Indian Institute of Technology Kanpur

Present

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NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Environmental Degradation of Materials

Module Lecture 010

Broad Subject: Mod-01 Lec-10 Kinetics of corrosion, Rate expression, Solved problems

Prof. Kallol Mondal

Dept. of Materials Science and Engineering

Now we need to see the kinetics of corrosion. So let us start with kinetics of corrosion. When we start talking about kinetics of corrosion, first of all we need to know how to express the corrosion rate. Whenever we talk about kinetics that means we involve the rate of corrosion, so we need to know how to express corrosion or dissolution rate. So this corrosion or dissolution rate can again be further bifurcated into two modes; one is weight loss for unit area per unit time. The another mode is the current density.

Now the weight loss per unit area and per unit time is simply you have to measure the weight of the metal in the solution for a particular duration and then see the loss in weight divided by the area of the surface area which is exposed to the solution and the time duration; that would give me the weight loss per unit area per unit time. Now again, the current density also can lead to the same thing weight loss per unit area per unit time and these two units these two modes can be related through some conversion factors. Now first let us come to this weight loss per unit area per unit time. This mode is simply let us say you have weight loss of about one milligram and the area exposed is 1 decimeter and the time duration is one day then I can measure this unit as one milligram per decimeter per day which is expressed in the form of mdd which is a very popular unit to express the corrosion rate or the dissolution rate.

Now this looks peculiar but this is the convention we took it as milligram per day per decimeter per day. Now the point is here one important factor is why we need to divide it by – divide this weight-loss with area? Now let us say you have two beaker and now you have kept the same solution HCl solution let us say you consider HCl solution of same concentration of same purity. Now you put a iron piece of same composition let us say it is a pure iron, it's 99.999% pure iron and here also you are keeping the same metal iron with 99.999% pure iron, but the area which is exposed to the solution is different in both the cases. Let us say in this case the area is more. So both the cubes of iron same composition same solution same concentration but you have a different area which is exposed in the cases.

Now in this case the area exposed is less so if you consider A1 and A2, so A2 is greater than is greater than A1. Now if you try to measure the corrosion rate in terms of weight loss per unit time or let us say milligram lost per day in this case and in this case also you measured in the form of milligram per day, let's say one day you have kept it the species are kept for one day in the same solution. Now since we are using the same metal same solution we are not changing anything else, only thing that is changed is the expose area but since the material is same, metal is same so we should get the same corrosion rate but you will see that the corrosion rate in this case is more than the corrosion rate in this case. It should not happen like that. Why it is happening because you have more amount of exposed area area in the HCl media of the same concentration. Now how to make it same if then this would be more because since we have more expose area and the one important factor with the corrosion is corrosion always happens on the surface. So if it is happening on the surface so more surface of the same material would lead to more dissolution. Okay.

So in this case the dissolution is more that means weight loss is more but since the corrosion rate should be same for both the cases because you are not changing anything except you are changing the area so how to make it same. So the main thing is we have to normalize this corrosion rate with respect to area. How to normalize it? You just have to divide it by another parameter which is area and then day. So you have also you just need to divide by area and per unit day. So then this inequality will not be there then this will be equal. So corrosion rates are becoming equal since the material is same. That means you have to have this area factor associated with the corrosion rate expression.

And now once you know this then it is very clear that why we are introducing the area. Now the SI unit for rate expression is basically nothing but gram per meter square per day. So you can express in the form of mdd or gram per meter square per day and the experiment what how to do this, how to get to this unit for that you need to do a little bit of experiments. The simple experiment is expose this iron piece in HCl for a day or some few more days and then take the sample out, measure the weight, final weight, initial weight minus final weight is the weight loss and then you know what is the area exposed to the solution. So that divide by area divide the number of days that would give me the mdd.

Now this is very clear because whenever we have iron in HCl medium HCL's acid then you are going to get dissolution. But now we see that there are two modes; one is weight loss per unit area per unit time, the another one is current density. Let see where from this current is coming. Now whenever have let us say a small section let me consider a small section I just blow it up, let me blow this section. The cross-section wise let us say this cross-section I am blowing it so now this is my cross-section, this section is exposed to the solution medium and this side is also exposed. Now if you cross it at this side now we can have somewhere you can have the dissolution of iron and when you dissolve iron in the form of ion so you release two electrons, two electrons are released and this two electron will go through the metal piece to a section where you have cathodic reaction.

