Indian Institute of Technology Kanpur

NP-TEL
National Programme
On
Technology Enhanced Learning

Course Title

Environmental Degradation of Materials

Lecture – 07
Broad Subject: Pourbaix Diagram

By
Prof. Kallol Mondal
Dept. of Materials Science & Engineering

In the last lecture, we have seen a position of one reaction that is Ni++ +2e in pH, potential pH diagram and there we have seen that let me draw the potential pH diagram which is nothing but the Pourbaix diagram. Pourbaix diagram it's basically nothing but potential versus pH and the relative position of all the species that are forming in H2o that can be graphically represented with E versus pH diagram which is nothing but the Pourbaix diagram. Pourbaix diagram, here E is nothing but the reduction potential and we will place all the reduction, all the potential in the form of reduction potential.

Now we have noted eight reactions, and we have also come to know their chemical potential standard chemical potential of those species ionic as well as the reaction product, let say ionic species for example mu0 of Ni++, mu0 of H+ or product phase let us say mu0 of Ni(OH)2 all those things we have noted. Now the reaction number one, which is Ni++ +2e = goes to Ni, this reacts reduction reaction we have also seen that it can be placed in potential versus pH diagram and for a particular ionic concentration, because this reaction is a potential dependent pH independent because there is no where we have H+ ion so this can be related, can be expressed in the form of Nernst equation, which is Ni++ Ni = E0 Ni++ Ni + RT nF, NF they had a two electron 2f Ln Ni++ concentration of Ni or activity of Ni, so here Ni is 1, because it is a pure metal. Now this one we can consider it as 1, you can consider this 10 to the power – 2, you can consider 10 to the power – 4, so we have seen with the help of standard chemical potential data that this is coming close to 0.24V - now this is when Ni++ ion activity is 1. Now if you change the Ni++ ion activity to Ni to 10 to the power – 2, it will go down like that as you decrease the concentration of Ni++ this line will go down.

Now we have already seen the position of Ni and Ni++ we have seen that position of Ni would be below this line and position of Ni++ would be Ni++ this is the position of Ni++ in this E versus pH diagram and we have already seen why the position of Ni would be below this, why the position of Ni++ would be above this. For example, if we consider the concentration what we can measure in the solution let say that is 10 to power – 6, let say this curve corresponds to do 10 to the power – 6, concentration, unit concentration, okay, so for Ni++. Now if we have a concentration which is less than 10 to the power – 6, let say 10 to the power – 8, if the concentration is 10 to the power – 8 of Ni++ then we cannot measure this, so that in other way it means that if the concentration of Ni++ is 10 to the power - 8 unit in the solution then actually it is basically saying no ionic formation, no ion formation or if it is no ion formation then it should remain as Ni, so below this concentration everything would be Ni, not Ni++ so that suggests that the concentration below this always should be Ni region, because below that concentration we cannot do anything. Now let say I consider the concentration to be 10 to the power – 2 unit which is basically saying that considerable amount of corrosion because corrosion means the ion formation from metal, so consider my amount of corrosion is 10 to the power – 2, below that it is not at all considerable amount of corrosion or we can say that if the corrosion, if the concentration is less than 10 to the power – 2 we can say that the corrosion is not happening. Then below this concentration everything would be nickel, the concentration of nickel ion plus plus is having some value, some finite value but that is considered to be a negligible corrosion, so we can say that below this line always would be Ni. So then what would be the position of Ni++? Ni++ position would be always above this line and this line is coming because it is a pH independent, because this is my equation and if this equation I would like to plot in E versus pH diagram then it should be a horizontal line, parallel to the pH axis.

