Corrosion - Part II
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Lecture - 10
Explanation of Corrosion Processes on the basis of Mixed Potential Theory: Part 3

Hello everyone, today we have lecture 10.

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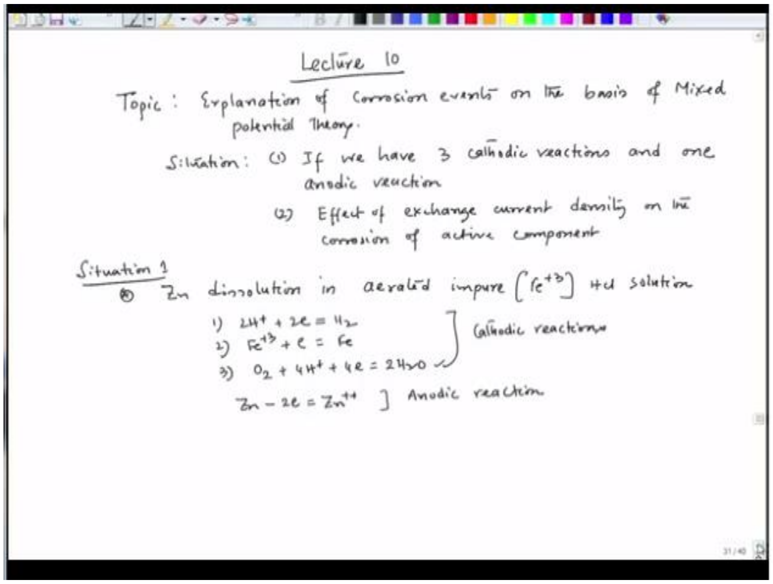

Lecture 10

Topic: Explanation of Corrosion events on the basis of Mixed potential Theory.

Situation: (1) If we have 3 cathodic reactions and one anodic reaction

(2) Effect of exchange current density on the corrosion of active component

Situation 1

(a) Zn dissolution in aerated impure (Fe^{+3}) HCl solution

1) $2H^+ + 2e = H_2$
2) $Fe^{+3} + e = Fe$
3) $O_2 + 4H^+ + 4e = 2H_2O$

Cathodic reactions

$Zn - 2e = Zn^{++}$ Anodic reaction

And the topic we will continue our discussion on explanation of corrosion event on the basis of mixed potential theory and today we will try to see couple of examples mainly we will talk about this situation 1 is if we have a 3 cathodic reaction and one anodic reaction. And 2 we will take 2 situations today, so another one is effect of exchange current density on the corrosion of active component.

So, these 2 situation will look at in this case it is very clear that we have in a system we have 3 cathodic reactions and 1 anodic reactions. In lecture 8 and 9 we talked about 2 cathodic reactions and 1 anodic reaction and the second see the situation will consider is the effect of exchange current density on the corrosion of active component. So, in this case it could be possible that the cathodic reaction or the anodic reaction that are taking place on that particular metal in that particular environment could be higher than the exchange current density of those cathodic or anodic reactions on that active component.

This is one situation, another situation is we can have in normal circumstance, so that means engineering case engineering applications many a times we have galvanic couples or contacts between active metal site and noble metal site. One classical example is when we have combination of copper and steel like if we have a say like steel rivet joining 2 copper plates that is 1 combination where the exchange current density of the cathodic reaction on copper surface will be higher than the exchange current density of the cathodic reaction on the steel.

So, this is 1 case another case could be platinum, if platinum or gold or caladium those are noble metals. Those are galvanically coupled with or connected to steel or iron. So, that case iron dissolution rate will be much higher in acid because hydrogen exchange current density on platinum or gold or palladium is few orders magnitude higher than the exchange current density of hydrogen evolution on iron surface.

So, that also increases the rate of dissolution of iron, so we will consider that part, so the first let's see the situation 1 what we have considered here. So, let's say the situation where we have zinc dissolution in aerated impure and the impurity is nothing but Fe+3 ion Hcl solution in ambient condition. So, that time if this is the consideration let's say here the situation 1 here, so we have 3 cathodic reactions one is

$$2H^+ + 2e = H_2$$
$$Fe^{3+} + 3e = Fe$$
$$O_2 + 4H^+ + 4e = 2H_2O$$

So, these are the three cathodic reactions possible in that particular electrochemical process and there is only one anodic reaction since zinc is dipped in that particular impure aerated acid, aerated means it is freely aerated. That means oxygen is there dissolve oxygen is there, so that is what these reaction is possible. So, the dissolution reaction this is the dissolution reaction or anodic reaction 1 anodic reaction so this is possible.

So, that case we have to consider all the reactions over zinc because that is the only metal surface that is all those 3 cathodic reaction will face as well as of course this anodic reaction.

