Corrosion – Part II
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Lecture – 21
Numerical Problems and Passivation

Hello everyone, today will have lecture 21. We have been discussing several corrosion events on the basis of mixed potential theory. In parallel we have been solving numerical problems and find to assess the effect of several factors like a number of oxidizing agents present in an electrolyte on the corrosion of active metal, effect of exchange current densities, effect of galvanic couple and at the same time effect of increase in area of either cathode or anode.

And then see the change in the corrosion rate of the active component. We have also discussed cathodic protection and we could see that there are 2 modes of cathodic production. 1 is ICCP that means, impressed current cathodic production as well as another 1 is sacrificial anode. And we could see the analysis of cathodic process protection on the basis of mix potential theory. We could also see the effect of velocity and in all those situations.

We could see that the effect is in the active zone of the metal which is dissolving. And that interaction point between the polarization graph of cathodic polarization as well as anodic polarization. But all the time we have considered the anodic polarization to be activation controlled. And then we sorted solving some problem when we on the particular situation that if the potentials are not measured with reference to hydrogen electrode.

Rather than if we measure the potential of the polarizing electrode. On the with the respect to some other standard reduct standard electrode like Ag/AgCl, silver/silver chloride, copper/copper sulfate or saturated calomel electrode. Then what could be how we could solve a problem to find out the potential as well as the corrosion rate. And in fact, in the last lecture, the later part we start we try to understand some of the scale factors, when we use saturated caromel electrode.

And one problem we also solved that if platinum is polarized to some certain voltage and that polarization with reference to oxygen reduction oxygen evolution reaction that means it is an anodic polarization. And the potentials were measured with reference to saturated calomel electrode. And we wanted to and the part that we wanted to find out the amount of over voltage. So, we put 2 scales standard hydrogen electrode scale.

As well as standard saturated calomel electrodes scale and we could see that how to change those scales to find out the potential as well as over voltage. Now, before we move to another important aspect, which can be analyzed with refer with respect to mixed potential theory that is the passivity. We need to solve one more problem just to make it clear that how to make use of electrode reference electrodes other than standard hydrogen electrode. So, first lecture 21.

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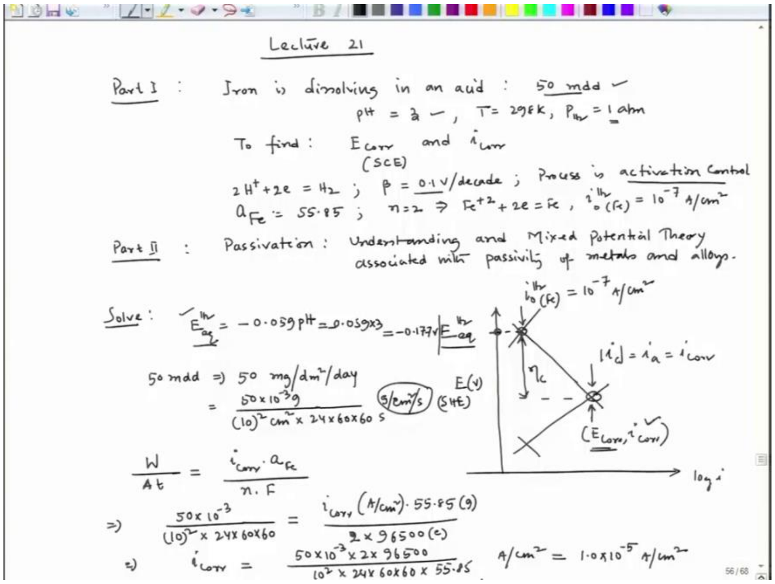

Lecture 21

Part I : Iron is dissolving in an acid : 50 mdd
pH = 3, T = 298 K, $P_{H_2} = 1$ atm
To find : E_{corr} (SCE) and i_{corr}
$2H^+ + 2e = H_2$; $\beta = 0.1$ V/decade ; Process is activation control
$a_{Fe} = 55.85$; $n = 2 \Rightarrow Fe^{+2} + 2e = Fe$, $i_{o(Fe)}^{H_2} = 10^{-7}$ A/cm²

Part II : Passivation : Understanding and Mixed Potential Theory associated with passivity of metals and alloys.

