Corrosion Failures and Analysis
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Lecture - 09
Galvanic corrosion (Part 4)

Welcome back. We will have lecture 9 for the course Corrosion Failures and Analysis. And, we will continue our discussion on Galvanic corrosion.

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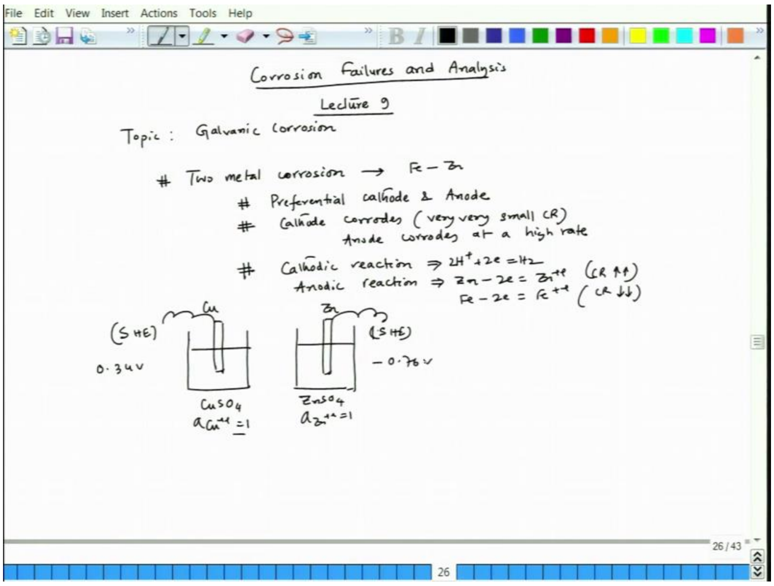

Corrosion Failures and Analysis

Lecture 9

Topic : Galvanic Corrosion

\# Two metal corrosion → Fe – Zn

\# Preferential cathode & Anode

\# Cathode corrodes (very very small CR)
Anode corrodes at a high rate

\# Cathodic reaction ⇒ $2H^+ + 2e = H_2$
Anodic reaction ⇒ $Zn - 2e = Zn^{++}$ (CR ↑↑)
$Fe - 2e = Fe^{++}$ (CR ↓↓)

So, the course is and topic Galvanic corrosion. Now, if we see that, in case of galvanic corrosion, it is basically is defined as two metal corrosion and one example we have provided is iron and zinc ash. And, we have seen couple of observation. So, observations were preferential cathode and anode.

And, second observation was cathode also corrodes, but very very small corrosion rate and anode corrodes at a high rate fine. And, interestingly one more observation we can make out of it, if we see that zinc and iron situation. The cathodic reaction is nothing, but H2 and anodic reaction was plus plus plus of course, its corrosion rate is very very small; its corrosion rate is very very high, but it does not stop.

$$Cathodic\ reaction = 2H^+ + 2e^- = H_2$$
$$Anodic\ reaction = Zn - 2e = Zn^{++}; Fe - 2e = Fe^{++}$$

Now, interestingly if we consider a situation like, what we had in case of Daniell cell, that we have one end copper is dipped in copper sulfate and copper ion activity was maintained at one. And, another end we had zinc and zinc activity and it was dipped in zinc sulfate, and activity of zinc ion was maintained at 1.

And, we develop some potential and that potential we measured by standard hydrogen electrode. And, here also we also maintain standard hydrogen electrode and then we measure the potential. Now, interestingly this potential if we maintain this condition, it is coming out to be 0.34 volt and here it will be minus 0.76 volt.

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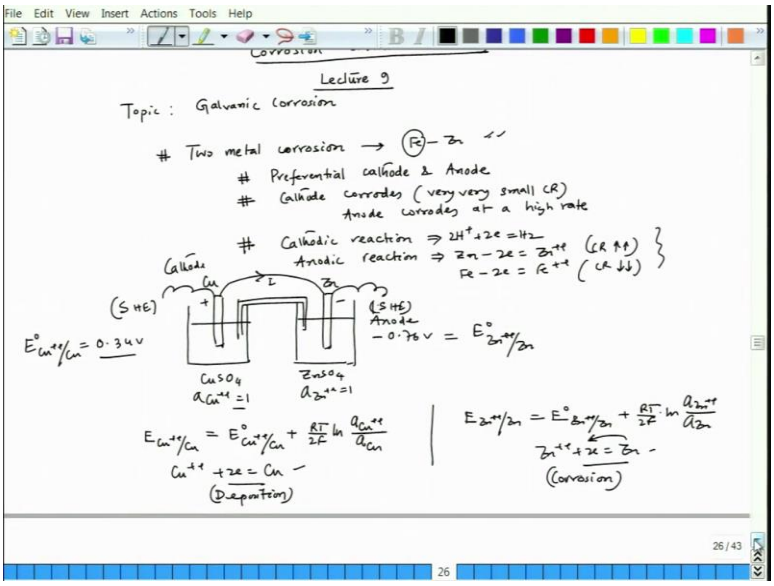

