

**Corrosion - Part I**  
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**Lecture - 26**  
**Estimation of Corrosion Rate – I**

Let us start lecture 26.

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Lecture 26  
 Kinetics of Corrosion (Rate of Corrosion)  
 Rate of dissolution of metal (Electrochemical mode)  
 loss

$T, P, \text{Concentration}$   
 Acid ( $C_1$ )

$Zn$  99%  
 $Zn \rightarrow Zn^{2+} + 2e^-$   
 $2H^+ + 2e^- \rightarrow H_2 \uparrow$   
 $Zn^{2+} + 2Cl^- \rightarrow ZnCl_2$

U.A. (de-aerated)  
 99% Pure Zn

0 time  $\rightarrow W_1$   $W_2 < W_1$   
 t time  $\rightarrow W_2$

$(W_1 - W_2) = \text{rate of dissolution or wt loss}$   
 $= \frac{\Delta W}{A \cdot t}$

Corrosion rate of metal dissolution or loss of wt per unit area  
 $= \frac{\Delta W}{A \cdot t} = \text{mass/area} \cdot \text{time}$

$A_1 < A_2$   
 Area over which reactions are taking place

Rate I  $\neq$  Rate II  
 Corrosion Rate I = Rate II (Without considering A)

Till now, we have looked at thermodynamics of corrosion and then while talking on thermodynamics of corrosion or rather the possibility of corrosion in a particular solution of certain pH, we discuss we have discussed forebay diagram in that context. Now, forebay diagram as we have mentioned that it tells us the stability of different phases in water or aqueous medium. But, it cannot tell us one of the important aspects of corrosion what is that is called the rate of corrosion or the kinetics of corrosion.

So, now onwards we will start talking on the kinetics of corrosion or rate. So, while talking on the rate of corrosion; that means, we are talking about the rate of dissolution of metal and of course, while we talk about dissolution of metal we have to consider electrochemical mode or electrochemical mode of dissolution of metal or loss of metal.

So, our dissolution we can also consider it to be loss of metal. Now, when we talk about loss of metal; that means, it is a basically loss of mass of that metal. For example, we have a beaker and we have taken let us say de-aerated HCL solution de-aerated.

And there if we put a small zinc piece let us say a commercially pure zinc which is let us say 99 percent pure zinc and then we will see that there will be bubble formation on top of it. And after some time if we take this zinc piece out and then measure the weight we will see that there is a loss of weight; that means, let us say the at 0 time, now weight was  $w_1$  and let us say  $t$  time the weight is  $w_2$  we see that  $w_2$  is less than  $w_1$ .

So, the rate of loss is nothing, but  $w_1 - w_2$  divided by  $t$ . This is the rate of dissolution or weight loss. Now, this is also rate means there is a per unit time part is coming there. Now, question is we have to see that where the reactions are taking place. If you see the reactions, the reactions are always taking place on the surface of that metal. It is not that entire body of that particular metal piece; that means the bulk of the metal piece is also reacting only the surface the hydrogen evolution is taking place.

And the reaction of course; zinc going to zinc plus and  $2e^-$  and hydrogen will take care of this  $2e^-$  and then form  $H_2$ . So, this gas will generate and then this  $Zn^{2+}$  plus  $Cl^-$  will react with  $Cl^-$ . So, it will form  $ZnCl_2$ , this is the reaction and this entire reactions are taking place on the surface of the metal.

Now, let us have one situation if we consider that these reactions are taking place at a particular temperature, pressure and then concentration of this acid is something like let us say  $c_1$  mole per cubic meter. And then we consider that the zinc has some purity which is 99 percent.

And now if we consider that the entire processing parameters or the surrounding parameters are same, so, we have 2 beaker; one beaker we have a small zinc piece, another beaker. We have a big zinc piece both of the same quality. Rather you have a zinc piece of 99 percent purity we take out 2 cubes out of it, one cube is smaller cube, another cube is much bigger cube. And then we are exposing them to HCL solution of same concentration and also the pressure and temperature both are same.

So, then we will notice that the weight loss or  $\Delta w$  this is nothing, but  $\Delta w$  by  $t$  which is nothing, but the rate of corrosion. So,  $\Delta w_1$  this is let us say set 1, this is set 2 and  $\Delta w_2$ . For a particular time, interval let us say the time is  $t$  for both the cases we would see that in this case and in this case these 2 are different. And we would see that this is greater than this, this will be much more greater than this. Because, here the zinc piece is

much bigger than the zinc piece what we have here and the quality of every other parameters are same.

