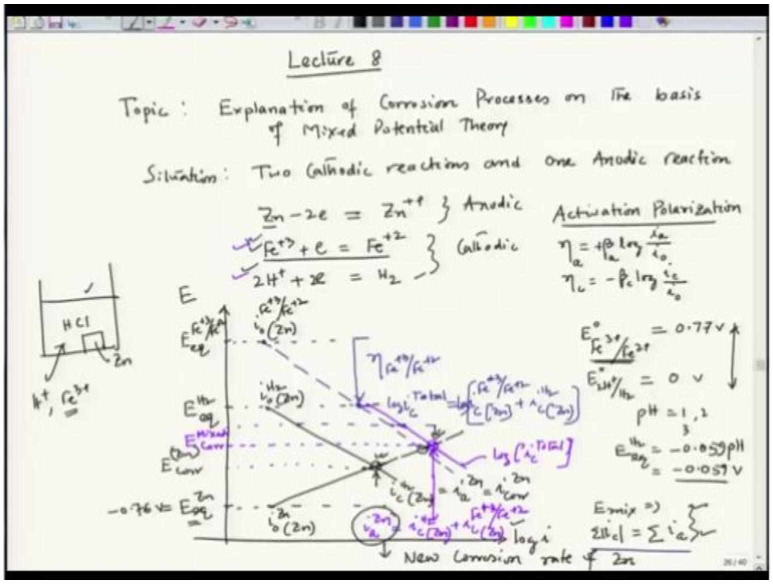
Corrosion - Part II
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology - Kanpur

Lecture - 08
Explanation of Corrosion Processes on the basis of Mixed Potential Theory: Part 2

Hello everyone, today we have our lecture 8.

(Refer Slide Time: 00:21)



Lecture 8

Topic: Explanation of Corrosion Processes on the basis of Mixed Potential Theory

Situation: Two Cathodic reactions and One Anodic reaction

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

$Fe^{+3} + e = Fe^{+2}$
$2H^+ + 2e = H_2$ } Cathodic

Activation Polarization

$\eta_a = +\beta_a \log \frac{i_a}{i_0}$

$\eta_c = -\beta_c \log \frac{i_c}{i_0}$

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77 V$

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

pH = 1, 2, 3

$E^{H_2}_{eq} = -0.059pH = -0.059 V$

$E_{mix} \Rightarrow \{\sum i_c = \sum i_a\}$

New Corrosion rate of Zn

Today’s topic will continue our discussion on explanation of corrosion process on the basis of mixed potential theory and today we will consider 2 instances I think it will be both lecture 8 as well as 9. We will consider situation: 2 cathodic reaction and 1 anodic reaction. We have already covered situation where cathodic reaction is 1 and anodic reaction is also 1.

So, that means single cathodic and single anodic reactions. Now here we are considering 2 cathodic reactions and 1 anodic reaction and the example being zinc dissolution and iron ferric iron reduction and also if we put zinc in impure acid which is deaerated that means there is no dissolve oxygen. But if we have a very small quantity ppm level content of Fe+3, so then we can have these 2 cathodic reaction.

So, these are the 2 cathodic reaction and this is 1 anodic. Now we have to draw mixed potential theory. We have to draw those interactions of these reactions apply mixed potential theory, so again the plot would be E versus log i and here we are only concentrating activation polarization. So, our equation to indicate these 3 equations should be general equation over voltage equal to the tafel slop log i versus i zero this is the general equation.

If it is anodic that time there would be positive and beta a, if it is cathodic negative beta c log i and here also since it is anodic in this case it would be cathodic reaction. So, since let's see where are those equilibrium potentials. Let's assume that the equilibrium potential of zinc let's make it is equilibrium it is reversible potential, let's say this is my reversible potential which is if it is E equilibrium zinc.

And since zinc is very active and if we consider this to be - 0.76 volt which is the standard reduction potential. So, even if the zinc ion content decreases that means if we do not keep the concentration as 1 because when you are inserting into the metal, the concentration of zinc in the beginning will not reach to 1. So, it will be less than that, so this equilibrium potential would be further down there if it is not unit concentration in that particular solution.