Solve : $E_{eq}^{H_2} = -0.059\,pH = -0.059 \times 3 = -0.177\,V$ $E_{eq}^{H_2}$

50 mdd $\Rightarrow$ 50 mg/dm²/day

$$= \frac{50 \times 10^{-3}\,g}{(10)^2\,cm^2 \times 24 \times 60 \times 60\,s} \quad (g/cm^2/s)$$

$$\frac{W}{At} = \frac{i_{corr} \cdot a_{Fe}}{n \cdot F}$$

$$\Rightarrow \frac{50 \times 10^{-3}}{(10)^2 \times 24 \times 60 \times 60} = \frac{i_{corr}\,(A/cm^2) \cdot 55.85\,(g)}{2 \times 96500\,(c)}$$

$$\Rightarrow i_{corr} = \frac{50 \times 10^{-3} \times 2 \times 96500}{10^2 \times 24 \times 60 \times 60 \times 55.85}\ A/cm^2 = 1.0 \times 10^{-5}\ A/cm^2$$

In lecture 21 the first part the part 1 a problem will be solved and that problem statement is like iron is dissolving in an acid at a rate of let 50 mdd and the pH of the solution is 3 and we need to find out. So, the to find E corr and I corr and the E corr will should be with reference to standard calomel electrode and the other data which are provided these are the 2 things. We need to find out other data this is hydrogen evolution is basically the reduction process.

This is one, second part is pH of course is 3, beta which is the tafel slope is 0.1 per decade of volt per decade of current density and the process is activation control. So this problem we will try to solve and we have to find where to also see the other another data which is iron, atomic weight of iron is 55.85 gram and we are taking n to be 2 that means, it indicates that this reaction is this reaction we are considering.

That means 2 electrons are participating for the anodic process. So, this is the part 1 and part 2 we will start passivation, passivation understanding and mixed potential theory associated with passivity. So, these are the 2 parts will try to do today. In fact, once we solve this first problem. And this second half of the topic will just introduce passivity and then in subsequent lectures will keep continuing our discussion on passivation.

So, let’s try to solve the problem. Now since it is mentioned activation control, that means we can draw mixed potential theory. This is log i potential. Now, let me draw everything with reference to standard hydrogen electrode. And since hydrogen reduction, hydrogen and reduction is the cathodic reaction. So we can have mixed potential theory like this. And one more data that is missing is i zero Hydrogen over iron surface = 10^{-7} ampere per centimeter square.

So, if we see this so that means, this point is i zero hydrogen over iron surface = 10 to the - 7 ampere per centimeter square and this potential is E equilibrium hydrogen and this can be this particular quantity can be found out. Because, we have mentioned pH to be 3 and this is at temperature T = 298 Kelvin that means room temperature and pressure hydrogen = 1 atmosphere.

If it is not 1 atmosphere then the calculation becomes a little tricky because that time we have to consider reduction Nernst equation with the partial pressure of hydrogen also, but if this is maintained at 1 atmosphere pressure. So my equilibrium hydrogen this becomes 0.059 pH = 0.059*3 = - 0.177 volt, fine. So, this is the voltage that this particular point is - 0.177 volt.

Now, since, beta is considered 0.1 volt and if this point coordinate if I tried to find out E corr, i corr, so i corr can be found out from this data because we have already measured this is the value that is given 50 mdd which is nothing but 50 milli-gram per decimeter per day. So, I can convert this one into gram and decimeter can be converted into centimeter square. So, I can make it 10^{1} square centimeter square.

And day I can convert to second, 24 hour into 60 minutes into 60 seconds. So, second this becomes my gram centimeter square per second. So, mdd can be expressed with this W by At = i corr iron divided by nF. Now this side is 50 into 10^{-3} divided by 10 square into 24 into 60 into 60 = i corr. That time would be i corr ampere centimeter square is 55.85 divided by n is 2 and F is 96500 coulomb, okay.

So, I could see that this unit both sides the units are same, because ampere is nothing but coulomb per second. So, then it will match this unit. This unit it will match. So, I can find out i corr = ($50*10^{-3}$ *2*96500)/(10*10*60*60*55.85) ampere per centimeter square. So, this would become, if you calculate, it will become $1.0*10^{-5}$ ampere per centimeter square.