Now that means the electron is flowing from **anodic** section current flows in the opposite direction. So the current flow would be in this way so if current electron flow is this way and flow would be the reverse way and then you have a circuit in the solution the current will also flow from the anodic side to the cathodic side you can have the same analogy in case of galvanic cell where you have the copper cathode, you have zinc anode, and external flow through the external circuit you have electron flow from the zinc side to the cathode side and in the solution you have current flow from copper side to the anodic side which is zinc. So now you can have a current flow.

Now this amount of iron that is dissolving that would be having a direct relation with this current that is flowing inside flowing in this circuit. Now that relation is given in the form of there are two laws which tells you the relation between – the two laws which give you the relation between the metal dissolution and current that is flowing in the circuit. Now how to these two laws; the first law says now let me get into the two laws. The first law says it's the amount of chemical change the chemical change here it is metal dissolution which is also can be considered as electrochemical change where metal is dissolving. So the amount of metal dissolution or iron dissolution in this case particular case would be strictly proportional to the amount of current or the amount of electricity that is burst through the electrolyte.

Now that means it says that the amount of chemical change here in case of corrosion let me put it as dissolution. I am saying that amount of chemical change or the dissolution or the corrosion, dissolution is nothing but corrosion, would be proportional to the amount of electricity. Let us say if the loss is metal loss or the metal dissolution is W, then W would be proportional to Q amount of charge and now we know that Q is nothing but iT which is proportional to iT. i is nothing but the current and T is the time for which the current is passed through the – current is passing in the circuit.

So now this is one and send then W is basically nothing but ZQ and Z it is electrochemical equivalent for a material. How to know Z? Let us say let's in case of silver so this reaction is possible since silver is highly electropositive metal. So it is a noble metal so reduction process is taking place and we know what is the atomic weight of silver 107.88 gram per mole, now here we know that the number of electron that is involved for this reduction process is one so one now if we would like to find out what is my electrochemical equivalent that means how much metal silver will be deposited on the silver electrode per Coulomb so now from this we can measure what is the gram equivalent in this case since one electron is involved so gram equivalent would be for silver would be equal to aAG/n which is nothing but the number of electrons that are involved for the reduction process here n is one so let me put one so which is nothing but the molecular weight and we know that if we supply one Faraday of electricity then the change would be equivalent to one gram equivalent, one gram equivalent weight so if you supply in this case one Faraday electricity then this much gram of silver will be deposited since here gram equivalent is equal to the molecular weight. I'm sorry in gram equivalent is equal to atomic weight.

Now in case of iron here two electrons are involved and iron we know what is the atomic weight atomic weight is 55.85 and that case equivalent gram equivalent would be 5500.85/2 since they're two electrons are involved for the reduction process or other way around if iron is coming out as iron ion so it's oxidation process now that means 1 Faraday is equivalent to aAg since gram equivalent is equal to aAg so one Coulomb would be equivalent to aAg by 96500 Coulomb would be equal to you can measure this then 0.000118 gram so here Z is equal to which is nothing but Z of silver. Now we have some relation between the weight loss or the dissolution dissolved weight is equal to the gram equivalent into the total charge.

Now second law, first law would be enough to have a relation between the weight loss per unit area per unit day with the current let me also put forward the second law. Second law says that let's say if you are supplying the same amount of electricity then the amount that would be deposited or dissolved would be chemically equivalent. That means in case of voltaic cell let's say you have this zinc in case of this is zinc sulfate solution and this is zinc plate now you have connected to a copper plate, in copper sulfate solution and you have completed the circuit with a salt bridge, this is copper sulfate solution and if you maintain the activities of zinc and copper constant and if you connect it these two terminals you will say that current will flow from this end to this end this is current flow and this end to this end there the electron flow and copper will be deposited here zinc will be dissolving in zinc sulfate.

Now when you have this then the if you supply the same current for the same amount of time same duration of time then you will see that amount that would be deposited on the copper side an amount that would be coming out from the zinc electrode to the zinc sulfate solution will be chemically equivalent that means that -- let us say e is my chemical equivalent okay would be proportional to Z which is my electrochemical equivalent. So this is the second law but the first law would be enough to have a relation between the current and the corrosion rate let us get into that part. Now I know what is i? i is nothing but dq/dt. So rate of charge flow or the electron flow is basically the current now if you know this now we also know that if let us say for this reaction Mn+ plus let us take a general reaction Mn+ ne plus equal to M in case of metal M now this is a reduction process now we are concerned with the corrosion. So instead of reduction let us write in the other format where the metal will be dissolving in the form of Mn+ ion and then an e number of electrons will be released.