So, anyhow, so this is if we assume that this is to be that particular situation this is assumption, completely assumption this is the potential. Now this particular reaction if we consider this is a very strong reduction reaction. So, we know

$$E^o_{Fe^{3+}/Fe^{2+}} = 0.77$$

which is very strong reduction potential very high reduction potential and E zero this is zero volt.

So, it means that the equilibrium let's also consider the situation that pH let's say 1. If we keep ph should be 1 or 3 or 2 any pH we consider in the acidic medium considering that in the acidic medium this reaction would happen. So, this particular potential let's say E hydrogen equilibrium, so depending on pH this equilibrium potential would vary would be equal to - 0.059 pH.

So, now if I consider pH to be 1 then it should be 0.059 volt, now depending on the pH this potential would vary that equilibrium potential. Now if this particular concentration Fe+3 concentration is very low still if we assume that this potential since there is a huge gap between zero and 0.77. This is a huge gap between this reduction potential. So, it would lie this equilibrium potential Fe+3, Fe+2 equilibrium. It should lie above this point.

Now we have to consider their respective i zero. Let’s say this is the point of i zero of zinc on zinc. Let’s say this is the i zero, hydrogen on zinc. Because if we have a solution deaerated HCl let’s say HCl, so there we have those ions H+ as well as Fe3+ and now we have zinc, zinc block. Now these 2 reactions this reaction as well as these reactions they must find some surface on which this reaction can happen.

So, these are the surface over which this reaction would happen is basically the zinc surface. So, now that is what i zero hydrogen over zinc surface, similarly this ion is getting reduce to Fe+2 that reduction process would also happen on zinc surface. So, we can write this is the point because these are the equilibrium potential and i zero always lies on equilibrium potential for the respective reactions, so this point is i zero Fe+3 Fe+2 over zinc surface.

Now as per the mixed potential theory they must reach to a point where this condition is met where summation of ic = summation of ia. Now if there is no Fe+3, so then it would have its own corrosion potential that means this is as per the single cathodic and anodic reactions. This is E corr and I just put this particular situation zinc because zinc is dissolved and i corr is so that means at this condition ic hydrogen on zinc = ia zinc = i corr zinc.

Now the other reaction is also following its own polarization let’s say this is the polarization of the other reaction which is Fe^{+3} + e = Fe+2, so this is going like this. Fine. Now we have to maintain this particular criteria that suggest that whenever 1 polarization line a particular polarization line. For example, here it is the cathodic polarization the blue line is the cathodic polarization line for Fe+2 to Fe+3 to Fe+2.

So, whenever it experiencing another cathodic polarization those currents are to be added up, so that means once it is coming to this much polarization. So, that means if the polarization level is this much which is+ 3 to Fe+2 this is the polarization level for this reaction. So, here it is experiencing another cathodic reaction which is hydrogen reduction. So, now as per this mixed potential criteria we have to add up those currents and then at this point we have to add total equal to ic of Fe+3, Fe+2+ ic hydrogen, this is on zinc surface.

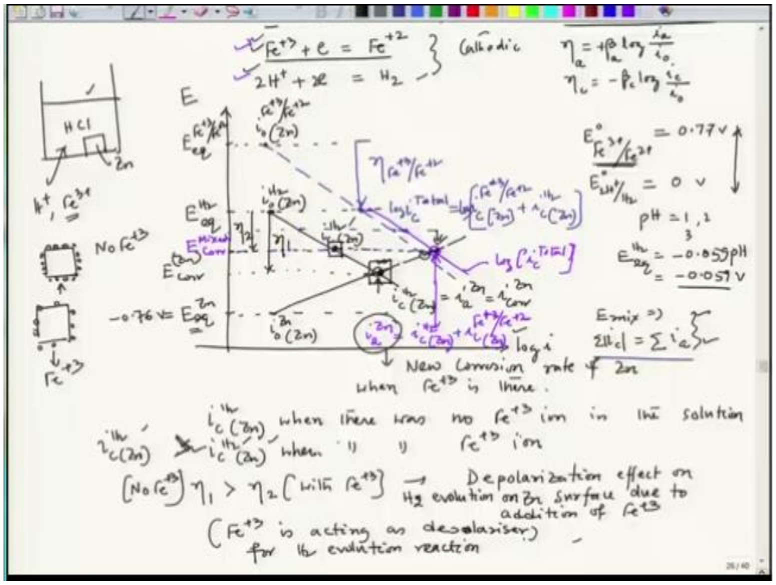
This is to be added up and then we will take log and so that means that log point will shift to the right. Because the actual this total ic would be following a different line which should be the current value should be at a particular potential. If I consider the particular potential that current value should be little higher than that because here this one and this one these are added up and then taking log, so it will come here.