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$E^\circ_{Cu^{++}/Cu} = 0.34\,V$

$-0.76\,V = E^\circ_{Zn^{++}/Zn}$

$a_{Cu^{++}} = 1$

$a_{Zn^{++}} = 1$

$$E_{Cu^{++}/Cu} = E^\circ_{Cu^{++}/Cu} + \frac{RT}{2F} \ln \frac{a_{Cu^{++}}}{a_{Cu}}$$

$Cu^{++} + 2e = Cu$
(Deposition)

$$E_{Zn^{++}/Zn} = E^\circ_{Zn^{++}/Zn} + \frac{RT}{2F} \ln \frac{a_{Zn^{++}}}{a_{Zn}}$$

$Zn^{++} + 2e = Zn$
(Corrosion)

Now, this potential how it is coming from Nernst equation. Considering this reaction and every time we are considering reduction potential that is what I have written in terms of reduction fine, where the reaction was zinc.

Interestingly this would become, if we connect them and remember there should be a salt bridge to maintain electrical connectivity. And, here we connect this with a conductor with a, and then current will flow from this copper end to zinc end. And, this is positive or cathode and here it is negative for anode.

Now, if you see cathodic and anodic reactions, the same ion is depositing and same metal is forming the ion. In case of zinc surface it is zinc, which is going to the anodic situation, when the it is connected so; that means, preferentially anodic reaction would happen here. And, preferentially cathodic reaction would happen here.

And, interestingly here since we are not having any other species rather than copper plus plus, only this cathodic reaction can take place and only this anodic reactions can take place this is corrosion and this is deposition. Since, copper has a higher reduction potential that is what it actually reduction process is preferred here.

Now, this case and this case is different. So, this is also galvanic corrosion galvanic, corrosion of zinc, but here we have ions of both the metals in the solution. But, in this case iron of iron is not present, iron of zinc ions of zinc also not present in the solution. Initially to start with it was only H plus, but still we ended up getting this reactions.

So, that is another important aspects, because these things are coming that the because this value is this and this is nothing, but which is standard reduction potential of zinc. But, in practical cases we experience the situation what we had in case of iron zinc ions of individual metals may not be present in the actual actual situation or practical situation.

So, that time we cannot judge that, which type of reaction would happen from the reduction potential. For example, here we cannot judge from the iron reduction potential, which is minus 0.44, the standard reduction potential for iron and zinc it was minus 0.76 volt standard reduction potential, because those ions are not present in the solution. So, in this case it is very easy, how to decide anodes and cathodes.

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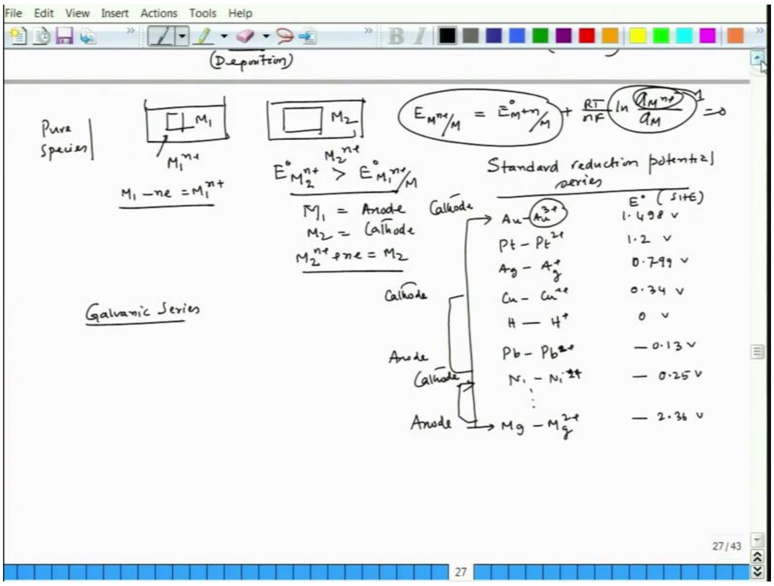

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M}$$

M_1^{n+} M_2^{n+}

$M_1 - ne = M_1^{n+}$

$E^{\circ}_{M_2^{n+}} > E^{\circ}_{M_1^{n+}/M}$

M_1 = Anode
M_2 = Cathode
$M_2^{n+} + ne = M_2$

Standard reduction potential series

	E° (SHE)
Au – Au^{3+}	1.498 V
Pt – Pt^{2+}	1.2 V
Ag – Ag^{+}	0.799 V
Cu – Cu^{2+}	0.34 V
H — H^{+}	0 V
Pb – Pb^{2+}	– 0.13 V
Ni – Ni^{2+}	– 0.25 V
⋮	
Mg – Mg^{2+}	– 2.36 V

For example, if, we have two metals M1 and another case M2 and they are in their respective ions in connection with respective ions of that electrolyte, where we have that respective ions this is M1 n plus and it is M2 n plus both ions are present in those electrolyte.

