# Corrosion - Part I
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## Lecture - 28
## Estimation of Corrosion Rate – III

Today we will have lecture 28.

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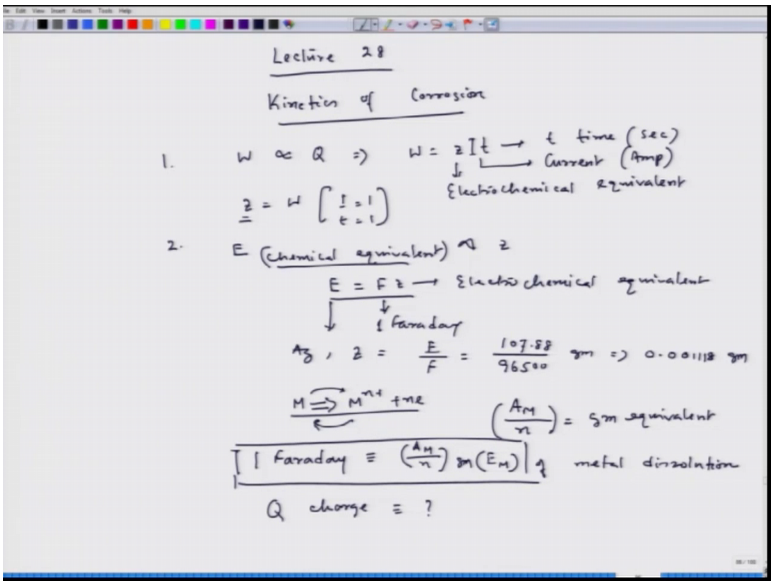

Lecture 28

Kinetics of Corrosion

1. $W \propto Q \Rightarrow W = z I t$ → t time (sec), I → Current (Amp), z ↓ Electrochemical equivalent

$z = W \left[ \begin{matrix} I = 1 \\ t = 1 \end{matrix} \right]$

2. E (chemical equivalent) $\propto z$

$E = F z$ → Electrochemical equivalent, F ↓ 1 Faraday

Ag, $z = \frac{E}{F} = \frac{107.88}{96500}$ gm ⇒ 0.001118 gm

$M \rightleftharpoons M^{n+} + ne$

$\left( \frac{A_M}{n} \right)$ = gm equivalent

$\boxed{1 \text{ Faraday} \equiv \left( \frac{A_M}{n} \right) \text{gm} (E_M)}$ of metal dissolution

Q charge ≡ ?

We will continue our discussion on kinetics of corrosion and in the last lecture, we just started looking at the corrosion rate in terms of current flow since for corrosion. That means, the metal ion formation we have to have electron generation and per unit time if we see that electron generation, we can get some idea about the corrosion rate and some correlation with the current flow during corrosion. Now, while doing that we started looking at laws of electrochemistry and the first law says that w is proportional to Q and where we finally we got W equal to z I t. This should be capital I which is the current in ampere. So, this is electro chemical equivalent and I is current in ampere, ampere t is time in second.

Now, there we saw that z is nothing, but the value of W when I equal to 1 t equal to 1. Now, then in order to find out z, we started looking at second law. It says that E which is the chemical equivalent is proportional to z. Why? Because we saw that we had taken two examples. One was electrolysis of aqueous initial solution and another one is the electrolysis of aqueous AGNO 3 and we saw that in case of NaCl, we had chlorine gas on the positive electrode that is the anode and on the negative electrode we had hydrogen generation that was basically H2O reduction of water reduction and then, in case of HNO 3 AGNO 3 we had silver deposition on cathode. That means the negative electrode and oxygen evolution on the anode and this oxygen evolution is coming because of OH minus oxidation.

Now, when we saw that and then, finally we realized that if we send 1 Faraday of electricity or the charge chemical reaction or the deposition or the evolution of gases on the cathode or anode, they are all equal to chemical equivalent or the gram equivalent of that particular substance. For example, in case of AGNO3 we had 118 where around 1 or 7.88 gram of silver deposition because of the because of that 1 Faraday of charge flow in that particular circuit as well as around 8 gram of oxygen on the anode. So, we see that every time this 1 Faraday of electricity or the charge is nothing, but equal to the chemical equivalent or the gram equivalent of that particular substance. Now, if we say that e is proportional to z that then E equal to F z. So, F is basically 1 Faraday and z is electrochemical equivalent.

