Corrosion Failures and Analysis
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Lecture - 08
Galvanic corrosion (Part 3)

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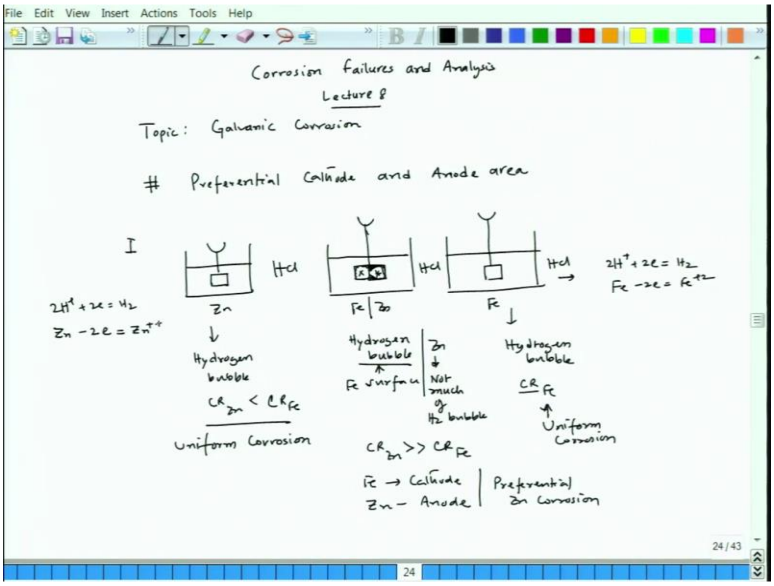

Corrosion failures and Analysis

Lecture 8

Topic: Galvanic Corrosion

Preferential Cathode and Anode area

Welcome back. We start lecture 8 today for the course Corrosion Failures and Analysis. Lecture 8 and topic we will continue discussion on Galvanic corrosion. And if we summarize what we have done in lecture 6 and 7, if you recall that in lecture 6 we talked about several possibilities, that even if we have the same metal or the same alloy surface, we do get galvanic effect.

And due to difference in concentration of active species, due to stress effect one section could be highly stressed, one section could be least stressed and then highly section stress section might get corroded, then we could have a situation like local concentration change of the alloy like, what we experience in case of 18/8 stainless steel, where chromium depletion happens across a grain boundary and that lead to inter granular corrosion.

So, that is also there also we have galvanic effect. Even you would see later that gravies as well as pitting corrosion we have galvanic effect. The pit portion is specifically anode even, the crevice portion is specifically anode around that area will be cathode. So, for the galvanic corrosion we have to see that this particular condition should be met preferential cathode and anode area, ok.

So, this is very important in case of galvanic effect. It need not be a for example, of course, as per the common definition we say that it is a two metal corrosion, where two different metals are electrically connected and then if we expose that electrically connected two metal component into an electrolyte, the active metal which is anode area dissolves and cathode, which is noble metal which is protected, but it does happen in other cases where it is the same plate where two metal condition does not exist ok.

So, for example, one example if you recall that I wanted to show you that if it is a stressed condition, then the corrosion happens on the stress part, because of the galvanic effect. So, one example let me just show you see if you place this particular component say this is a bent rebar which is ribbed rebar ok.

So, if you see that this bend portion this portion as well as this portion they are specifically corroded red rust is more in those cases these two segments, because whenever you bent it that particular portion experiences more stress and the, and that leads to differential cell formation, this particular part would be preferentially anode and the rest of the part which is not bent, will be preferentially cathode and that leads to a galvanic effect like this ok.

So, this bent portion if you see it is more reddish rather than the rest of the portion. So, rest of the portion also we have corrosion, but not that pronounced if we consider the bent portion. So, this is one example I just wanted to show you. Now interestingly, if you see that this is the same metal part there is no different metal parts joined here, but still we do experience galvanic effect.

Now, coming to the experiment the virtual experiment what we have been doing, if we see that there are two parts three parts one is first experiment what we did, we have a HCl medium and there we have dipped zinc and we have weight there ok. Another experiment we had iron as well as zinc same area, let us say this is iron and this is zinc.

So, this is a two metal contact and in the two metal contact and we also measure the weight here. And we could see that here also weight is reduced, but the majority of the weight loss is basically coming from the zinc surface and the corrosion pattern if we see that it is like this. And iron also do get corroded some portion and zinc would be more, but the corrosion would be more close to the joint rather than away from that joint.

Another experiment we did same HCl medium, we had iron block and we measured the weight and we saw that weight is lost. Now, if we all are HCl and observation what we had in this case? Hydrogen bubble preferentially formed on iron surface you do get hydrogen bubble, but if we consider zinc surface not much of hydrogen bubble. But these two cases observations would be almost similar lot of hydrogen bubble, here also hydrogen bubble.