Now the second reaction we have started thinking that is another reaction which is Ni + 2H2o going to Ni(OH)2 + 2H+ +2e now this reaction we can also consider in the form of reduction potential, if we consider it in the form of reduction potential, then we can write this equation instead of this, let us write in the form of reduction potential. In reduction process Ni + 2H2o, now in for this reaction I can also express in the form of Nernst equation and here I am putting at ox/red because ox this is my ox, and this is my reductant, this is my oxidant, this is my reductant, so this should be equal to E0 red + here 2 electron is involved, 2 electrons are involved so RT nF, n is 2, 2F Ln concentration of oxidant Ni(OH)2 concentration and concentration of H+ square because 2 hydrogen ions are involved in this reaction and then it would be concentration of Ni and concentration of H2o whole square.

Now if you see this, this is precipitating out, so the concentration I can consider it as 1, this is the pure substance so this is also 1, this is a pure metal 1, now we have to see what is the concentration of H+ ion in the media, now this also we can express as E0 ox/red + RT 2F x 2, I am just taking 2 out Ln H+ ion, so this 2, 2 is getting cancelled and then finally I can write it as E0 ox/red +, now I am putting the value of our R, R is 8.314, T is 25 degree Celsius so which is 298 Kelvin and F is 96500 Coulomb per gram equivalent, so it would come if you just put all those values it would come 0.059 x now instead of Ln I put log H+, if i put log H+, sorry there is a small mistake, so if i put log H+ and all the values I put R, T and F, and if I consider Ln, now if I consider Ln H+ then it would be 2.303 log H+, so if i put this formula so 2.303 that factor also will come out, so finally we will get 0.059 log H+. Now instead of that let me put a minus sign here, and then in the bracket I put another minus, so it would be like this. Now minus log H+ is nothing but pH, so I can modify this entire equation and put it like this, minus sign will remain 0.059, and then it would become pH so this is my relation.

Now you see if we would like to plot this equation let say this is my equation number 1, this is my equation number 2, if I would like to plot this equation I need to know what is E0 and I need to know the pH of the solution. And if you see this there is a negative slope and the slope is 0.059, so it should be something like this, this line with a negative slope and the slope is 0.059, but if we would like to pinpoint that equation we need to know what is this, so how to find out this? This is the standard reduction potential, for this reaction when the activities of those species should be 1, now that case I can find it out let me remove this part, I can find out now NIOH I know so Del G0 for this reaction Del G0 would be Mu of the product Mu0 Ni, Mu0 Ni + 2 Mu0 H20 - Mu0 Ni(OH)2 - 2 Mu0 H+, so now let me put all those values Mu0 Ni is 46398 + there should be a minus sign, there was also a minus sign because Mu0 Ni++ is nothing but - 46398 Joule per mole, then this should become 2 x 216 sorry, this is 452, I am doing a mistake, okay, sorry, so it would be 236964.2 - this is minus, since this is a minus sign also this value is minus so it would become plus then 452694, then here also this is already zero we have consider, convention is this is considered to be zero, so now this is my, what would be the final value? Final value it would become, so let me calculate it, this is 2 x 236.964.2, 236964.2 x 2 + 46398 = - 452694, 64-, 64632.4 Joule per mole, and this is nothing but – nF E0, and n is here is 2, so then E0 would be ox/red would be equal to – 64632.4, there will be a minus sign by 2 x 96500, F is 96500, this should become to type in 96500, just a minute let me see, where I'm making mistake, sorry, I made a mistake here, because this is also 0, this is also 0, so there should not be any value here, so instead of that, this value would change, this value would become 2 x 236964.2 – 452694, it should be 21234.4, so this would also change 21234.4 divided 2, divided by 96500, so it would be 0.11, so this is my volt, so I can calculate E0 for this reaction, so the finally I can replace this, this E0 because when I am considering E0, considering the standard chemical potential of all the species for this reaction, then the activities of all the species also would become 1, so there the activity of H+ ion would also become 1 so pH would become 0, so if pH becomes 0, so E ox/red = E0 ox/red.