So let me put this reaction in other format, M would be equivalent to Mn+, this. So in this case let's say I supply one Faraday of electricity then this would be equivalent to gram equivalent. So in this case the gram equivalent would be if aM is my atomic weight of metal M and there are n number of electrons that are involved for this oxidation process then it would be n, this would be my one Faraday would be this much gram of a metal M will be coming into the solution. So if this is the situation then if we supply Q amount of charge then what would be the total what would be the number of moles that would be released into the solution, if Q is the charge then Q by nF would give me the number of moles then this would be my let me put n dash to be the number of moles that would be released in the form of metal Mn+ ion.

So now if we know this and this n dash is nothing but let me put this n dash is a number of moles and aM is nothing but the atomic weight of metal n. So if you we can get this relation from this now this relation I can take it as dq by dt nF if I am taking out since n and F both are constant for this particular reaction, F is always constant so now this would be equal to dn dash by dn dash dt the rate at which the metal is dissolving or the rate at which the number of moles of metal M is dissolving in the solution would be equal to this.

Now from this we are now relating to the amount of metal that is dissolving, that means this n dash. Now dq/dt would be nF dn dash/dt. Now let me replace dq/dt with this. So let me put now let me consider this so here I would be equal to 1 by nF dn dash/ dt. Now so what is my dn dash/dt it would be equal to I divided by nF. So dn dash/dt which is the rate at which the number of moles is dissolving in the solution in case of metal would be equal to the current divided by number of electrons that are – that is involved for this oxidation process and F is one Faraday. Now n dash is nothing but I can have a small relation for n dash. n dash is nothing but the weight let us say W is my weight loss, if W is my weight loss now what would be the number of moles would be equal to aM. aM is basically nothing but the atomic weight of metal M. so I can replace n dash in the form of W divided by atomic weight of metal M. So it would be equal to now I just replace this n dash. Now I can put W aM. Now I can take the M part which is atomic weight of metal M to that side so I put it as aM. Now this is another relation which tells you the weight loss per unit time equal to current into the atomic weight of metal M divided by nF.

Now we have already come across from this that it is not good to express corrosion rate in the form of weight loss per unit time because the corrosion process is happening on the surface. So it's better to divide it by the area to have a better representation of corrosion rate and which can be comparable. We have seen that process in case of the same metal piece two pieces of metal, two pieces of iron dissolved in HCl of same concentration and the only change is the area in one case is smaller the other case is bigger so that case in order to have the comparable corrosion rate it's always better to divide it by area.

So now same way we can put it as we can divide by area of the metal piece which is exposed to the solution I put a which is the area that is exposed to the solution. Now similar way I can also divide this part with a and here a is nothing but the area. So now I have this relation. Let me write it here. So dw/Adt would be equal to dw/Adt divided by area be equal to current into aM which is the atomic weight of the metal M divided by nFA and this is done just to have the unit weight loss per area per time. Now this part if you see if you consider if you want to see the value of aM, n and F all are constant for a particular process. So that case I can take this aM part, nF part on the left side separately I can consider these two parts aM these values and then I can have I by area. Now for a particular metal M these are constant. So only variable is this. Now if these are constant and now you see that the rate of corrosion is exactly proportional to I by A, and I by A is written in the form of i small i which is considered as current density. Now if this is a constant so now from this relation it's pretty clear that the corrosion rate is proportional to current density.

So now I can write that I can let's say if we remove all those dw/dt term and if we integrate it with respect to time so then we can get W divided by area into time would be equal to aM/nF(i) or I can write corrosion rate proportional to current density because this part is constant. So now if you see these two modes these are basically the same thing. In one case you find out the weight loss and in many cases you will come across that the weight loss is so marginal it is better to find out what is my current density. So once you know the current density you can express this current density in the form of weight loss per unit area per unit time. Fine. So this is one important relation which combines these two different modes of expression for corrosion rate, weight loss and current density.