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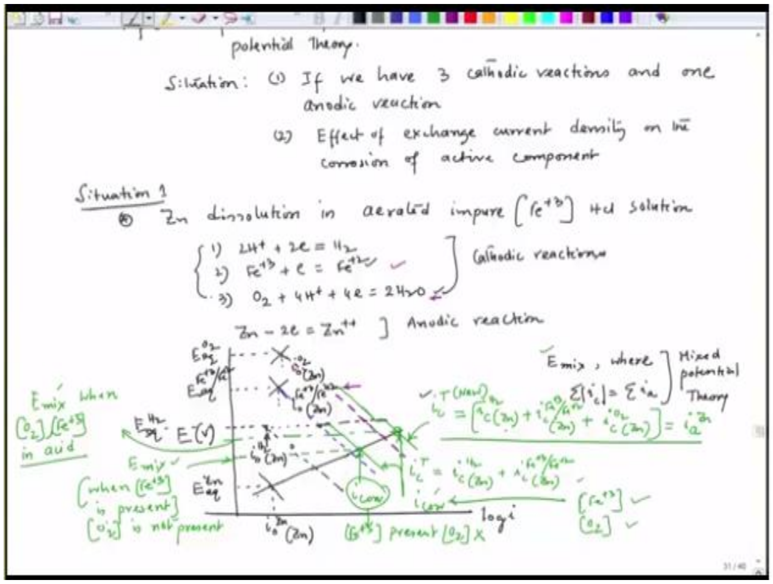

potential Theory.

Situation: (1) If we have 3 cathodic reactions and one anodic reaction

(2) Effect of exchange current density on the corrosion of active component

Situation 1

Zn dissolution in aerated impure [Fe^{+3}] HCl solution

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] Cathodic reactions

$Zn - 2e = Zn^{++}$] Anodic reaction

E_{mix}, where $\Sigma|i_c| = \Sigma i_a$] Mixed potential Theory

$i_c^{T\,(New)} = \left[i_{c(Zn)}^{H_2} + i_{c(Zn)}^{Fe^{+3}/Fe^{+2}} + i_{c(Zn)}^{O_2}\right] = i_a^{Zn}$

$i_c^{T} = i_{c(Zn)}^{H_2} + i_{c(Zn)}^{Fe^{+3}/Fe^{+2}}$

So, that time we can draw mixed potential theory. This is the plot between log i versus E which is volt and we will consider this voltage with reference to standard hydrogen electrode. Now let's say this is the point which is E equilibrium of zinc corresponding i zero zinc over zinc surface. Then we will have another reaction which is basically hydrogen evolution reaction on zinc surface, so this is E equilibrium hydrogen.

Then we can have E equilibrium iron + 3 Fe+2 and then we might have another we will have another one which is E equilibrium O2 and corresponding value this is i zero O2 over zinc surface. This is i zero Fe+3 Fe+2 over zinc surface and this is i zero H2 over zinc surface, so now all the 3 reaction cathodic reactions we have to consider in order to consider the concept of mixed potential theory that will reach E mix where summation of ic = summation of ia.

So, that condition is to be met, so this is the mixed potential achievement or concept mixed potential theory as per the mixed potential theory. So, now we have to extend those lines and then keep adding up those similar lines like cathodic lines wherever there will be a experience of new reaction while cathodic polarization takes place. So, then if we consider for example black colour for zinc, so this is my zinc it will go up like this.

Then this will be extension of this, this is hydrogen line dotted line is the hydrogen line let me draw with the blue colour the line for iron. So, this is the iron line but at this particular voltage when this Fe+3 this particular reaction is polarizing towards cathodic side. So, at this point it will experience another cathodic reaction which is hydrogen evolution reaction, so we have to add it, so I am adding all the things like a blue green colour.

So, this is addition part, so this line is ic total = ic hydrogen over zinc surface + ic Fe+3 Fe+2 over zinc surface. So, that means if we have no oxygen dissolve oxygen but only oxidant is a strong oxidant like Fe+3 then the mixed potential would be this only will be mixed potential E mix when Fe+3 is present. Now we have to consider let's say with a pop up colour, so if we continue this oxygen line this is the oxygen line**.**

Now it will when the oxygen line is this cathodic reaction is polarizing at this potential it will experience another cathodic reaction which is this one. So, add it, so if we add that where it and then keep going down parallel to the purple line. So, you will come there and then it will so if I change this line little shallow the slope becomes if I change this slope little bit I have change the slope little bit, so that I can have the effect of hydrogen polarization also.

So, that case this line will have to be change, so that the new just doing little bit of modification, so this will be my mixed potential when Fe+3 is present. Now at this point when it come to this line which is hydrogen evolution start point it will further added up and then go down. So, this particular line is ic total new = ic hydrogen evolution on zinc surface + ic Fe+3 Fe+2 over zinc surface + ic oxygen over zinc surface.

So, this should be equal to there is only one anodic reaction ia zinc over zinc surface of course this is not needed at all. We have just put zinc because those are happening on the zinc surface, so this and the E mix should be, so this is the E mix let me put it as a prime when we have dissolve oxygen Fe+3 in acid. So, we consider in this case we have consider all those 3 processes and in this case we are considering when O2 dissolve oxygen is not present.