So, similarly this one and this one they are to be added up and then this point will come here and now you see that it will be parallel to that. So, then we have to draw this line, so this is the plot of log of ic total, so the ic this ic contains cathodic current density for this cathodic reaction as well as cathodic current density for this reaction. Now if we extend this line then I have to find out that point where this criteria is met, these 2 criteria is met.

Now if I consider there are 2 points, if I consider this point as well as this point then we could see that at this point only I could see that ia zinc = ic hydrogen over zinc+ ic Fe+3 Fe+2 over zinc and also it corresponds to a potential. So, this is E corr mixed, so this purple line actually and cross section of that purple line at the black line for the zinc, zinc anodic line that is the point we have to concentrate on and that is the point the system would try to reach.

And that corrosion rate of zinc would shift from this point to this point. Why? When we have when we do not have this Fe+3 in this, that means it is a pure HCl, my corrosion rate was here**.** But once we added Fe+3 into this solution then my corrosion rate has move to this position, so that means corrosion rate of zinc has increased and the criteria for the mixed potential theory is also met.

(Refer Slide Time: 15:54)



And now ia zinc is nothing but the new corrosion rate of zinc when Fe+3 is there. Now interesting part here if you look at if we see this particular mixed potential that in the new mixed potential when we have impurity in the form of Fe+3 I need to see the hydrogen evolution on zinc surface. Now if you see the hydrogen evolution rate when there was no impurity what is that hydrogen evolution rate. This particular point is the hydrogen evolution rate which is nothing but let's say this is term it has ic hydrogen on zinc surface when there was no Fe+3 iron in the solution.

Now once we have F+ 3 let's say this point is that is i total, so at that point, so corresponding to this point. Okay, this is the new point I would say hydrogen over zinc when there was Fe+3 on it. So, let me put it as prime, so this is ic hydrogen zinc prime, now what happens once we have this Fe+3 when it was pure the hydrogen evolution rate on the zinc surface was indicated by this particular rate.

Now once we have added Fe+3 when hydrogen evolution rate on zinc surface has reduced, now what could be the observation. The observation is unique, so in the beginning when there was no Fe+3 will see lot many bubbles of hydrogen on top of the zinc surface. But once we have Fe+3 since the rate of this rate is less than ic hydrogen on zinc surface when there was no impurity when there was this is the case when there was impurity and this is the case when there was no impurity.

So, now in this case no Fe+3 but once we have Fe+3 since the rate of hydrogen evolution is low on zinc surface. Because that time the current density corresponding to hydrogen evolution at that new E corr mixed is less. So, we would see that the hydrogen evolution on the surface is much less compare to this, so here we have Fe+3. Interestingly when we had no Fe+3 what was the polarization the total polarization the over voltage for the hydrogen evolution reaction.

So, the total over voltage was this much let’s say this is new one this was the over voltage when there is no Fe+3. Now once we have added Fe+3 the over voltage has gone with reference to the equilibrium potential of hydrogen evolution to this, so this is neeta 2. So, we can say that the over voltage 1 is greater than over voltage 2, so this is corresponding to with Fe+3 and this is corresponding to no Fe+3. Okay.