Now in case of, this is fine let me put forward another situation, let's say in case of crevice, crevice corrosion or pitting corrosion these two modes, the another mode is uniform corrosion. This and these two you will -- professor Chaudhary IIT Roorkee will cover this part but for the time being let me tell you this uniform corrosion means the corrosion is happening let us say if your this is my exposed surface the corrosion happening uniformly throughout these sections, throughout the areas. Now in case of pitting or crevice you will experience if you have the same thing here.

Okay now the corrosion would be happening if you consider the same piece of the same cross-sectional area and area expose to solution you will come across that corrosion is happening in some localized regions. These regions corrosion is taking place and the corrosion is penetrating inside the volume inside the metal. So if we would like to understand the rate expression corrosion rate expression for this and this let's say in this case I determine the corrosion rate in the form of mdd. So that is be fine because the corrosion is happening throughout the section and over all exposed area everywhere corrosion is happening but in this case few sections or the few localized regions we are experiencing corrosion. So this mode will not be proper in this case. So in this case we need to measure the corrosion rate in the form of depth penetrated divided by time since overall cross-sections are not coming into picture. Fine. So that case how would we convert this same expression this relation into the form of depth penetrated per unit time. Now let me write so you can understand that in case of uniform corrosion the rate expression what you are using for example mdd or metal loss per unit area per unit time will it be good for expressing the corrosion rate in case of crevice or pitting where the corrosion is happening in the localized region and corrosion is basically the pit what is forming that is penetrating inside the metal and overall our surface area remain intact.

So that case we need to understand how to express the corrosion rate so that case we express the corrosion in the form of depth of penetration by time. Now you will see that this expression can lead to the expression for the pitting or crevice. Now let me write W divided by A which is area into time would be equal to current density into aM divided by nF. Now if I divide this with the density of the metal let us see what happens to left side, to the left side what happens. Now I divide by row so I have to divide this type this right-hand side also with the rho which is the density. Rho is density of metal. Now that case what would be the unit that is coming out dimension for this left side. Now weight is mass then area is length square, time is second and this is mass divided by length cue which is the density so this is coming out to be length by time. And this is in second so let me put it as time.

So length by time. So now if I just divide this part with the density of the metal I can easily convert this mdd unit to a depth of penetration per unit time unit and so this would be then would be equal to W/A into T into Rho would be equal to i into aM nF Rho which is another important relation to express the corrosion rate for crevice or pitting or extremely localized corrosion or dissolution. So now this is another expression. So in this case I know what is the unit led by time and the convention, U.S. convention in order to understand the depth of penetration per unit time or the express the rate in the form of depth of penetration per unit time is nothing but will milli-inch per year and this also called as mils per year and in short form it is called as mpy.

Now in SI unit it's this is U.S. convention. Now SI unit it is written as milligram, millimeter per year. So now we have two units mpy and millimeter per year. So now we know that we can express the rate of corrosion in the form of metal loss per unit area per unit time. We can also do it in the form of current density. We can also put – we can also use the unit mdd which is milligram per decimeter per day. We can use the unit for depth of penetration, one is mpy, one is millimeter per year and that is used for crevice or pitting or extremely localized corrosion and mdd is used in the case of uniform corrosion.

Now with this concept let us chalk out some problems, solve some problems then things would be much more clear.

Now let me write this two expression on the right side corner. One is W/At to i aM/nF this is for uniform corrosion. This is one. Second thing is W/At Rho is equal to i aM/nF Rho which is for crevice or pitting corrosion. So let me remove other part and let us find out -- let us solve some problems.

Now first thing let us find out what let us say one convention is another convention is you can find out what would be the corrosion in the form of mpy if you know the weight loss, if you know the area exposed, if you know the time duration and of course if you know the density of the metal. So one convention is if you know the weight loss W in the form of milligram and T in the form of hour, density in the form of gram/centimeters cue and A which is area in the form of inch square. This is – there is no such meaning why we are using milligram, hour, gram per centimeter cube and inch square this is a convention we take. Now if you have this mode then we know what is my weight loss. Okay. We know what is my nF, what is my T, what is my area, what is my T, and what is my Rho. If you see the relation this is my relation which is again length by time and I have mentioned that this can be expressed in the form of mpy and the relation is says that this should be if these are the expression mode milligram, hour, gram per centimeter cube and inch square then this into 534 would be equal to mpy. This would be the number of mpy – this would be the mpy which is the corrosion rate in the form of milli-inch per year.