And interestingly it might be possible that the corrosion rate CR and here also CR if you compare zinc and this is iron, this would be might be less than corrosion rate of iron. But once we join them we see the corrosion rate of zinc in this coupled case is very high as compared to corrosion rate of iron.

And the last observation what we had is basically initially to start with the bubble will form on both the surfaces, but gradually you will see rather quickly you will see that the bubble only will form on iron surface not on zinc surface. And in this case iron becomes cathode, zinc becomes anode and in this case and that is what you have preferential zinc corrosion in this case and in those cases you will see uniform corrosion.

And if we try to see the reactions governing reactions, you would see that in this case you will see these two reactions and here these two reactions.

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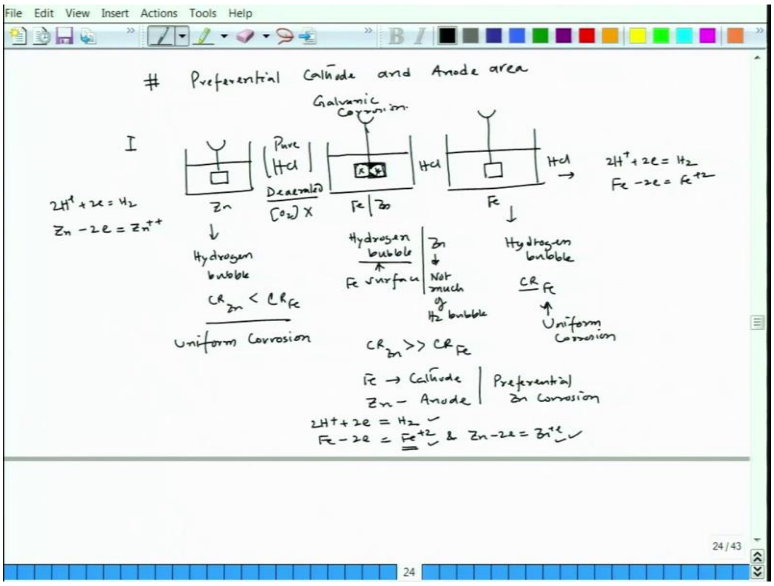

And if we see the center part, center part will have, but this the rate of this reaction would be very small compared to the rate of this reaction, but you would actually experience iron dissolution also. Now, interestingly the cathodic reaction if it is pure HCl and that to deaerated so; that means, there is no dissolve oxygen, no dissolve oxygen. So, the cathodic reaction would always be this one.

And in this case anodic reaction more of anodic reaction would be this less of anodic reaction will be this. Now, here you could see that though they are individually dipped in HCl both are acting as a anodic it is a very highly corrosive situation and both the metal should dissolve at a very high rate, but once we join together and expose to HCl iron dissolves less zinc dissolves more. So, that is what this is a typical example of galvanic corrosion.

Let us analyze this part little more with the help of mixed potential theory and in order to understand mixed potential theory you have to go back and try to check my other videos on galvanic corrosion on mixed potential theory rather. So, there also I have explained the same concept, but I am just in brief repeating the same thing ok.

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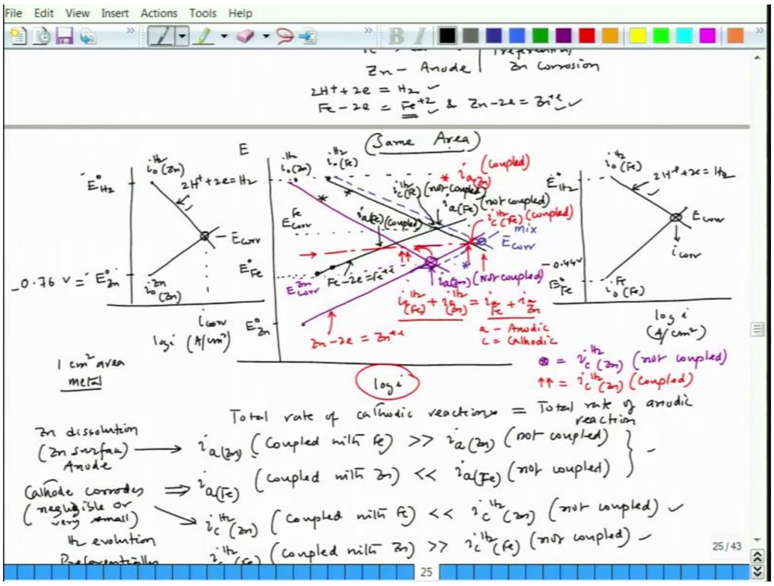