Now, then the rate of corrosion would be this or the rate of dissolution or the rate of weight loss. Now, we see that if the zinc piece is same and if the parameters are also same then we should expect that the both the rate should be same. Now, here this rate 1 is equal to rate 2 that should be the situation because it is the same zinc piece and all the other factors like temperature pressure concentration all are similar.

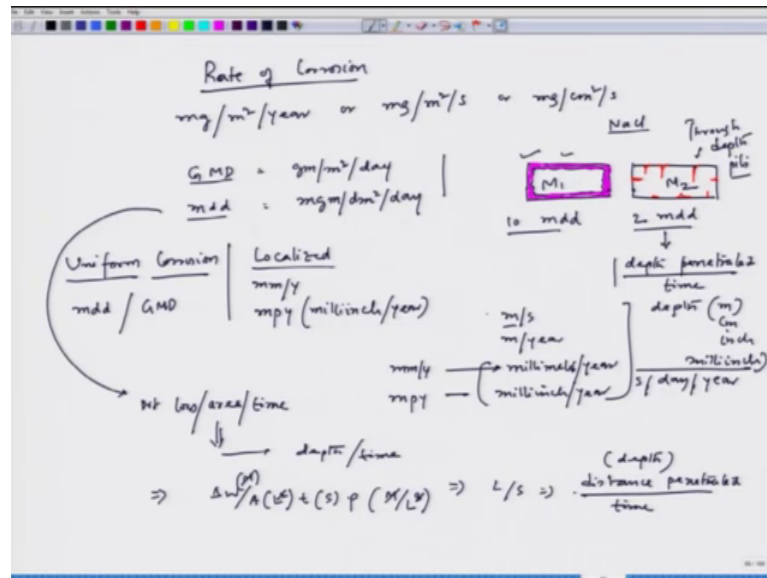
So, but it is not like that because you see this quantity and this quantity they are different. Now where is the problem? The problem is since we are considering that the surface reactions are taking place and the bulk of the system is not participating in the reactions. So, we have to normalize with area, when you normalize with area because only the area is taking part and here it has got much higher area than this particular situation.

So, that for the weight loss should be also higher and when we divided by the same time duration that this particular factor would become much higher. Now, once we divided by  $A_1$  so, this is  $A_2$  and this is  $A_1$  and  $A_1$  and  $A_2$  the relation is like this and these are nothing, but area over which reactions are taking place ok.

So, now, whenever we consider this normalized factor area we would see that these 2 are equal which was not there before, but now after this is without considering area. Now, once we consider area, then we will see that rate 1 equal to rate 2. So; that means, the corrosion rate or the dissolution rate of that particular metal per unit area they are equal.

So; that means, this area is extremely important factor while we consider that the rate of corrosion. And we have to consider that the corrosion is nothing, but rate of metal dissolution or loss of weight per unit area. This is extremely crucial factor and; that means, our formula would be  $\frac{\Delta w}{A t}$  or you can say mass per unit area per unit time.

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Hence, the rate corrosion can be considered as like if we consider the unit part, we can considered as milligram per meter square per year or milligram per meter square per second or milligram per centimeter square per second like that anything. We can consider only thing is we have to consider in the form of loss of metal or loss of weight per unit area per unit time.

Now, there are some units available to express rate of corrosion those units are G M D, we considered as gram per meter square per day these are some of the expressions or the units that are available in order to express rate of corrosion. m d d we call it as milligram per decimeter square per day. So, these are the 2 rates that are available.

Now, when we talk about these rates let us seek a which at some point of time whether these particular way of expressing rate of corrosion would give us suitable corrosion rate or not or suitable information about corrosion.

Now, when we talk about this let us say we have 2 surfaces, 2 metal block one is M 1, one is M 2 they are exposed to that say NaCl solution. Now, after some time we might experience that in one case if we see the if we analyze we will see that dissolution has been more or less uniform over the entire cross sections or surfaces of surfaces available for that particular metal exposed to the NaCl solution. So, this is the situation so, these pink color regions are basically the loss of metal. So, that much amount of metal has dissolved in the particular solution after some time some particular duration.

Now, in the other case we might notice that macroscopically there is nothing on the surface, the surface looks absolutely clean. But, if we see microscopically we can see that in some portions some cases the dissolution has gone deep into the material so, like this.