So, I can decide which will act as cathode and which will act as anode. If, the such situation arises. Simply by looking at the Nernst equation, which is generalized form this is a generalized, form we can use. And, we know that there is a series exist for example, here if this value is greater than. So, then M1 would be anode, M2 would be cathode ok. And, the reactions would be in this case and in this case M2. So, these will be two reactions, that way we can judge.

So, in so, pure cases so it can possible, it can be possible when it is a pure case pure species. And, here we can judge by looking at standard reduction potential series. And, that series for example, if I try to point out here you will get like this Au, Au 3 plus E0 value would be 1.498 volt and this is all with respect to standard hydrogen electrode. This is gold 2 plus is basically like that; way you can go up to magnesium.

So, like that way we can have a series which is based on finding this value by putting the same ion of that particular metal, maintaining that ion concentration to be activity to be 1. So, for example, here if this concentration is 1, this activity is 1, then of course, potential of that particular electrode would be same as reduction potential, standard reduction potential, because this lone part would be 0, if the activity of metal ion concentration is 1.

So, like that way we can find out these values. And, here if I try to see this if we connect it to this 2, when there ions are present, then this would be cathode and this would be anode. Similarly, if I connect magnesium with nickel this should be cathode magnesium would be anode. Similarly, if I connect nickel with copper, nickel would be anode copper would be cathode, fine it is very easy to find out, but it is impossible to get in practical situations.

So, that time we have to generate another series that is called galvanic series, galvanic series. And, in that galvanic series we have to just find out that which one in a two metal contact. Those two metals could be alloy, those could be metal could be pure metal, those could be pure metal and alloy all those combinations are possible. Even it could be same metal, but the reactions would have different activity ok, I will come to that.

So, galvanic series how and it starts with this particular discussion, that cathodic reaction and anodic reaction if you see, cathodic reaction is always this. Even if iron remains cathode. Why we say this? Because catholic reaction, wherever catholic reaction happens it is basically cathode, but that does not mean that, that particular metal will have a cathodic reaction. Here it is not happening rather that cathode is actually going through anodic reactions.

So, that is what we need to have a kind of comparative series, which will not get bound by the values what we have in standard reduction potential series. And, these series could be different for different electrolyte. Let us see, how you find that series ok.

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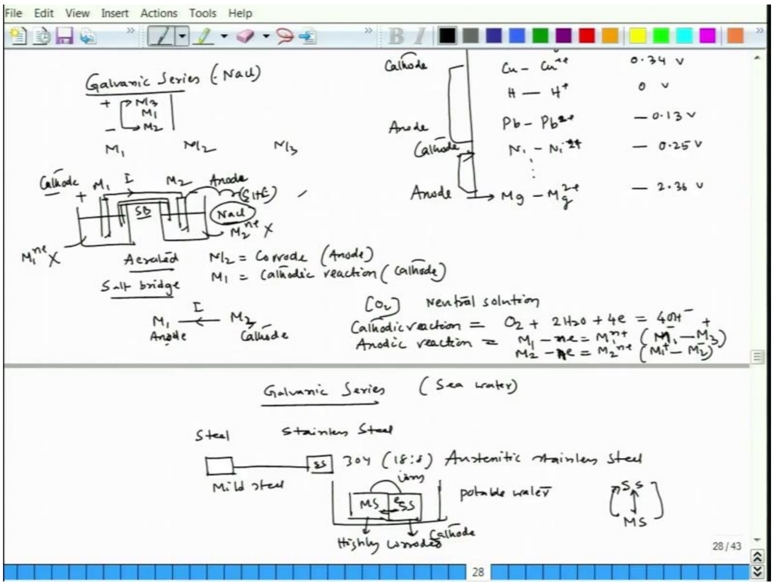

So, let us say we have a metal 1 M1 and M2, and another metal M3. Let us say all are M1 this M1 and metal M1 metal and M2 metal, they are dipped in let us say Nacl solution or seawater solution this is a M1 this is M2. And, let us say this is aerated, aerated solution. And, if we connect them, this is a salt bridge.

Now, we have to just check which way current moves, if current moves from this end to this end. So, the current flows from this end to this end, and we know that in galvanic connections current always moves from positive end to negative end. So, this will be cathode and this would be anode. So, this is anode and this would be cathode.

