to this is nothing but the galvanic coupling between zinc and iron.

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Even we can have the same situation when we connect magnesium with iron or aluminium with iron where aluminium zinc and magnesium all will be acting as anode and iron will be acting as cathode. And this particular technique of protection of iron is called cathodic protection and we have also seen that there are two segments of cathodic protection one is sacrificial anode, where zinc or magnesium or aluminium are connected to or is to iron piece which is to be protected.

And zinc will act as or magnesium or aluminium will act as anode and iron will act as cathode, because we have also seen that that preferentially that iron will act cathode because the cathodic reaction will take place on iron surface but on the anodic surface the dissolution of that

particular metal takes place. And we have also seen that that particular mixed potential theory that base of that particular protection root that mixed potential root is based on basically the main mixed potential theory.

Where we could see that yes that hydrogen evolution reaction on iron surface increases and the hydrogen evolution reaction on zinc surface decreases when we connect zinc and iron. Similarly, we have also seen that if it is oxygen reduction process that is basically the cathodic reaction then on iron surface oxidation reaction oxygen reduction takes place.

But on cathodic surface on anodic surface dissolution of zinc take place preferentially so it is not that iron dissolution is not taking place rather iron dissolution is taking place at a much slower rate than in the situation where iron is separately placed in that electrolyte. So this, so we today we will talk about little more on cathodic protection. So the situation will be talking about effect of magnesium and zinc on iron corrosion so this particular when they are galvanically coupled.

Fine and what we have seen in case of and this is also an example of cathodic protection and remember our discussion will be only confined to the application of mixed potential theory will not talk detail about cathodic protection that means the technical part of cathodic protection only the mixed potential theory will be talked about. Now when we talked about cathodic protection we could see that there are two modes one is sacrificial anode another one is impressed current cathodic protection.

So this is in short we call it ICCP and if we try to see their mixed potential mode in one case we will just draw schematically you try to follow the previous lecture. So this is $\log I$ this is E in volt. We have two active metal joining, this is 1 and so this c is cathodic reaction and $M1$ and $M2$ these are the two active metals. If we have this situation. Now in one case, we talked about hydrogen evolution reaction to be the cathodic reaction.

Another case we talked about oxygen evolution reaction to be the oxygen reduction reaction not evolution oxygen reduction reaction to be the reduction cathodic reaction. So both the cases we explained our protection of iron because of galvanic coupling of iron with an active metal more higher active metal, rather I would say that zinc corrode, zinc if we see the equilibrium

M2. So this is M1 and M2 are two metals, this M2 could be zinc, magnesium aluminium these are the and here M1 is nothing but iron.

And then we followed our mixed potential theory. Fine, so this point is my point where $i_c = i_a$ we have already realized that and then we have seen the mixed potential is this one and our statement was the iron would preferentially act as cathode. Because the cathodic reaction would take place on the iron surface at a higher rate than the rate of cathodic reaction on zinc. Here also you could see that cathodic reaction this is basically summation i_c and this point is nothing but respective I zero point of cathodic reaction.

And this is summation of I zero point. Now this line is summation of i_a point where this is i_a is M1 and M2. Now I could see that hydro if it is hydrogen evolution reaction or oxygen reduction reaction, the rate of i_c of cathodic reaction whether it could be hydrogen or oxygen reduction hydrogen evolution or oxygen reduction that is at a much higher rate than the i_c of c on M2 or zinc surface. So iron becomes cathode and dissolution rate if I try to see so this line is nothing but i_a of M2 and M2 of course we could see that it could be zinc magnesium aluminium.

So the rate at which zinc dissolution or M2 dissolution would take place this is the rate so had it been the situation where zinc is separately placed in that electrolyte the dissolution of zinc would have been here so this is i_{corr} zinc. Since we are talking about M2 so this is M2 this is i_{corr} . So I could see that i_a of this is i_a point i_a of zinc or I could see M2 has gone up.

Whereas, the dissolution of iron has gone down. So this point is nothing but i_a of M1 and had it been separately placed that M1 the corrosion rate of M1 would have been i_a of M1. So I could write it like this so this is M1 or this is M1 when it was separately added separately placed in that electrolyte. So this is the mode of sacrificial anode, where M1 is M2 is dissolving and M1 is protected rather I would say that M1 is corroding less as compared to the situation where it is not connected to connected to M2.

Similarly, and so there I could see that the corrosion potential if I consider for iron is this is the corrosion potential of iron when it is not connected to zinc or the corrosion potential of M1 so that case my corrosion potential of iron has gone to this particular difference so I could see that

iron is polarizing towards negative side with reference to the corrosion potential or we can say the free corrosion potential.