So, we did not have the situation what we faced here the dissolution was overall uniform; that means, the thickness reduction for the particular block is uniform over the entire area or the surfaces that are exposed to NaCl. But here, we see that the surface has not changed much, rather surface character, surface nature or surface appearance does not look different after dissolution study. Rather than if we see microscopically, we see that there are pits these are called through depth pits.

Now, these pits are basically progressing through the depth and the surface thickness has not changed much. Now, would it be fine if we express this one as  $m/d$  and at the same time this one also  $m/d$ . By looking at this data let us say this is  $10\ m/d$  and this is  $2\ m/d$  by looking at these two data can anybody understand that the character of corrosion is different? No, nobody would understand..

Now, in this case it is not about uniform dissolution it is basically localized dissolution. And in order to understand the localized dissolution we have to understand the what is the depth that has penetrated for that solution that has penetrated into the material.

So, here the unit should have been depth penetrated per unit time. So, that case  $m/d$  may not give us the actual information. So, now, in that case we have to consider a different unit and that time it is basically depth some unit let us say meter or centimeter or inch or milli inch, milli inch and then time we can consider it to be second, we can consider it to be day, we can consider it to be year.

So, here the unit becomes either meter per second, meter per year, millimeter, year, milli inch per meter and these are all this dimension is nothing, but the depth that is basically up to which the solution has progressed into the material. And here two units are popular, one is millimeter per year, another one is milli inch per year which were we call it as  $m/y$ .

So, when it is uniform corrosion we can express the corrosion rate in the form of  $m/d$  or  $G M D$ . We can express like the situation what we have seen here. But, in case of

localized we have to consider we can consider as millimeter per year or m p y means milli inch per year fine.

So, these are two different rates now, question is we have the information about weight loss per unit area per unit time. Now, we have to convert this one into depth by time. How can we do it? Now, it is very easy if we know the density of that particular material.

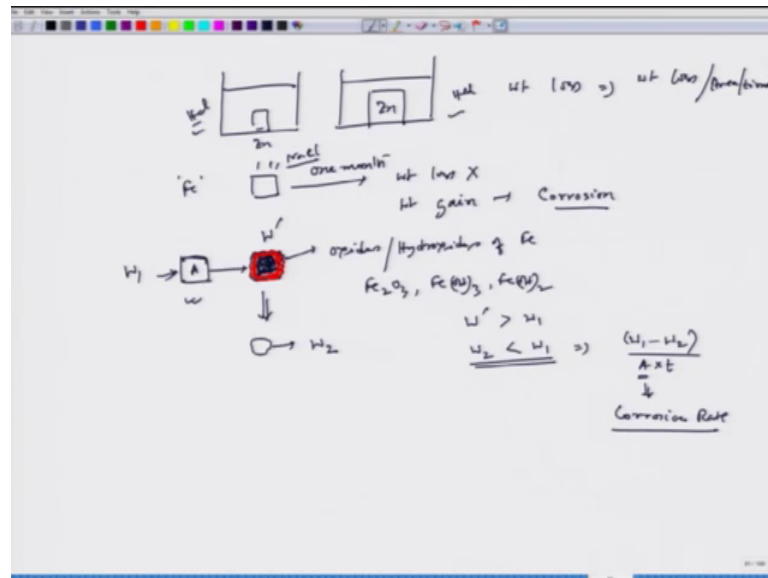
Now, this is  $\Delta w$  by area which in the form of let us say  $L^2$ , this is mass and then we have time in the form of second and then if we divided by density which is  $\rho$  this is  $M$  divided by  $L^3$  these are the dimensions.

So, now, if we see that so, it comes about  $L$  by second or distance penetrated per unit time or we can call it as depth is not it. So, it is simply the dividing the  $m d d$  by the density of that material say then we will convert the uniform mode of corrosion to localized mode of corrosion. Now, one example I we can cite that is you have also seen it we have shown one stainless steel plate you might have noticed that that stainless steel plates have got lot of pits and those are true pits.

And the surface looks absolutely fine not much of corrosion product, but it has it has got perforated because of the corrosion attack localized corrosion attack. So, that case it is better to express the corrosion rate in the form of depth penetrated or the distance penetrated into the material by time. But, in case of zinc when it is dissolving in HCL, we can definitely consider it to be more or less uniform dissolution that time we can express the corrosion rate in the form of mass loss per unit area per unit time. We can express the unit in the form of  $G M D$  or  $m d d$ .