Now how would we get 534? Now the 534 is nothing but the conversion factor. Now since this is in milli-inch per year I need to convert everything in the form of milli-inch in the form of so that we come across this unit. Let's see if we know this if we know this W/At Rho if I put all those units let's see what happens. This is one milligram. This is one inch square into this is hour, one hour, into this is one gram/ centimeter cube. Now this would be I just convert it into gram so that gram, gram can get canceled. So this would be equal to 10 to the power -3 gram divided by 1 inch square. Let me put it in the form of millimeter, milli-inch. So if we take it in the form of milli-inch so it would be 1 -- 10 to the power 3 square, just a minute let me first put it in the form of inch. Inch square then hour let me put converted into year because here we have year. So one hour would be one by 24 into 365, one year is equal to 365 days and 24 is the number of hours in a day. So one hour would be equivalent to this year and one gram and inch let me convert it into centimeter cue in the form of inch cue.

So one centimeter is equal to one by 2.54 inch so it will be equal to 1/2.54 by cue into inch square. So this inch cue so this things are getting canceled. Now this should become, so now this inch will go in the numerator so 10 to the power -3 now let me convert this inch into milli-inch into 10 to the power 3, this would become milli-inch and then this this term will also go to the numerator so milli-inch into let me put it this term, let me put it on top. So 10 to the power -3 gram, gram is getting canceled here into 10 to the power 3 milli-inch into this part will go above so 24 into 365. This would be, this is per year and this would be divided by 2.54 cue. So if you do this calculation you will see that this value is coming out to be 534. Yes 534.

So this is nothing but milli-inch per year which is nothing but mpy. So then you see that this conversion is coming because of the unit conversion. So now this is one way to express the corrosion rate. Now let me also this is the problem number one, why we get this 534 conversion factor in order to convert this W by At Rho in the form of mpy. And the second problem let me chalk out here let's see the problem says that iron is corroding at a current density of 1.69 into 10 to the power -4 ampere per centimeter square. So what would be the corrosion rate in the form of mdd and in the form of mpy? So these two things we have to find out.

Now we know these two relations. These two relations will give me the corrosion rate in the form of mdd and mpy because we know the relation between current density and weight loss per unit time per only day weight loss per unit time per unit area. Now let me chalk out the same problem here. Let me remove this for understanding mdd or express mdd the corrosion rate in the form of mdd so we have to use the first expression because here we know that this part gives me the weight loss per unit area per unit time. So I will use first term, and here I know only thing I know that is the current density and other things what we know in case of iron we know that iron is dissolving in this way and I know what is my aFe 55.85 gram per mole. So this is equal to i aM/nF so here i is 1.69 10 to the power -4. So 1.69 into 10 to the power -4 and I know this right side we consider, the right-hand side into I know what is aM, a 55.85. I know what is n, n is 2, F is 96500 now I need to find out what is this is basically let me put it in the form of units. This is ampere per centimeter square into 55.85 gram. This is Coulomb.

Now this I can write it in the form of 1.69 into 10 to the power -4 Coulomb per second per centimeter square into 55.85 gram divided by into 10 to the power 3 milligram since mdd is nothing but milligram per unit per day per unit time per unit per decimeter. So this would be equal to 2 into 96500 Coulomb. If you this will get canceled now second you convert it into day, centimeter square you converted into decimeter square, then you will get if you convert all those things you will get that this value would come for 422.54 mdd. So only thing what you have to do second you have to convert into day, centimeter square you have to convert it into decimeter square because one centimeter is equal to ten centimeter is equal to 1 decimeter. This conversion if you do here then you will get that the corrosion rate is coming in the form of mdd and this would be equal to 422.54 mdd. Thank you.

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Prof. Phalguni Gupta

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CO Co-ordinator, NPTEL, IIT Kanpur

Camera

Ram Chandra

Dilip Tripathi

Padam Shukla

Manjor Shirvastava

Sanjay Mishra

Editing

Ashish Singh

Badal Pradhan

Tapobrata Das

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Shikha Gupta

K.K Mishra

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Sweta

Preeti Sachan

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Ashutosh Kumar

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Puneet Kumar Bajpai

Priyanka Singh

Office

Lalty Dutta

Ajay Kanaujia

Shivendra Kumar Tiwari

Saurabh Shukla

Direction

Sanjay Pal

Production Manager

Bharat Lal

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