So there from it is polarizing negatively. So that is what it is called a cathodic polarization. This is also a cathodic polarization of iron and that also and because of that I could see that i_c that the cathodic current density over iron surface is increasing so that is what it is also coming under the influence of cathodic protection. But when we talk about impressed current cathodic protection I could see that this theory of impressed current put in cathodic protection.

There I am not having any dissolving electrode rather I would have an electrode which will be just used to supply negative current to the supply, just used to have a completion of circuit.

So what we are doing let's say this is the metal object which is to be protected in an electrolyte and that electrolyte could be soil solution or seawater. So there I could have not seawater in there we've to remember this impressed current cathodic protection may not be suitable for seawater.

Because this is not high resistance path. Generally impressed current cathodic protection is used where the resistance of the electrolyte is very high that is what it is mainly in soil application and then this is let's say the this is iron which is to be protected and in this case protected and then this is unprotected by supplying negative current. So if I try to supply a negative current to this that means I have to supply i_c to this, so I have to connect it to and a cell which is supplying a DC current to the system.

And then that circuit is to be complete. Since here we do not have a dissolving metal which will dissolve or sacrifice itself and then protect the iron piece. Here we are having an electrode which will be acting as an auxiliary anode. So this is connected to this so the positive end is connected to some metal which is generally high silicon steel. High silicon steel that is used silicon percentage could be almost about 16 to 17 percent so though that steel will not dissolve rather it will just complete the circuit.

And the current negative current which will be sent to the iron piece for protection by external power source so this is my circuit current and the current is leaving this anode and going to metal surface. So the current in that electrolyte is leaving anode surface so this becomes anode and entering the cathode surface and i_c is entering into the metal surface so since i_c is entering

so that means we are sending electrons to the metal surface and those electrons will be used up for cathodic reactions.

This is the mode of impressed current cathodic protection. Where if this is my i_c and this is my i_a then this could be this is my free corrosion potential and this will be the steady corrosion potential if electrolyte condition is maintained similar. So how can I reduce this corrosion rate so this becomes my $i_{corr} = i_c$ and this is a mod sign because i_c sign is negative. Now if I try to do that I have to go down, okay.

So in order to reduce the rate of corrosion of iron so if I go down then only the current density will move this way. So here if I do this way if I take the potential downwards that means I have to polarize the iron surface towards negative side and that means polarize towards cathodic side. So that is what it is basically the cathodic protection. When you do that I could see that if I go to this potential this is my potential E_1 .

So my polarization is nothing but $E_1 - E_{corr}$ since this is my E_{corr} which is negative. So I can term it as η_c , fine. So this is the cathodic over voltage. This η_c is over voltage. So corrosion current density was here and now it comes to this so the corrosion rate has reduced. So this is also cathodic protection but here we are sending current from external source that is called impressed current cathodic protection. Now the main difference between these two, these two is in the way the current is sent to the negative current is sent to the iron surface.

Now in this case the negative current or the electrons are sent to the iron surface because of the dissolution of the more active metal which is zinc or magnesium. But here the negative current is sent by applying, by supplying current from an external DC power source. Now if I try to see other differences now here if I see the potential difference the potential difference is driving or not potential difference the polarization.

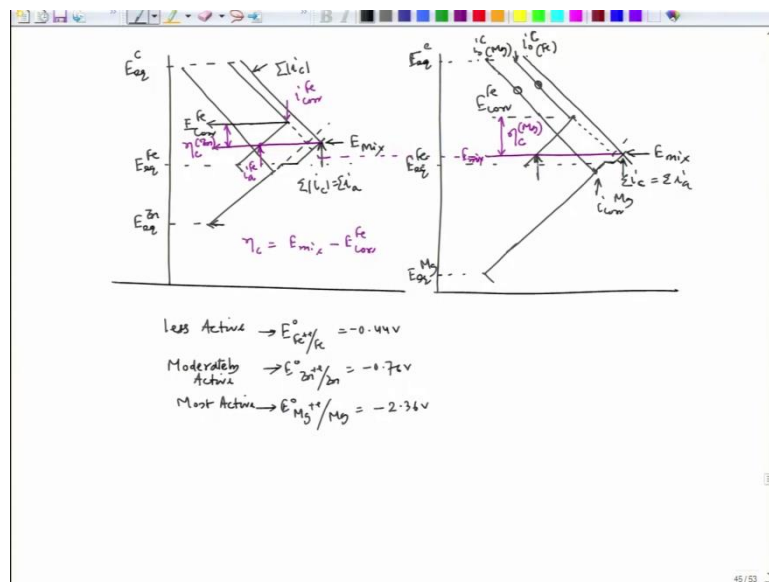
So here is this much but here the polarization is if this is my corrosion potential of iron. when it is not connected to any acting any other active metal now after connecting to M2 which has lower equilibrium potential than iron so then in this particular situation I have this much so this much would be my over voltage. So this is η_c for this case and η_c for this case cannot be changed anymore because that is decided by the self-dissolution of the M2.

