Corrosion – Part I
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Lecture – 29
Exchange Current Density

Let us continue our discussion on kinetics of corrosion.

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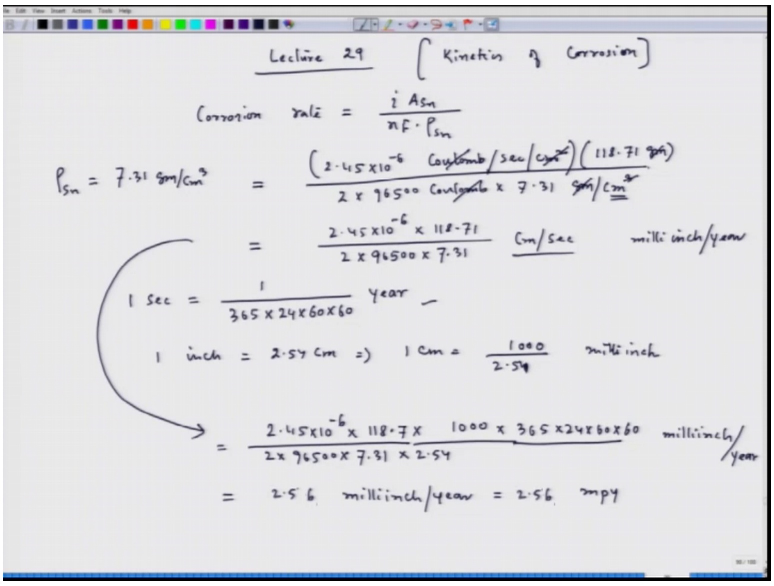

And today we will have lecture 29 and we will continue our discussion on kinetics corrosion.

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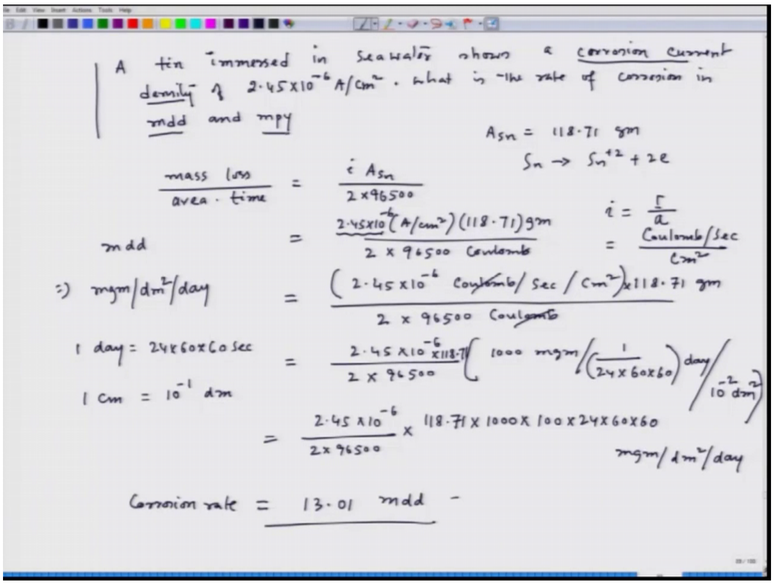

Now, if I recall our last lecture we started this problem and then there we address the first part, we had to calculate the corrosion rate in the form of m d d by using the corrosion current density, what is provided to us. And then we found out and we have actually did little bit of conversion of the units and then we got the value which is 13.01 m d d.

Now, we have to find out the corrosion in the form of m p y there are two ways one is you once you know m d d you can convert that m d d into milli inch per year or you can start with the basic equation, which is corrosion rate is equal to i A m here m is nothing, but the s n n F into rho s n and rho is the density A n A s n is basically the atomic weight of tin and then we can write it as 2 .45 into 10 to the power minus 6 it is basically ampere per centimeter square.

Now, I will write it directly in terms of coulomb per second per centimeter square. So, this is coulomb per second per centimeter square weight is atomic weight is 118.71 gram and n is equal to 2 F is equal to 96500 coulomb into rho the rho of s n is equal to 7.31 gram per c c or centimeter cube so, 7.31 gram per centimeter cube.

Now, I could see that this one will get we can cancel out coulomb coulomb can be cancelled out and this gram gram also would get cancelled out. So, you are left with 2.45 into 10 to the power minus 6 divided by into 118.71 divided by 2 into 9 6 5 0 0 into 7.31 gram per second.

Now, we have to convert this gram per second into milli inch per year. So, 1 second equal to 365 a year consists of 365 days each day consists of 24 hours and then 60 minutes and each minute 60 seconds so, this much here. Now, 1 centimeter we can convert 1 inch equal to 2.54 centimeter.