Zn – Anode | (preferential) Zn Corrosion

$2H^+ + 2e = H_2$ ✓

$Fe - 2e = Fe^{+2}$ ✓ & $Zn - 2e = Zn^{+2}$ ✓

(Same Area)

$i_{c(Fe)}^{H_2} + i_{c(Zn)}^{H_2} = i_{a_{Fe}} + i_{a_{Zn}}$

a – Anodic
c = Cathodic

⊗ = $i_c^{H_2}(Zn)$ (not coupled)

↑↑ = $i_c^{H_2}(Zn)$ (coupled)

Total rate of cathodic reactions = Total rate of anodic reaction

Zn dissolution (Zn surface) Anode ⟶ $i_{a(Zn)}$ (Coupled with Fe) >> $i_{a(Zn)}$ (not coupled)

Cathode corrodes (negligible or very small) ⟹ $i_{a(Fe)}$ (coupled with Zn) << $i_{a(Fe)}$ (not coupled)

H₂ evolution Preferentially → $i_c^{H_2}(Zn)$ (coupled with Fe) << $i_c^{H_2}(Zn)$ (not coupled) ✓

$i_c^{H_2}(Fe)$ (coupled with Zn) >> $i_c^{H_2}(Fe)$ (not coupled) ✓

Just to analyze this virtual experiment. See, if we consider zinc case. So, this is exchange current density on the zinc surface. And I am considering this is an assumption, but it should not be it should not be true value I am assuming that this is starting with its standard reduction potential both the cases just to analyze this part, but this value would be different this value would be different depending on the ph of the solution ok.

Now, in this case, if you see here also it will be same like this on iron surface and here this is my icorr and this is Ecorr, this is Ecorr and this is icorr and let us see this is log I, this is log I ampere per centimetre square, this is ampere per centimetre square. And remember we are taking one centimetre square area metal in all the cases. And we know this value is 0.76 volt and in this case this value is minus 0.44 volt ok.

Now, we have to put them on this scale. So, this is log i this is E. So, this position does not change. So, this is let us say this is i0 hydrogen on zinc surface, this is i0 on iron surface, and if I see the position of this, this is E0 Fe and let us see it is here this one and here it is, this is individually there like this. So, this is for iron, this is for iron individually and this is zinc. Now, once we have mixed potential so, we have to consider this concept the total ok.

So, now if you see this, let me drop it little more bit, that is what you have to practice it ok, it is very important to practice. So, now, here you have to add this hydrogen reduction reactions, and you also add the total metallic oxidation. So, here it is meeting. So, it will go like this ok. So, now this is the part Ecorr mixed Ecorr mixed.

Now, if you want to know ok what will be my corrosion rate of iron as well as, zinc after consideration of mixed potential for the case where, both the iron and zinc plate blocks are joined together and placed in HCl.

So, you just need to draw a line here from here ok. And at this point you have i on iron surface hydrogen reduction should be plus i on zinc surface hydrogen reduction should be equal to i of iron plus i of zinc and here it is a I am just putting a because a is anodic and here I can put c, the c is cathodic ok.

So, now total cathodic reaction rate is equal to total anodic reaction rate. And we have to see across this red line that red line, wherever it cuts the anodic line of zinc. So, this is the anodic line of zinc, where zinc minus 2 equal to zinc plus plus ions are forming and that point is this one.

Now, you could see that previously the corrosion rate of zinc was individually what is here, it was here which is ia zinc when it was alone not coupled ok, but after coupling you see the corrosion rate of zinc it is at this point which is i.

So, this point so, this point is ia zinc when coupled. And if we consider the corrosion rate of iron before coupling, it was here. So, this is ia iron not coupled and after coupling the corrosion rate of iron is because this is the line, which talks about anodic reaction of iron. So, the corrosion rate of iron is now this one is the corrosion rate of iron after coupling.

So, this is ia iron coupled and of course, this line is nothing, but cathodic reaction lines, this is hydrogen similarly these two lines are, these two lines are this and this now interesting part is let us see so; that means, it is very clear that ia of zinc when it is coupled with iron has gone up i a zinc when not coupled as well as ia iron when coupled with zinc is less than less than iron not coupled.

And if I compare so; that means, first the observation what we had that once we joined together iron corrosion rate would reduce to a drastic level and zinc corrosion rate will increase to a drastic level, and interestingly exactly it happens like that.

Now, question is in order to another observation what we had was that, i ic of hydrogen on zinc surface when coupled with iron should be less than ic hydrogen on zinc surface when not coupled. Let us see whether that condition satisfies. Now, if I see the hydrogen evolution reaction rate, when it was not coupled for the zinc case, it was here.

So, this is the that round part this part is basically ic hydrogen on zinc surface not coupled and let us see what is the hydrogen evolution rate on zinc surface after it is coupled with iron. So, again that red line you have to see this particular line, this particular line you have to look at and you have to see where that line cuts with the hydrogen reduction line in case of zinc, it is cutting here it is cutting here.