Now if I have a different pH value, so I will just put this value and with the pH, so the final equation, let me remove this, the equation would become this equation I can modify I can write it like this, now I know the value 0.11 volt - 0.059 pH, so this is my equation number 2, so this 2 equation is becoming, now let me put it as 3, because from 2 I am getting this, so now I can plot this on this, so here this would be 0.11 if the pH is 0 here, if I consider pH to be 0 here so my value of potential would become 0.11 because I have considered that this is my standard reduction potential when all the species activities of all the concentration of all the species become 1. Now this is my line, let me put it in the form of green color, let me put a dotted line, dotted line, now this equation is basically telling the equilibrium between this species and this species. Now you see here the species are H+ Ni(OH)2 and Ni and H2o, so this and this if you remove, because these are basically the constituents of the water medium, now then this tells you the equilibrium between Ni and Ni(OH)2, so if it is between Ni and Ni(OH)2 then we have to see where we are getting Ni and Ni(OH)2.

Now this line is passing through two regions, one is Ni++, another one is Ni, now but we have already seen that this is the equilibrium between Ni and Ni(OH)2 so in fact this line will not have any existence, because this line is going through Ni++ and which is not a part of this reaction, so then the part of this reaction Ni and Ni(OH)2, so then the part where, the part of the line which goes through the Ni region that should be existing. So let me put a thick line, in this region the other region because then this, if this is Ni the other part of course would be Ni(OH)2, the logic is this reaction tells you the equilibrium between Ni and Ni(OH)2, so this line can exist in the region of Ni not Ni++, so that's why in the region of Ni++ I am putting a dotted line and in the region of Ni and Ni(OH)2 I am putting a solid line, the solid line indicates that this line indicates the equilibrium between Ni and Ni(OH)2, and this region is invisible because we cannot have any equilibrium between Ni++ and Ni(OH)2 from this equation. So now we can have a region of Ni and Ni(OH)2 so then this part cannot exist, because this part if I extend then Ni is going into Ni(OH)2 region which is not possible, so left of this line should be Ni, right of this line should be Ni(OH)2.

Now I know another reaction which is nothing but Ni + 2 + 2H2o going to Ni(OH)2 + 2H, this is another reaction this is let say third reaction and this reaction we have already seen that this is not a potential guided reaction, because there is no electrons which are involved or you can say that this is not an reduction reaction, not a reduction reaction, so now this reaction if I would like to see the we can make use of all the thermodynamic data, now for this reaction I can calculate what is equilibrium constant at 25 degree Celsius, because we have considered 25 degree Celsius in the beginning, so that case this should be equal to Del G0 / RT with a minus sign, because Del G0 = - RT Ln K, so this is Ln K, now for that I need to find out what is Del G0, so Del G0 again I can find out which is nothing but the Mu of Ni(OH)2 mu0 + mu02, mu0 H+ 0 - mu0 Ni+2 – 2 x mu0 H2o, so if you put all the values of this species, this chemical potential, standard chemical potential you would get, this would be close to, this would be close this would be, you would see that the value would be come, I am not putting all the values, I am straight wave, I am jumping one step, so this should be 452694 + 46398 + 2 x 236964.2 divided by 2 x sorry R, R is 8.314 x 298, you would see that this value becomes close to – 12, so this is becoming – 12, just a minute, so this would become let me calculate, so this is Del G0 would become 2 x 236964.2 = + 46398 = - 452694 = 6463, so just let me put it by 8.314 x 298 = 27.297, there would be a minus sign, there would be a plus sign, because this is becoming plus, so now Ln K equal to this, now I can find out what is K log, log K would become divided by 2.303 = 11.85, now I will put a, if I then this plus sign would become minus because I am putting a log K now, so this would become minus or it is close to 12, let me put 12, now K would become then, this K would be then, so log K is 12, now let me remove this part. So I can put K, K is NiOH concentration of Ni(OH)2 H+ 2 log equal to – 12. Now this is 1, this is also 1 now this equation would become log of H+ square Ni++ would be equal to – 12. Now this would become pH = 6 - 0.5 log Ni++,so this is another equation so if you simplify it then you would become pH which is nothing but the log minus log H+, if you take if you extend it then it would be 2 log H+ ion concentration – Ni++ log of Ni++, then if you simplify it then it would become, this is my another equation let me put it as equation number 4.