So, 1 centimeter equal to 1 divided by 2.54 I can make it milli inch by putting here 1000 because 1 inch is equal to 1000 milli inch. So, now, I will put these values here so, 2.45 into 10 to the power minus 6 into 118.71 into divided by 2 into 9 6 5 0 0 to 7.31 into 1000 sorry, we made a mistake here it should be centimeter because only this part is left out. So, 1000 by 2.54 so, that is 1 centimeter equal to 1000 by 2.5 for milli inch.

And then 1 second is equal to this much here so, per second so that means, this will be multiplied here so, this much inch per year. So, this becomes milli inch per year or so, we could see that we can express the corrosion rate by using the corrosion current density and then we can convert it into either m d d that is gram per area per weight loss per area per unit time and also we can converted into m p y which is milli inch per unit per year. So, we can convert it into uniform as well as localized depending on the surface nature of that particular metal in that particular corrosion corrosive environment. So, now let us get into little deeper into the current density part.

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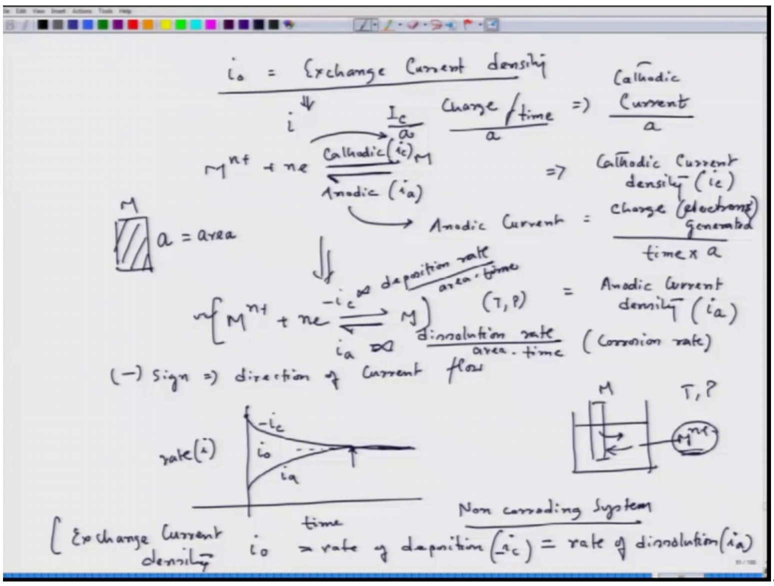

Now we have already started mentioning this particular term called i 0 which is nothing, but exchange current density and this has a relation with i. Now, if I try to look at this particular reaction and if it reaches equilibrium and before it reaches equilibrium so, then this is anodic this is cathodic.

So, this direction we have cathodic reaction and this reaction sorry we have just reverses this would be cathodic and this side would be anodic. Now, this is reduction the forward reaction and the backward reaction is the oxidation reaction or corrosion reaction. Now, part if I see the cathodic part the rate at, which electrons are consumed if we express that we can convert it in the term of Ic or the current per unit time or equal to charge it is not current it is basically charge per unit time is equal to current and this current is involving cathodic reaction. So, that what we call it as cathodic current.

Now, if we divide this particular reactions let us say this is the metal surface on top of which the cathodic reaction is taking place. So, we can divide this area and then we will get or a is nothing, but area divided by area a. So, I get cathodic current density similarly on the anodic side we can get anodic current or charge in the form of electrons generated divided by time and then if I divide it by area of the anodic surface we get anodic current density I we will try to term it as ic and this one would be i a.

Now, this is i a, this is i c now we will talk in terms of current density only because we have seen the rate at which this deposition or dissolution that will be directly proportional to the their mass loss per unit area per unit time or mass gain per unit time mass deposited per unit time per unit area that we have already noticed. Not in the form of current because current will not give us the actual information because, it does not involve the area into does not take the area into consideration.

Now, so, this reactions M n plus plus n e M this reaction is taking place simultaneously and then they will reach equilibrium. So, i c i a now if I consider this particular direction the current density to be i a so, the reverse direction which is cathodic reaction rate is we shall mention it in the form of minus i c. Now, this minus sign indicates the direction this negative sign indicates direction only of current flow. It does not tell that current density is actually negative magnitude is positive, but negative means it is flowing opposite to the anodic current.

So, whichever you take to be positive the other one should be negative, but our what we will take it i a we will take it as a positive current and i c we will take it as a negative current so; that means, its flowing opposite to the anodic current.