Since, this is a galvanic mode of situation and here the corrosion is taking place. So, that case M2 would corrode and M1 would act as this is anode, M1 would be the surface for cathode or cathodic reaction cathode. and interestingly when we have this initial there we did not have MN plus here also we did not have M2N plus.

So, that way we can see that by looking at the current flow, we can check which one is active, which one is less active. So, the less active metal in this series in Nacl solution whatever 3.5 percent of sea water in this series M1 would move on top of M2.

And, here we are not putting any values. You can also find out the values here, by joining standard hydrogen electrode you will get some potential, but we are not mentioning that. We are just comparative we are making a comparative statements that we are actually, which one is acting as a positive end, which one is acting as a negative end. So, accordingly we decide which one is cathode or which one is anode.

Similarly, if we have a joining like if a condition like the same condition, instead of M1 if we put M1 and M2. Let us say, when we join this, like this same situation what we have here. If the current moves from M1 to M2 in the external circuit, then definitely M2 is cathode and M1 is anode. So; that means, we can see that if we compare M3. If, we compare M1 and M3 definitely M3 is less active and M1 is more active.

So, more active 1 dissolves and less active metal will act as cathode, where cathodic reaction happens. And, here so; that means, M3 would stay on top of M1. So, now, we have a series which is M3, M1 and M2. So, if we join then M3 and M2 definitely this would be positive this will be negative.

Now, interestingly what are the cathodic and anodic reactions? Since, I have said that this is aerated. So, we have dissolve oxygen and if we consider Nacl solution it is a neutral solution. So, the cathodic reaction would be an anodic reaction, M 1 minus n e equal to M1 n plus sorry it should be M2 ok. Even, if it is M1 no problem in that case this is joined M1 and M3, because M3 is acting like cathode.

And, another anodic reaction would be M2 minus 2e equal to any. So, let us make a generalized statement Mn number of electrons are associated. So, it would be M 2n plus that time M1 and M2.

So, in this case this is positive this is negative; in this case this is positive this is negative. And, that is what it is followed in that galvanic series. So, now, in the galvanic series this M1, M2 and M3 could be metals, could be alloys, and could be some reactions also ok, fine now, but if we consider only metals so, we can have a series like this; in let us say sea water.

And, interestingly before I get to that particular thing so; that means, you could see that if you change this Nacl solution, you can change it to some other solution, you might find that M3 might become active compare to M1. So, it is not sacrosanct that in one particular electrolyte one metal or alloy is less active or noble does not mean that that will remain noble in other solution ok.

So, in order to understand the industrial applicability of galvanic series, we have to see a complete galvanic series and see, how we select materials in order to prevent corrosion related problems. And, whenever we select materials we try to select materials, which are close by in the galvanic series in that particular environment ok.

So, in order to understand that we will take this galvanic series discussion because it involves lot of engineering applicability in the next class because this particular class we have I think hardly left with 10 minutes. So, 10 minutes will not be sufficient to understand this galvanic series situation.

But at least I could tell you that, what is the implications of galvanic series and standard reduction potential series. Because in case of standard reduction potential series, we always deal with same metal, same species, and unit activity is maintained, but in case of galvanic series it is not needed.

So, for example, if we consider steel and stainless steel fine. So, let us say you have a stainless steel SS and 304 standard in the standard form of 18 8 white austenitic stainless steel. Austenitic stainless steel and in this case if we have another steel which is mild steel and you let us say you have made an electrical contact.

So, you have one is mild steel, another one is stainless steel. And, if this couple if we expose to normal portable water, you would see that the SS would become cathode, hardly any corrosion will be noticed there and, but this will be highly corroded ok.

Why this situation happens? Because, if we compare the galvanic series in portable water; SS would always stay on top of mild steel.

And, their difference in potential if even, if you measure the potential in the portable water, this difference in potential is large. And, in fact, when you connect them the large current will flow from SS to the mild steel from the through the conductor or to the external circuit. And, here the conductor is nothing, but this and this is the electrolyte. So, here ions move and here electron moves ok.

So, SS would become cathode and MS is image becomes anode, but here interestingly they are not pure metals these are, they are highly the SS is highly alloyed metal and ms is less alloyed metal fine. So, this is very important, because this tells me that we cannot have such kind of situation where, highly noble and highly active metals cannot be joined for an engineering applications ok.

So, we have to be very careful that part, that we have to select materials. So, that their galvanic series in the galvanic series they are close by, but in this case they are wide apart. So, wide apart means it will be highly cathode and highly anode ok. And, if it is they are close by the galvanic effect will be hardly noticed ok. So, we will talk this part in our next lecture.

So, till then let us stop here we will continue our discussion on galvanic series. Galvanic series as well as galvanic corrosion, because this I this galvanic corrosion like consider to be one of the fundamental corrosion forms.

Thank you.