Now, this equation can enable us and e is nothing, but the chemical equivalent ss we have said, this equation will enable us to find out the z value. So, in case of silver, we can find out z is equal to E divided by F which is E is nothing, but 1 gram equivalent which is same as the molar atomic weight of that particular silver because it has got the atomic this oxidation number to be 1. So, 107.88 divided by 965500 gram and this is coming out to be 000.00118 rather 1118. If we check this yes it is 0.001118 gram per coulomb now. So, with the help of second law we can find out the value of z. Now, we try to understand this importance of these two equations on corrosion rate. Now, whenever we talk about M going to Mn plus ne that time it is gram equivalent would be M which is the atomic weight of that particular metal divided by M. This is equal to gram equivalent, fine.

Now, when you see that, then we could see that whether it is this way or this way. If I send 1 faraday of electricity or 1 faraday of charge, that means 965500 coulomb of charge. It will always liberate when it transforms to metal ion or well, it will also deposit the metal of this amount which is m divided by n. That means, this is e value of metal or chemical equivalent of this metal. Now, if the deposition is in the chemical equivalent if I send 1 faraday of electricity on the other way, the dissolution of metal ion would be same as the deposition. That means, 1 faraday would be equivalent to this gram of metal dissolution. Is not it? So, that much gram of metal dissolution would take place if I send 1 faraday of electricity. Now, electricity or 1 faraday of charge now if I take this particular concept to understand if we send Q amount of charge, what would be my, the amount of mass that will be lost in the form of ions into the solution; so, that we can easily find out.

Now, let us see if I try to put it in the form of differential mode.

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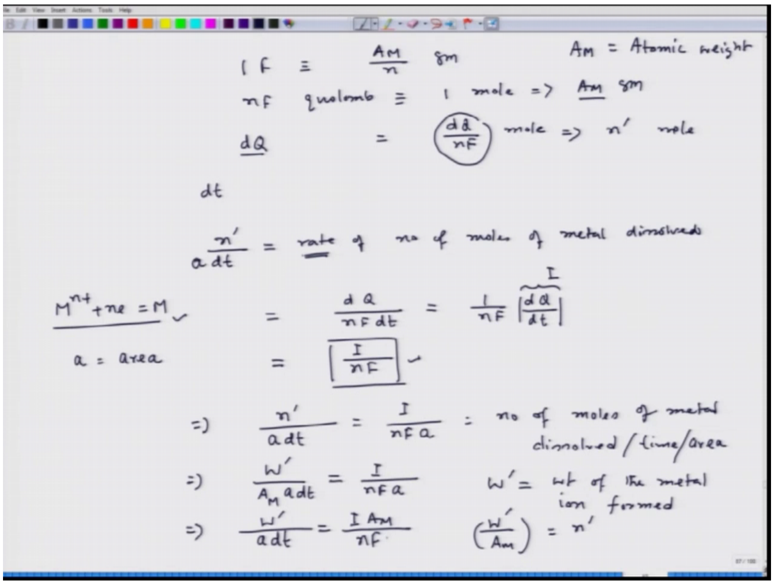

$1F \equiv \frac{A_M}{n}$ gm $\qquad A_M$ = Atomic weight

$nF$ qulomb $\equiv$ 1 mole $\Rightarrow \underline{A_M}$ gm

$\underline{dQ} = \boxed{\frac{dQ}{nF}}$ mole $\Rightarrow n'$ mole

dt

$\frac{n'}{a\,dt}$ = $\underline{\text{rate}}$ of no of moles of metal dissolved

$\underline{M^{n+} + ne = M}$ ✓

a = area

$= \frac{dQ}{nF\,dt} = \frac{1}{nF}\overbrace{\left|\frac{dQ}{dt}\right|}^{I}$

$= \boxed{\frac{I}{nF}}$ ✓

$\Rightarrow \frac{n'}{a\,dt} = \frac{I}{nFa}$ : no of moles of metal dissolved / time / area

$\Rightarrow \frac{W'}{A_M\,a\,dt} = \frac{I}{nFa}$ $\qquad W'$ = wt of the metal ion formed