Now, when they reach and also we see that this is proportional to the deposition rate per unit area, per unit time and this is proportional to dissolution rate per unit area per unit time. So, the rate of corrosion rate, since they are taking place at a particular temperature and pressure and they will reach equilibrium because, if we consider time and the rate and if we tell this rate in the form of i then initially, if we consider if we say that our particular solution has M n plus ion. So, once I dip this particular metal into that solution at a particular temperature pressure see this metal will start depositing and at the same time opposite process would also start.

So, now if I consider that this is the initial concentration of initial rate because, since metal ion concentration is very high in the beginning when we dip that particular metal into that solution containing metal plus plus n plus ion. So, there are lot of supply of metal in class so, the rate at which the deposition would happen would be very high rate.

So, and then gradually this one would deplete gradually, but at the same time there would be a dissolution also the metal ion will form from metal surface and these two opposing process will try to equilibrant or they will try to reach to a particular rate, where the rate of deposition and the rate of dissolution would be equal. So, initially this is the rate which is let us say i c and I am on putting a minus sign because, I am considering the direction of flow of that particular current and it is a deposition.

Now, the opposite current would also start immediately after putting that particular metal into that solution. So, this is i a and then after reaching the same value they will maintain that value if we do not disturb that particular solution. So, if you do not change the temperature pressure that metal surface quality is same solution is same so, it will maintain that particular rate. So, this indicates these particular value indicates i 0, which is the exchange current density.

Now, interestingly and whenever we are reaching to this equilibrium in that particular situation do we get the dissolution or deposition to be different no they are same. And in fact, that situation is called non corroding system so; that means, the metal is not dissolving preferentially or the deposition is not going on preferentially. So, both are happening same rate so, whatever metal is dissolving that particular that amount is again going back and depositing on the metal surface.

So, that is called non corroding system and that time we see the rate of deposition or i c with a minus sign because, I am considering it to be the opposite to the anodic current flow is equal to rate of dissolution, which is i a and that particular situation this is called i 0 or exchange current density.

So, this exchange current density is the unique situation at a particular temperature or pressure on a metal surface for that particular reduction or the half cell reaction. So, remember this is for half cell reaction because, whenever we are considering this rate of deposition and rate of dissolution we are not taking into consideration of other species dissolving or depositing or other reaction which is either reduction or oxidation.

So, it is the same metal ion and metal these two species one is this depositing one is dissolving. So, one is reduction another one is oxidation this is basically with reference to the half cell reaction. If we consider that in a particular cell the two situations are taking place one is preferentially reduction, one is preferentially oxidation. Then we say that the one part becomes half cell because this these are because the full cell consists of two half cells that what we have understood. So, this is related to the one single electrode system or the single reduction or oxidation process.

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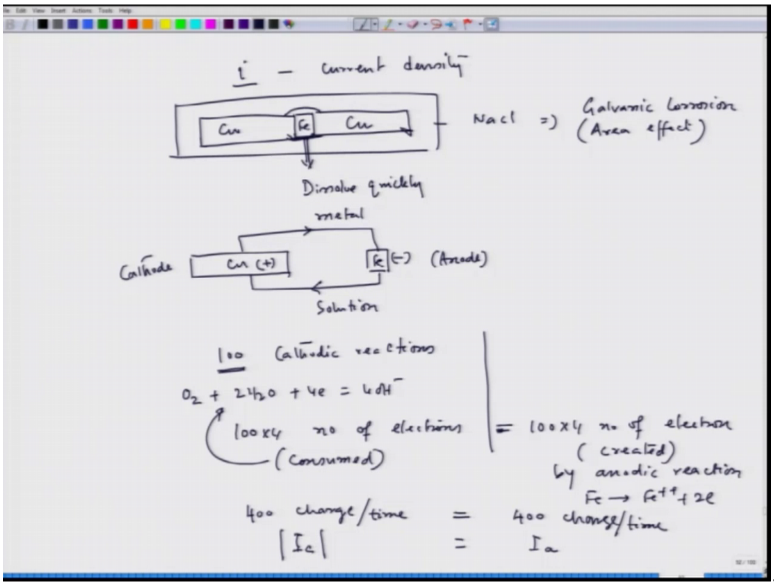

Now, before we go deep into this discussion, I would like to just state the importance of this rather current density. If we recall we saw that in case of galvanic corrosion, if we have a copper this is copper plate, this is copper plate and if we have a kind of iron rivet which is connecting these two copper plates.

And if we put it in N a c l solution and according to the galvanic corrosion this one will dissolve quickly and then finally, the rivet would lose it is strength joint strength. So, this is the example what we have put in while discussing the galvanic corrosion and that to we that time we consider the area effect.