So, this is one important aspect while we talk about kinetics of corrosion or the rate of corrosion. How to express the rate? What should be the best unit we should put to understand at least by looking at the unit give? What should what is basically the mode of corrosion attack? Whether it is a localized or it is uniform. Now, there are another aspect, when you talk about the loss of metal we are considering that every time there will be a loss of after for example, the example what we have cited is HCL medium and we have two zinc piece, one big one small and then after some time we are taking it out and then measuring the weight.

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. And we could see that there is a loss of weight because, it is dissolution when it dissolves the zinc does not form any corrosion product on the surface. It actually the, it produces zinc chloride also it has got a very high solubility. So, it dissolves in the solution.

So, when you take it out we do see the weight loss, now this is in HCL and heat is also HCL. So, this is uniform water corrosion, but many a times for example, in case of atmospheric corrosion of iron we do not see that actually if we start from 0 time and after spending certain days if you take out that particular metal space without disturbing the surface conditions. That means, you are carefully taking the sample without disturbing the surface and weighing the weighing the particular small item or the plate if you have a exposed it to the environment, you might see that there is weight gain rather than weight loss.

So, in certain cases we see that this is weight loss and it becomes straight forward, but when we have weight gain then we have to have to mention that it is basically no corrosion is taking place? No, it is not. Like that for example, in case of iron let us say iron piece the example what we have provided if you have expose it to the environment; that means, atmospheric corrosion if you led that atmospheric corrosion to happen. Let us say some one month you have expose it and then you measure the weight and that

time you also spray a little bit of NaCl solution. You would see that the weight loss is not there, rather there is a weight gain.

So, now we are confused, but actually it is there is no point in getting confused, rather there is also corrosion. Here, the particular block is covering with a kind of surface layer, surface layer. Only the center part remains to be the iron and the rest of the iron let us say you have started with this is the size, initial size and then it has grown in size, but actual metal piece is nothing, but the center part. Rest of the layer is nothing, but oxides or hydroxides of iron..

And since it is  $\text{Fe}_2\text{O}_3$  or  $\text{FeOH}$  whole 3 or  $\text{FeOH}$  whole 2, now one mole of iron if it forms oxide or hydroxide the weight will be increasing if they are not getting detached from the surface.

Now, how do you get the corrosion rate then? In those cases you have to carefully remove the outside layer of the surface layer. And that removal should be done so, carefully that the inner part which is the metal part should not get damaged or should not get removed. So, that is what we have some standards, how to remove the oxide layer which is mostly done chemically and then after removal we are left with this much small piece and that what we have to take the weight. So, this is  $w_2$  and here the weight was  $w_1$ . Now, and this one is  $w_{\text{prime}}$  so,  $w_{\text{prime}}$  greater than  $w_1$ , but  $w_2$  is less than  $w_1$ .

So, now we have to consider this one after removal of the oxide layer and then we have to find out the corrosion rate. Now, this area should be the area what was initially considered ok. So, the area of this particular block should be considered because the dynamic change in area it was very difficult to understand what could be the dynamic change in area.

Because, it may not happen completely uniformly there could be some localized attack or there could be some uniform attack. So, it is a mixture of things so, that is what it is always better to consider the initial area in order to consider the corrosion rate. So, this should be my corrosion rate.

Fine so; that means, we have what we have gained from this particular lecture is we need to consider corrosion rate in the form of loss of metal per unit area per unit time and area



is important factor for the normalization because the surface reactions are leading to the dissolution of metal, not the bulk of the system.

This is one part, second part is whenever there are 2 ways of expressing corrosion rate, one is uniform corrosion mode where we can consider weight loss per unit area per unit time. And there is one more way to express corrosion rate is basically the depth penetrated or the distance penetrated into the metal or in the basically depth directions of that particular metal or the perpendicular to the surface.

We have to put in the form of depth per unit time or the and the units are one case uniform case we can consider G M D gram per meter square per day or m d d milligram per decimeter square per day. And in the other case where we consider depth penetration that time we have to consider the unit in the form of m p y or millimeter per year m p y is nothing, but the milli inch per year. So, these are the usual practice the way we have to express the corrosion rate.

Now, in the second part we have to consider. So, these are basically the experiments we have to do; that means, in this experiment the kind of experiments what shown here is basically nothing, but the immersion experiment and this is basically exposure or experiment.

So, now, other than that we have to also look at the electrochemical nature of this particular dissolution or the electrochemical nature of the corrosion rate. So, in the next lecture we will talk about the electrochemical nature of this corrosion rate thank you very much let us stop here.

Thank you.