$\Rightarrow \frac{W'}{a\,dt} = \frac{I A_M}{nF}$ $\qquad \left(\frac{W'}{A_M}\right) = n'$

Let us say 1 faraday of electricity is equivalent to AM divided by n. This is basically amount of metal that will be dissolving. Now, if I send n F amount of charge or coulomb, so it will be equivalent to 1 mole of that substance. Why? Because this is nothing, but a n gram of metal or the weight, the atomic weight of that particular metal. So, one particular atomic weight, so this much of metal ion if it forms, then we would definitely have 1 mole of metal dissolution. So, if we send Q d Q amount, so it will be simply 1 by n F d Q, so this much of mole that dissolves.

So, now you see if we send d Q amount of charge, we get this much, this much of mole, loss of mole of that particular metal that is dissolving in the solution. Now, if this d Q charge is sent for del t time or d t time which is a very small miniscule time ah, then we can find out what is the number of mole dissolved per unit time. So, let us say this value is the number of mole would be then w or this if I note it down as n prime which is the number of moles that is dissolving, so this mole it is equivalent to n minus mole. So, n minus divided by t is nothing, but the rate of number of moles of metal dissolved per unit per unit time which is same as because n prime is nothing, but d cubed by n F. Now, n F is a constant, n is nothing the oxidation number for this particular reaction. Now, F is 1 faraday which is also constant. So, now I can write this. Now, if I see this quantity, this quantity is nothing, but I. So, I can write this 1 equal to I divided by n F.

Now, when I write this, it says the rate of I can rate of number of moles of metal dissolved or in that case I do not have to mention this per unit time because when I am using this rate, time is taken care of. Now, this particular is also indicating the corrosion rate only in the form of number of moles dissolved per unit time, but it is not taking care of the area because area is very important as we have discussed in our last lecture because whenever corrosion happens, it is basically surface phenomena. So, the exposed area on top of it, this reaction will take place not in the bulk of the system or the bulk of the metal. So, until unless we normalize it with area; we will not be able to get the proper indication or proper expression for the corrosion rate.

So, in order to do that, we have to divide it with area. So, let us say small a is basically area this is area. So, I can put it as n prime a d t equal to I n F a. So, now it becomes number of moles of metal dissolved per unit time per unit area. So, this is the proper indications. Now, it is in the number of moles. Now, we can convert this into grams per unit area per unit time. So, in order to do that n prime is basically the number of moles. So, this w if w prime is the amount of metal that has dissolved divided by a which is basically AM rather is AM is the atomic weight divided by a m a d t is equal to I n F a I can write this way, where w prime is the weight of the metal or the mass of that metal coming into solution formed and then, w and a n is nothing, but equal to n prime or the number of moles, then w prime a d t equal to i AM n F a.

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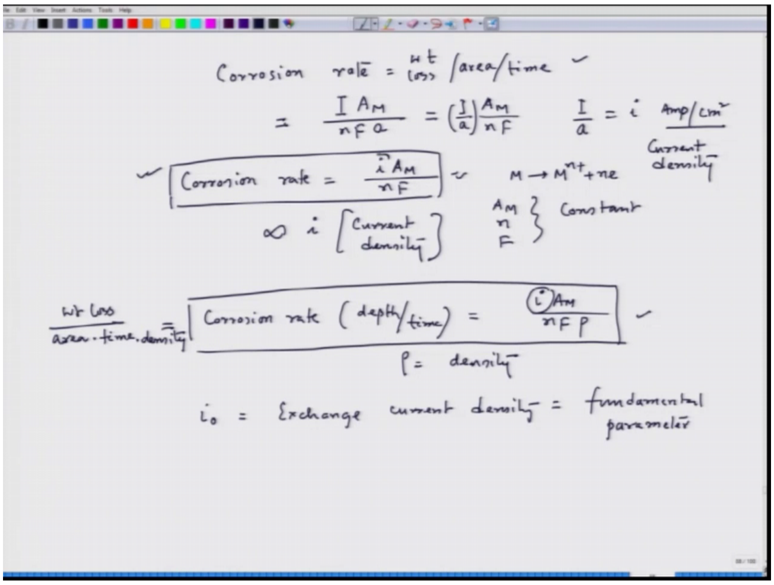