So, we analyze this particular area effect saying that if we have a higher cathodic area in connection to a smaller anodic area then the rate at which, the anodic area would dissolve or the dissolution would be faster in case of that situation rather than a situation where anodic area is larger than the cathodic area. And we said that the m number of cathodic reactions, that are taking place on cathode area will be soo high in order to meet that much of electrons supply we need to have a more and more metal ion that should form from the anodic region and the dissolution becomes faster.

Now, can we prove it through i which is current density small i we can do that. So, this is a circuit let us say this is a circuit so, you have a copper and you have a iron. So, now, you have this is the closed circuit let us say this is copper. So, here the current flow is taking place, this is positive this is negative because, this is anode in case of galvanic cell this will form definitely a galvanic cell, this is cathode. And this is through the metal this current through the metal and this is through the solution That way the total circuit is complete.

Now, if we see the area the total area of copper is so large. So, assume let us assume that 100 oxidation cathodic reactions are taking place, some number arbitrary number were taking cathodic reactions. And the cathodic reaction is nothing, but O 2 plus 2 H 2 O plus 4 e equal to 4 o H minus and in order to see this cathodic reactions you have to meet this number of cathodic reactions we need 100 into 4 number of electrons.

Similarly, on the anodic side we have to meet this total number of electrons. So, we have to create into 4 number of electrons so, this should be created by anodic reaction and here it should consumed for this cathodic reactions and here the anodic reaction is F e F e plus plus plus 2 e. Now, you see in order to meet this so, now, I see that here also the charge is 400 charge and here it is equal to 400 charge in the form of electron of course.

Now, in order to meet that, we have to so, this is let us say per unit time. So, that is the current this is c equal to I a which is anodic reactions and now in order to maintain that we just mentioned it as mod I c which is the I am taking the we I am taking care of that negative sign.

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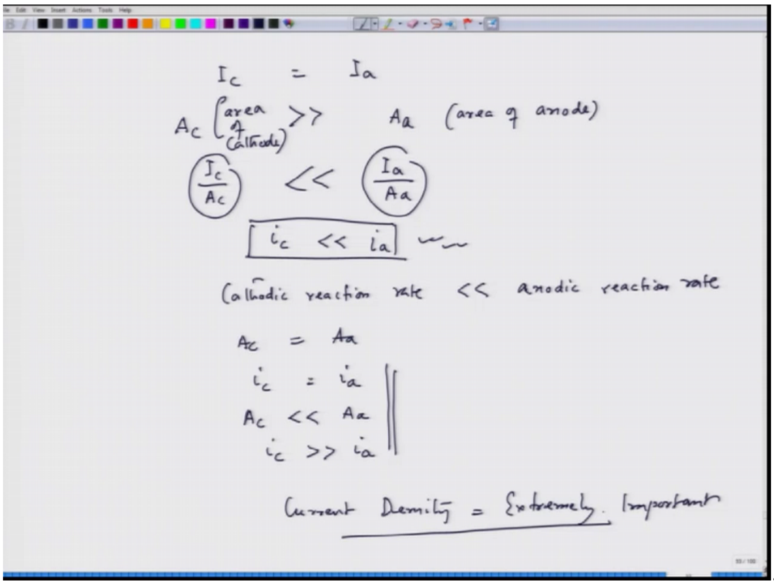

Now, this is I c equal to I a now we have to take care of that area factor. So, the area of cathode and area of anode is very large. Now, we know that current flow if we see this circuit this circuit the current is same entering into the metal or going out through the metal from the metal. So, this is same, but when I try to understand the rate at which this cathodic and anodic reactions are taking place so, I have to divide I c with A c and I a with A a. So, these are area of anode and this is area of cathode.

Now, since A c which is the copper area in this particular situation you see the area that is exposed to the solution this is the cathodic area copper behaves as a cathode in that situation, that case area of cathode is very large. Now, if we see this ratio then as per the ratio this should be like this because, A c is much greater than I a. So, then i a should be greater than i c or I would say cathodic rate reaction rate is much lesser than the anodic reaction rate. Now, if A c equal to A a then I would say that i a equal to i c or i c equal to i a and if A c is less than less than A a i c would be greater than greater than i a.

Now, interesting is in this situation we are saying that the anodic current density is very high as compared to the situation what we have considered here. So, the dissolution rate of that anode would be so fast if we have a larger cathode area compared to the anodic area. So, the anode will dissolve in order to meet that many electrons requirement for the anodic cathodic reactions to happen on the cathode surface.

So, this is one interesting fact is when we see that current density we are able to analyze or understand this particular phenomena more clearly or more better and scientifically it is more intriguing rather than considering from analytical point of view so; that means, this i c or the current density is extremely important consideration. So, let us stop here we will continue our discussion on this very topic in our next lecture.

Thank you.