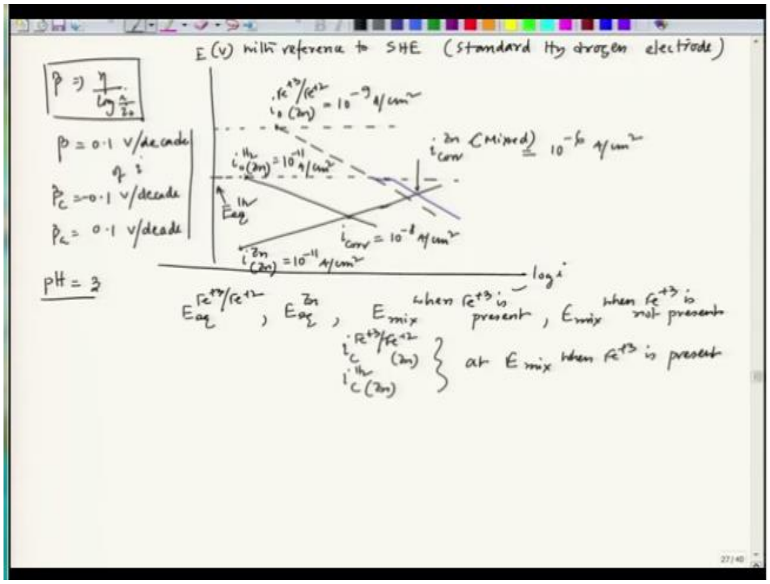
So, now which one is larger, so this one is definitely larger, so that means once we have added Fe+3 the total polarization for the hydrogen evolution reaction on zinc surface has gone down. So, we can say that it has got depolarized, so we can clearly say this is the kind of depolarization effect on zinc surface due to addition of Fe+3 and depolarization of what hydrogen evolution. So, actually I can say that depolarization effect on hydrogen evolution on zinc surface due to addition of Fe+3.

So, we can also say that Fe+3 is acting as depolarizer. Further so I can say that depolarization for the hydrogen evolution reaction. Now interestingly so if we consider that the hydrogen evolution rate over zinc surface is the observation for zinc corrosion. That means if you say that the more the hydrogen evolution on the zinc surface more will be the corrosion of zinc that may not be true.

That means when we have a strong ion strong reduction reaction when we have a strong reduction. For example this case are oxidant the strong oxidant because Fe+3 in this case is a strong oxidant which has a tendency to go to Fe+2. So, if we have a presence of strong oxidant then there could be a situation that the zinc hydrogen evolution of zinc surface would be low. But the rate at which the zinc dissolution happens would be much faster than the rate at which when the observation was the hydrogen evolution on zinc surface was high.

So, this is the reason for that situation because when we have a lower polarization for the hydrogen evolution I have much higher dissolution rate of zinc. So, on this particular ratio let’s have some numerical problem. Okay, so I have chalk down numerical problem on this.

(Refer Slide Time: 22:31)



That problem statement is like this let’s say situation where log i and this is potential and remember this potential with reference to standard hydrogen electrode. Okay. So, that time I can put some of the so the same diagram let’s put this value is 10^{-11} ampere per centimeter square, this value is i zero Fe+3 Fe+2 over zinc surface is 10^{-9} ampere per centimeter square. When the there was no Fe+3.

And if there is no Fe+3 iron so then this is the corrosion rate of zinc which is i corr = 10^{-8} ampere per centimeter square, this value this i zero zinc over zinc surface = 10^{-11} again ampere per centimeter square. And the corrosion rate of zinc i corr of zinc I would say mixed I just put mixed when that the mixed potential theory is getting applied. So, these value becomes 10^{-6} ampere per centimeter square.

And few data that is given is beta = 0.1 volt per decade of i the current density why decade because beta can be considered as neeta by log of i by i zero. So, that is what I am taking per decade of because this is in decade, so now so beta c if we consider that time it will be - 0.14 volt per decade

I simply said decade of current density I just omit this of i rather I say this a volt per decade. And beta a = 0.1 there is a - sign when we consider beta c this is decade.

So, this is the data that is given and another data which is pH because will decide what should be the E equilibrium hydrogen. So, not this point, this is the point which is E equilibrium hydrogen that would be this pH let's consider pH to be 3. Now we have to find out what will be E equilibrium Fe+3 Fe+2 E equilibrium zinc and ic Fe+3 Fe+2 at. Okay.

So no this is not the case. So, the E mix when Fe+3 is present E mix when Fe+3 is not present as well as ic Fe+3 Fe+2 and ic H2 over zinc surface both at E mix when Fe+3 is present. So, these are the parameters are to be found out, so we will take this problem to our next lecture. let's stop here, thank you.