Corrosion rate = wt loss /area/time ✓

$$= \frac{I A_M}{nFa} = \left(\frac{I}{a}\right)\frac{A_M}{nF} \qquad \frac{I}{a} = i \quad \underline{\text{Amp/cm}^2}$$

Current density

✓ $\boxed{\text{Corrosion rate} = \frac{i A_M}{nF}}$ ✓ $M \rightarrow M^{n+} + ne$

$\propto i \left[\begin{matrix}\text{Current}\\ \text{density}\end{matrix}\right]$ $\left.\begin{matrix}A_M\\ n\\ F\end{matrix}\right\}$ Constant

$$\frac{\text{wt loss}}{\text{area}\cdot\text{time}\cdot\text{density}} = \boxed{\text{Corrosion rate (depth/time)} = \frac{ⓘ A_M}{nF\rho}} ✓$$

$\rho$ = density

$i_0$ = Exchange current density = fundamental parameter

So, finally we are getting the corrosion rate is equal to gram or I could say in the form of weight divided by area divided by time equal to I AM. This is the expression. What we are getting now, we can simplify this one AM IA n F and I divided by a is written in the form of i small i which is nothing, but ampere per centimeter square. I can mention in this fashion ampere per centimeter square which is nothing, but the current density. So, corrosion rate is equal to i n F. Now, AM for a particular metal n and F for M equal to M n plus plus n e, they are all constant.

So, now corrosion rate I would say is proportional to I or the current density. Interestingly it is not proportional to the current flow, rather it is proportional to the current density because if we take current, then we are actually not considering the area that is exposed to the solution for the corrosion reactions to happen on the on the metal surface, but current density will look when we consider it actually takes care of this area that is actually on top of which the reaction the corrosion reaction is taking place. So, hence the corrosion rate is directly proportional to the current density not I, but we get this particular information by using this electrochemistry, of the laws of electrochemistry. Now, once we get this idea, we can see that it is basically in the form of weight loss or I can say weight loss per unit area per unit time.

Now, this we have seen that in those cases where the dissolution pattern is localized, we have to use a different way, different way of expressing corrosion rate which is nothing, but the depth penetration depth divided by time. So, we can convert this particular expression in the form of the depth penetrated per unit time by simply dividing this corrosion rate with density of that particular metal. So, the corrosion rate in the form of depth per unit time we can put it as I a M n F rho where rho is basically density. So, we get another expression like this which is equivalent to weight loss area time density.

Now, we see that we have a very good idea that corrosion rate is electro chemical in nature and by using laws of electrochemistry; we can relate the current flow in the form of current density with the corrosion rate. Now, before we get to the details of this current density part because we have to now get to the exchange current density which is exchange current density is basically I 0 which is a very fundamental aspect in electrochemistry as well as in corrosion because while explaining corrosion in more scientific fashion, we have to use make use of a mix potential theory and there this I 0 will be extremely needed and this is a fundamental parameter fundamental parameter. So, before we get to this I 0 which is exchange current density, let us use this particular formulas and let us see whether we can find out the corrosion rate in different units and express them in different units.

So, let us solve some numericals. We are just giving some examples of those numericals t s will give you many more problems on these two formulas and then, you can solve them and practice.

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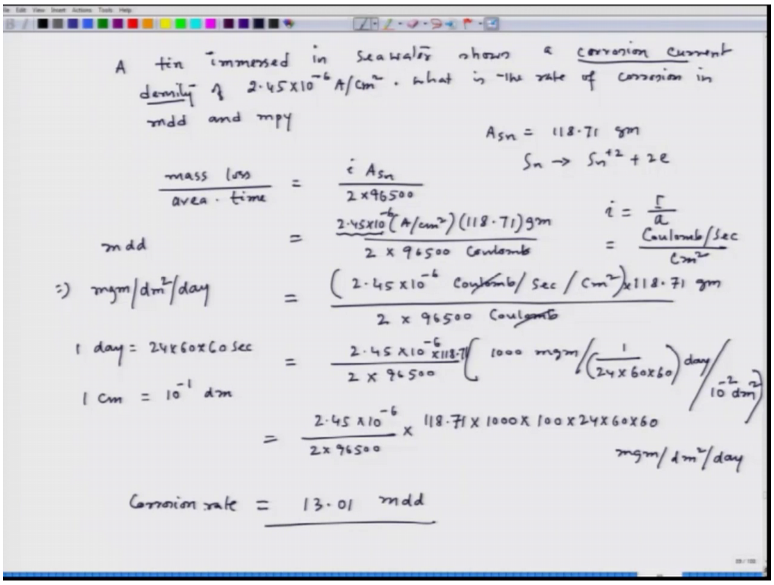