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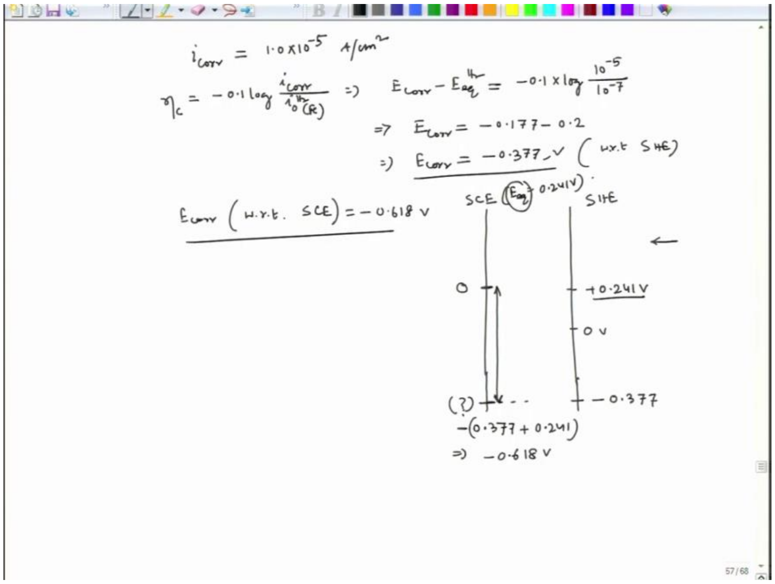

$i_{corr} = 1.0 \times 10^{-5}$ A/cm^2

$\eta_c = -0.1 \log \frac{i_{corr}}{i_o^{H_2}(Fe)} \Rightarrow E_{corr} - E_{eq}^{H_2} = -0.1 \times \log \frac{10^{-5}}{10^{-7}}$

$\Rightarrow E_{corr} = -0.177 - 0.2$

$\Rightarrow \underline{E_{corr} = -0.377\ V}$ (w.r.t SHE)

$\underline{E_{corr}\ (\text{w.r.t. SCE}) = -0.618\ V}$

So, i corr = $1.0*10^{-5}$ centimeter ampere centimeter square. So, that means, in at this point we know this value. So, now we have to find out this quantity. So, in order to find out we have to use

$$\eta_c = -0.1\ log \frac{i_{corr}}{i_{o,Fe}^{H_2}}$$

Since at this point ic = ia = i corr and this point is also known. So, I can find out over voltage of this amount.

$$E_{corr} - E_{eq}^{H_2} = -0.1\ log\ log\ \frac{10^{-5}}{10^{-7}}$$

So, E corr = - 0.177 - 0.2. So this E corr becomes - 0.377 volt. Remember, because when we calculate this E equilibrium hydrogen that is based on pH and this equation is with reference to hydrogen electron. So, that is what initially we have taken everything on the potential axis.

In hydrogen standard electrode with reference to standard hydrogen electrode. So, whose potential at room temperature is 0. So now, once we find out this value that is this is with reference to standard hydrogen electrode. So now in order to find out E corr with reference to saturated calomel electrode, so we have to find out 2 scales. So these are 2 scales this is saturated standard hydrogen electrode, where this point is 0 volt and this is standard calomel electrode.

So, the 0 point corresponds to - 0+241 volt. This is the standard calomel electrode E equilibrium = 0.241 volt. So, this is the standard voltage of standard calomel electrode with reference to hydrogen electrode. So that will be considered as zero when you measure any voltage with reference to standard calomel electrode. Now, so, this potential is with reference to standard hydrogen electrode. So, the standard hydrogen electrode, this is - 0.377 volt.

So, corresponding data, this is the potential we have to measure. So, that means, we see that with reference to standard calomel saturated calomel electrode, the potential will be this difference and since this is 0, so this potential also will be negative and this potential would be 0.377 + 0.241 with the - sign. So, this becomes 811 volts. So, this is could be = - 0.618 volt. So, this is the problem I wanted to show.

How to make use of different electrodes or reference electrodes. Now, in case of different reference electrodes, this value this equilibrium value will be different. In case of standard saturated calomel electrode this is the voltage. In case of silver/silver chloride electrode or in case of copper/copper sulfate electrode, the equilibrium potential of that reference electrode will be different.

And that particular equilibrium potential is measured with reference to standard hydrogen electron. And that becomes a 0 because we are taking that particular potential to be a reference potential. An accordingly you have to make use of and change the values as per this scale this particular scale side by side you put those two scales and find out what could be the potential that will be shown in the machine, okay.