So, this is my complete diagram and at this point this is the E mix and we could see that the total ic = total ia and here only one ia is present. And similarly in this case ic total is basically the combination of 2 reaction because 1 reaction is not taking place. Now we see that as the number of reduction reactions are increasing I could see that the corrosion rate is increasing this is i corr and this is i corr prime.

So, i corr is corresponding to the situation when Fe+3 present and O2 not present but in this case Fe+3 present O2 present. Now that means as we increase the number of reduction processes in that complete electrochemical process which is nothing but the corrosion of zinc our corrosion rate increases depending on whether these interactions are possible.

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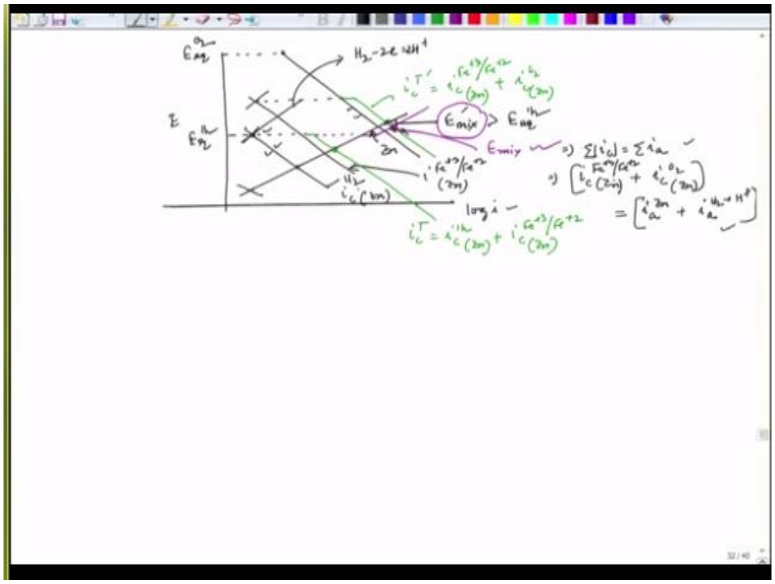

But there could be a situation like 1 situation I can think of, so I will just draw that same line without giving any without writing all those details this is the zinc one, this is the hydrogen one. I just simply write hydrogen and zinc this is ia this is ic hydrogen over zinc now if this is my ic Fe+3 Fe+2 over zinc then here I could see that we can have the existence of hydrogen evolution reaction.

So, this is the new corrosion point this is ic total = ic hydrogen over zinc surface hydrogen evolution of course ic Fe+3 Fe+2 over zinc surface. But if the another, that oxygen evolution reaction happens here depending on the E equilibrium oxygen, so that will go straight of course it will be decided by the tafel slope. And here one assumption is whatever things we are drawing 1 assumption is we are considering tafel slope to the same for either of that cathodic or anodic processes.

So, now here we could see that I could add this reaction which is ic total prime = ic Fe+3 Fe+2 + ic O2 over zinc surface. But before it intersects the where it intersects the anodic line, so that potential this is the E mix prime this point is above the hydrogen evolution line on the zinc surface. So, hydrogen reaction will not be effective here, so the only 2 reaction will take the will guide the entire corrosion process.

But one more important issue we will see with some numerical problem if this is in log scale if this line and this line they are staying quite farther from each other. So, then the effect of this line on this overall reaction rate of the zinc dissolution will not be felt. So, we will see that part in next class where we will be solving 1 problem. Now this is one typical situation where even though there are 3 cathodic reactions but 1 cathodic reaction is not participating.

But once we have this situation there could be addition of another anodic reaction because beyond this because this potential above this potential this E corr is greater than E equilibrium hydrogen. So, we can have addition of oxidation reaction, so here it will be added up, so it will go like this, so this will not be the actual E mix rather this point will be the E mix.

Because we could see that when anodic reaction is going up so we have anodic reaction for hydrogen is going on. So, this particular line talks about H_2 - 2e = $2H^+$, so at this point I will actually meet the mix potential concept which is summation of ic = summation of ia which is nothing but ic hydrogen on sorry this is Fe+3 Fe+2 zinc + ic oxygen reduction on zinc surface = ia of zinc over zinc surface ia of zinc + ia of hydrogen 2 H +.

So, and that is possible at this point, fine, so this is the possible changes in this case I could see that before this mixed potential line which is basically the this situation which is nothing but E mix prime before it meets that anodic line of zinc. It actually come across all the polarization cathodic polarization lines of all 3 cathodic reaction.

But here we see that if the situation is like this when it reaches to the mixed potential that potential lies beyond above one of the E equilibrium hydrogen line. So, this is the hydrogen is staying above, so we have to add the anodic current density of hydrogen with anodic current density of zinc. And then only we get the concept of mixed potential theory, so this is one variant for a situation when we have multiple number of cathodic and 1 anodic reaction.

So, let me stop here, we will continue our discussion on this particular topic in the next class. We will talk about a effect of exchange current density on the corrosion rate of an active metal, thank you.