So, that value is nothing, but ic hydrogen on zinc surface when coupled. So, definitely this value from here to here its, it has got reduced and remember this is in log scale. So, that is what the reduction is quite large. So, this condition is met.

Now, let us see the another condition observation was on iron surface the hydrogen evolution rate would increase so; that means, the statement is ic hydrogen on iron surface when coupled with zinc should be greater than greater than ic hydrogen iron surface, when not coupled let us see those two points. Again we have to see the red lines and the red lines if I see it is cutting the hydrogen line for the iron case this here ok.

So, this is ic hydrogen on iron surface coupled and let us see what was the ic hydrogen on iron surface when it was not coupled. So, that point is, is this point, which is ic hydrogen iron not coupled ok. And interestingly those two points not coupled cases are shown here. So, which is again mixed potential theory because the total reduction rate should be equal to total oxidation rate.

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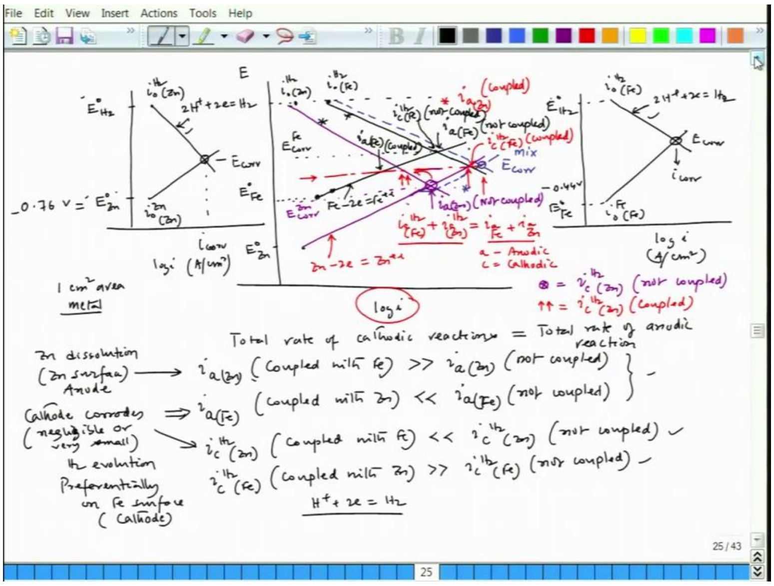

Total rate of cathodic reactions = Total rate of anodic reaction

Zn dissolution (Zn surface) Anode → $i_{a(Zn)}$ (Coupled with Fe) >> $i_{a(Zn)}$ (not coupled)

Cathode corrodes ⇒ $i_{a(Fe)}$ (coupled with Zn) << $i_{a(Fe)}$ (not coupled)

(negligible or very small) → $i_c^{H_2}(Zn)$ (coupled with Fe) << $i_c^{H_2}(Zn)$ (not coupled) ✓

H_2 evolution Preferentially on Fe surface (Cathode) $i_c^{H_2}(Fe)$ (coupled with Zn) >> $i_c^{H_2}(Fe)$ (not coupled) ✓

$H^+ + 2e = H_2$

So, here also this is matching so; that means, preferential and what is the cathodic reaction in both the cases? This is the cathodic reaction. So, cathodic reaction is preferentially taking place, hence this is cathode. Since we know that cathodic reaction takes place on cathode and in this surface on this surface hydrogen evolution reaction is very less, but zinc dissolution is maximum on this zinc surface.

So, this is zinc surface and that is what it is anode an interesting part is we could also see that hydrogen evolution on the zinc surface is less. And another important thing is whenever we say galvanic corrosion it does not mean that the cathode does not corrode cathode also corrodes.

Here you see cathode also corrodes, but it is negligible sometimes, but negligible or very small fine. So, that means, with the mixed potential theory we could analyze the entire this three virtually experiments and interestingly its all matching with the theory.

And we could see that two concepts, one is one part becomes preferentially cathode another part becomes preferentially anode, and cathode also corrodes, but at a much smaller rate, but anode corrodes at a much higher rate. And here the major one of the important conditions what we have imposed here remember that will come to the come for the discussion is same area.

We will see if the area changes for cathodes and anodes we will have a serious implication on anode galvanic corrosion.

So, let us stop here we will continue our discussion on galvanic corrosion in our subsequent lectures and remember we will explain galvanic corrosion quite a deep because you will see the subsequent lectures, whenever galvanic corrosion, whenever any type of corrosion forms comes in, we will see the galvanic effect needs to be considered. So, let us stop here we will continue in our next lecture.

Thank you.