So, this is the problem I wanted to tell I wanted to solve. Now, this is actually taken from a book similar type of problems are they are in another book which is an introduction to metallic corrosion and it is prevention by Raj Narain. In that book, some problems are there in case of the problem what we solved + that was available in the book principles of corrosion engineering and corrosion control by Zaki Ahmad, okay.

So you can read those two books where you can find our problems. In fact, in this course also you will be given a lot of numerical problems subsequent after subsequent weeks. So, you need to solve those problems and the TAs will be there and I will be also available for discussion. So, this actually we now gradually move to the second part which is the passivation. So, the second part is Passivation.

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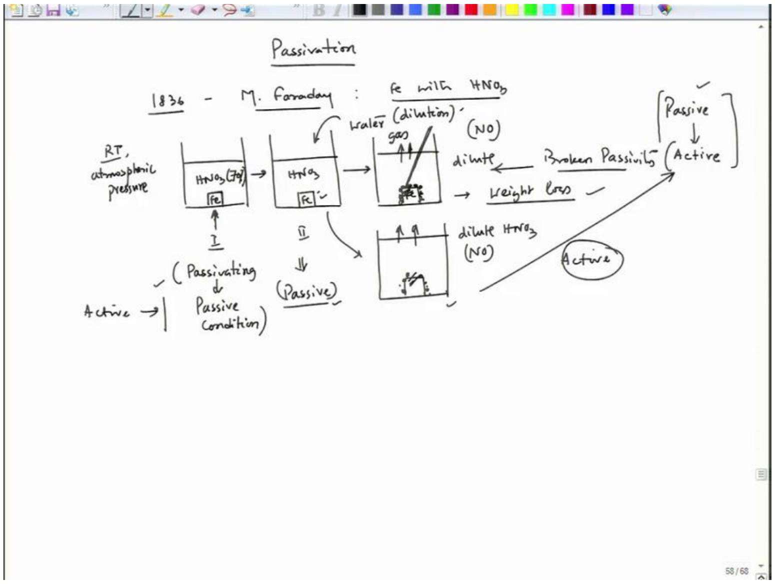

So this passivation is extremely important engineering field. For example, this is very popular that stainless steel we use stainless steel in many applications many critical fields like chemical industries, like acid making industries, and even our day to day applications the stainless steel utensils as well as stainless steel, bio implants, even stainless steel tools and everywhere we have this word called stainless.

Stainless means it does not get corroded. And we all from a normal textbook we have found out that we could know we know that stainless properties from the stainless steel comes due to the effect of chromium. Since stainless steel contains, let is say 304, which is a very popular grade of stainless steel it contains nickel and chromium is up the order of 18 to 8 percent, nickel of the order of 8 to 8 percent. And of course, carbon is very low, it ranges from point 02 to point 03.

And sometimes it contains little higher carbon content, which is point 08 percent it might go. So, the carbon is generally in the lower range. And the intention is always to go for a very low carbon, just to avoid sensitization because sensitization is a tricky problem as well as it is a very critical problem in case of stainless steel, where grain boundaries are attacked preferentially by the chemicals.

So, there this chromium tries to from chromium oxide on the surface. And once this chromium oxide forms on the iron surface, it becomes a near inert that means in the environment where it is used where once chromium oxide forms it does not participate in dissolution reaction. So, that means the rate of dissolution decreases to a great extent, the reduction in rate can reduce from let say, some orders of magnitude.

Let’s say in normal condition, iron if you expose it to some acid, it can dissolve at a rate of 10^{-5} ampere per centimeter square, which is extremely high corrosion rate. But once we add chromium, the corrosion rate can reduce to up to 10^{-8} ampere per centimeter square. So, that is the corrosion rate reduction is almost about 3 orders of magnitude. So that is the influence of chromium there.

And this particular behavior appears because of the very tendency of that metal with chromium content to passivate in that environment. So, this passivation is nothing but a reduction in corrosion rate, due to the influence of environment or influence of alloying elements in the metal, okay. So, for example, if lead is exposed to sulphuric acid, it can form lead sulphate that lead sulphate can give reduction in corrosion and that is also getting passivated, okay.

So, that is basically the environment is leading to sulphate formation, but in case of iron if you expose it to water and then if you anodized it. That means if we take it preferentially take it intentionally to the anodic side, let is say it potential equilibrium potential is - point 5 volt in case of iron if you deserve it, put it in water. And if you take it to a positive potential, let is say close to around 1 volt.