Yes, it can be changed only if M 2 is changed. For example, M 2 is changed from zinc to magnesium or zinc to aluminium, so I replace zinc with aluminium, if I replace zinc with magnesium, so that case this value would change so we will see how this value is changed because of change of anode material but in this case I could see that the over voltage is this much in this particular case. Now if I supply more negative current so that means if i_c is increased fine.

Then the potential will still drop, so I can drop it further so I can take it to this potential so now corrosion current density or the dissolution current density of iron would go from this to this initially it was here when it was there was no current flow in the system. But once we started current started connect once we started flowing the current into the system so we could see that depending on the amount of current we are sending I can change the over voltage and then accordingly I can change the rate of dissolution of iron.

But so that is possible in this situation in this case but in this case it is decided by the self-dissolution of the active metal and that can this over voltage amount can only be changed if we change the anode material. So we have to just look at that part so that is what the situation we have considered here the effect of magnesium and zinc on iron corrosion when they are galvanically coupled. So let us see that part, okay.

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So if I try to see that so let's say in case of zinc so we draw side by side cases. So one case was so this time we will just draw a possible situation so this is let us say zinc so this is E equilibrium zinc, this is E equilibrium of iron, this E equilibrium of cathodic reactions. Here I am not

specifying whether it is a hydrogen or oxygen hydrogen evolution reaction or oxygen reduction reaction so I am just simply mentioning the cathodic reaction in that situation I will have so this is summation of i_c , okay.

And this will flow this way and this will flow that way. This is my point where i_c summation = i_a summation, fine. This potential is the E_{mix} . Now before connecting iron and zinc this was the corrosion potential of E_{corr} iron and after connecting to zinc I could see that the E_{mix} is here. So over voltage is η_c . So the $\eta_c = E_{mix} - E_{corr}$ iron and correspondingly I could see that the corrosion rate of cathodic reaction on iron surface is increasing.

And corrosion rate of sorry not corrosion rate the rate of cathodic reaction on iron surface is increasing. But the rate of corrosion or dissolution of iron is decreasing from this point. So this is i_{corr} of iron when it was not connected to zinc and this is the i_a of iron when it is connected to zinc, fine. So this is the η_c . Now how can we increase it. Now let's say if I take magnesium and we know that if we compare E_{red} rather reduction potential = 0.44 volt. E_{red} of Zn^{2+} E_{red} rather - 0.76 volt. E_{red} of $Mg^{2+}/Mg = - 2.36$ volt.

So I could see that if I compares the potential so I could see that this is the most active and this is moderately active moderately active and this is active, fine. Moderately higher, so I should not say moderately rather I would say okay so I can put it as more active and this is less active I can say that this is less active. So that situation so this point in this case it was equilibrium point so I can change the equilibrium point. E_{eq} magnesium and this iron equilibrium point will not change.

And this point if we do not change. So this is iron this is magnesium. If I consider this situation let's say I if this is the situation. So when separately done so that time this is the corrosion rate of i_{corr} of magnesium and this is E_{eq} c, this is i_{corr} of c on magnesium surface, this is i_{corr} of c on iron surface. This is E_{eq} iron.

And then if I continue this same process I will follow. So this becomes my, this is my mix potential so summation of $i_c =$ summation of i_a this potential is E_{mix} and this is E_{corr} of iron. So if I try to see the E_{mix} . This is my new E_{mix} . Now η_c if I have to compare so this becomes my η_c . So I could see that if I extend this line extend this line I could say that

neeta c in case of with reference to magnesium and neeta c with reference to zinc, I could increase that neeta c or the cathodic polarization when we connected to magnesium.

When you connect it to magnesium. So that means the magnesium is highly active the most active if we compare the E zero values of iron, zinc and E node values of iron zinc and magnesium. So that case I could increase the over voltage cathodic over voltage or I could say I could increase the cathodic polarization and that would influence. So let me complete this so this is my individual cathodic reaction so this is i_c this particular line is i_c of cathode equation over iron this particular line i_c of Cathodic reaction on magnesium surface. But if we compare so the since we are getting higher over voltage in case of magnesium connection.

I could see that the corrosion rate is also of that iron the dissolution rate of iron after cathodically coupling with magnesium is also decreasing as compared to the corrosion rate of iron or the dissolution rate of iron when it is connected to zinc, okay. So this way we can actually increase the over voltage amount. But other ways we cannot but in case of ICCP we actually can increase it depending on the stronger or weaker power source whatever we wish to use. Let's stop here we will continue our discussion on the mixed potential theory and analysis of corrosion events in our coming lectures, thank you very much.