A tin immersed in Seawater shows a corrosion current density of $2.45 \times 10^{-6}$ A/cm$^2$. what is the rate of corrosion in mdd and mpy

$A_{Sn} = 118.71$ gm

$Sn \rightarrow Sn^{+2} + 2e$

$$\frac{\text{mass loss}}{\text{area} \cdot \text{time}} = \frac{i\, A_{Sn}}{2 \times 96500}$$

$$\text{mdd} = \frac{2.45 \times 10^{-6} (A/cm^2)(118.71)\,gm}{2 \times 96500 \text{ Coulomb}}$$

$$i = \frac{I}{a} = \frac{\text{Coulomb/Sec}}{cm^2}$$

$$\Rightarrow mgm/dm^2/day = \frac{(2.45 \times 10^{-6}\ \cancel{\text{Coulomb}}/Sec/cm^2) \times 118.71\ gm}{2 \times 96500\ \cancel{\text{Coulomb}}}$$

1 day = 24×60×60 sec

1 cm = $10^{-1}$ dm

$$= \frac{2.45 \times 10^{-6} \times 118.71}{2 \times 96500} \left( 1000\ mgm \Big/ \left(\frac{1}{24 \times 60 \times 60}\right) day \Big/ 10^{-2}\ dm^2 \right)$$

$$= \frac{2.45 \times 10^{-6}}{2 \times 96500} \times 118.71 \times 1000 \times 100 \times 24 \times 60 \times 60 \ \ mgm/dm^2/day$$

Corrosion rate = 13.01 mdd

So, the first problem let us let us say a tin immersed in sea water shows what is the rate of corrosion in mdd and mpy? Now, in this particular problem we have used a corrosion current density. Now, if we go back and see this particular formula, here the corrosion current density is nothing, but the current density at which the dissolution is taking place. So, this is nothing, but the corrosion current density this is nothing, but the corrosion current density. So, we will start expressing this or mass loss divided by area and time which is nothing, but i A sn tin is nothing, but the S n divided by n is 2 here and F 96500 coulomb where A sn is nothing, but 118.71 gram and S n is going into the solution as S n plus 2 plus 2 e. So, that means n becomes 2 and i is nothing, but in ampere per centimeter square A sn is nothing, but in gram 118 gram divided by and here I can put this value 2.45 into 10 to the power minus 6 n is equal to 2 into 96500 coulomb. Now, this quantity I can write in this way 2.45 into 10 to the power minus 6 coulomb per unit time per unit area because i is i is nothing, but i divided by area or coulomb per second per unit centimeter square.

So, then I can write this time as second area in centimeter square 118.71 gram and this becomes 2 into 96500 coulomb. So, this coulomb would get cancelled and then, 2.45 into 10 to the power minus 6 divided by 2 into 96500 and now, I will convert the units because it is in mdd which is milligram per decimeter square per day. So, this becomes gram. So, I have to convert this gram into milligram. So, 1000 milligram divided by second, I have to convert into days. So, the second becomes 1 divided by because one day is equal to 24 hours 60 into 60 second. So, one divided by 24 into 60 into 60 day divided by centimeter should be in decimeter. So, 1 centimeter is equal to 10 to the power minus 1 decimeter. So, it should be 10 to the power minus 2 decimeter square.

So, final expression would come as 2.45 into 10 to the power minus 6 2 into 96500 into 1 1. Sorry I miss this amount of gram 8.71 into 1000 into 100 into 24 into 60 into 60 this much milligram per decimeter square per day. So, finally this value would be 13.01 mdd. So, this is the corrosion rate.

So, we will solve the other part which is in the mpy in our next lecture. Let us stop here. We will continue our discussion on Kinetics of Corrosion.

Thank you.