It might passivate again because of the formation of different degrees of iron oxides or hydroxide, okay. So, and that will be decided by the pourbaix diagram of that iron. So, that means the passivation as we discussed that passivation is nothing but the reduction it in corrosion rate due to the influence of environment or the influence of the alloying elements into metal all it has a cell tendency due to anodic polarization, okay.

So, now on this passivation people while people have extensively worked, but the first time it was realized by the great Michael Faraday in 1836. He did one interesting and a very, very simple experiments those experiments can still be performed in normal condition in the in your house you can have this particular experiments of course, you have to take care of your safety because we have to deal with nitric acid concentrated nitric acid that is 70 percent nitric acid.

So, you have to be very cautious and always you have to put on gloves and all the safety at safety procedures before you do this experiment, but this experiment is basically the start of passivation discussion. So, in 1836 around that Faraday did one experiment iron with HNO3. This was a famous experiment the experiment starts with like with are the container containing HNO3 70 percent of HNO3 is very concentrated acid at room temperature.

And of course, atmospheric pressure, fine. So, this is the condition and there if we introduced one iron block. A freshly prepared polys iron block if we introduce into it what it does initially you will see that there are bubble formation initially. Of course, there will be a small bubble forming, but after maybe a couple of minutes, you would see that the bubble formation has receded and no more bubble formation is there.

Now, if 1 starts taking weight of this iron object 1 can see that the iron object weight reduction is not possible to measure with a normal weight machine if you want if you have a very sensitive digital weighting machine, you can check the weight loss you can get the weight loss, but otherwise it is almost negligible weight loss because that corrosion is nothing but the weight loss. But here you do not see any weight loss.

Now, if we continue that experiment in this fashion so, if we have HNO3 70 percent and that metal is still there, now add keep adding water. So, when you add water you are actually diluting it, when you dilute it that time you would see that there is no visible effect. That means and at the same time, if you keep measuring the weight of iron with time, it does not change. So, there is again negligible weight loss.

Now, once we take this iron again, now, we saw so the second time this is the second experiment, this is the third, this is first, this is second, and the third one said that dilute this is dilution. Now, this is still dilute and still that metal iron is there without any change. And now take a glass rod, a sharp glass object and then scratch this iron surface, is a scratch you will see that vigorous bubbles are forming on the surface.

And gases are coming out if you analyze this gas you will see this gas is nothing but NO and we see weight loss and this weight loss is substantial. Now, this particular metal this in from this condition stage 2 if you take it and then put it in the dilute acid HNO3 with a scratch on it. Then also you will see that gases are coming out and the bubbles are forming and the gas is analyzed you will see that this gas is NO and you will see a lot of weight loss.

So, this is the experiment what Faraday perform. Now, these experiment talks about passivity as well as later on it talks about when it converts passive to the active stage. So, that type stage 1 the metal is actually the iron is passivating and then reaches to passive condition and corrosion rate reduces to a have very large extent. Now, stage 2, since, that metal is has attained passivity that means on the surface something has happened and if you do not disturb it.

And this water when you add it should be added slowly. So that it does not create much of churning in the metal in that water in that solution. So, that condition is still passive, but once you create a scratch, that scratch actually removes the surface layer and that surface layer is actually introducing passivity into that particular metal. And once it is exposed, the passivity is broken.

So, this particular stage is a broken passivity and this particular stage, it goes to active from passive, so this is the phenomena will observe, okay. So that means passivating, still passive, and here also the same situation is taking place. So, this is active. So, we have passive and another interesting part is if the fresh iron metal, when it was first introduced into that concentrated HNO3, if it is introduced, instead of concentrated HNO3.

If you introduce the dilute HNO3 you will see that the bubbles are forming. So, it is not passivating and you will see that there is a huge water weight loss will be consistent and there will be substantial weight loss. So, that condition of course, is an active stage. So, we are getting active to passive, passive is maintaining and at the same time because of the surface disturbance, it becoming active again from passive state.

So, this is the very experiment of the great Michael Faraday and this talks about the passivity from active to passive as well as from passive to active and it gives a lot of information and that is the beginning of our extensive research on passivity as well as passivation because this particular aspect has got a huge industrial as well as practical implications. So, let me stop here, we will continue our discussion on passivation in our subsequent lectures. Thank you.