This was the equation number 3, this is equation number 1, now this 4, I can also plot it here, in this E versus pH diagram. Now here you will see that this is pH in potential independent, so if it is potential independent reaction then the line because also this indicates a straight line function and this is, which is also dependent on the nickel ion concentration, now this line is considered when the nickel ion concentration is Ni++ = 1, now also let me calculate this as a function of nickel ion concentration and when the nickel ion concentration is 1.

Now this is another line which should be vertical to this line, and should be parallel to this line because this is pH dependent, but potential independent, so this line would be something which should be going parallel to this line, so let me put this line parallel to this line, this is my line for equation 4, but let me pinpoint this all the pH values. Now if this is 1, so pH should be 6, so this line should pass through a pH value which is 6, fine, so that means this line will come pH value, when the pH is 6 and when nickel ion concentration is equal to 1.

Now we know that now we have to find out the equilibrium condition so that this line indicates the equilibrium between Ni+ 2n Ni(OH)2. It suggests that the line below this Ni and Ni++ line cannot have any existence, because this line indicates the equilibrium between Ni(OH)2 and Ni++ below this line there is no existence of Ni++, above this line there is existence of Ni++, so below this line it would be dotted, I am putting dotted because just to have reference where from it starts, and above this line there it should be a thick line, because this indicates the equilibrium between Ni++ and Ni(OH)2. And when the concentration of Ni++ is 1, so if it is 1 then this should pass through pH 6 and also this line should have a thick, I should have it, I have drawn it in the form of thick line and this line indicates the equilibrium between Ni++ and Ni(OH)2.

Now point is I have connected these three lines at this point, we have to see that whether these three lines are connecting here or not, that means when the pH is 6 and potential is - 0.24V, and how to find out? Now let me see whether this is a common point between this line and this line that means this is line number, line number, let me put it as 4 because corresponding to equation number 4, so this and this equation number 1, E=– 0.24 -, and if the activity is 1 for this reaction, for this reaction, so it is basically + RT 2F Ln Ni++ ion, so this is equation number one we have seen that this is equation number one.

Now equation number 1 and equation number 4 if we solve it when the activity or the concentration of Ni++ is 1, so then E= 0.24, just a minute, just a minute, if we solve this, this is at pH 6, what would be the value of E? At pH 6 the value of E would always be this much, this is at pH 6 at Ni++ concentration equal to 1, so this point if we see the coordinates for this one, this is 6, X is 6 and potential is 0.24, so definitely this two point will meet at this point, if the nickel ion concentration is 1, provided this is nickel ion concentration is 1, so we know that these two lines are merging here, when the nickel ion concentration is 1 and the pH is 6.

Now let me see whether this line is passing through this point or not, for that let me see the equation number 3, equation number 3 says that this is 0.11 - 0.059 pH, so this is equation number 3. Now if I solve equation number 1 and 3, then I would get at pH = 6, what would be the potential? At pH, let say when the activity of nickel is 1, so then at pH 6 E = 0.11 - 0.059 x 6, this equal to .11, .059 x 6 +.11 = 0.244V - which is close to 0.24V, so that means when the pH is 6, this potential is also becoming close to 0.24 that means this line as well as this line both are meeting at this point so this line and this line are meeting at this point, we have to see whether this line and this line are meeting, so solving equation number 3 and 4 you would see that again these 2 lines are cutting at this point, so that means this is the common point. And now we know the complete picture of the diagram, here we see that the position of Ni++ is within this boundary, position of Ni is within this boundary and position of Ni(OH)2 is within this boundary and each line indicates the equilibrium between the species that are existing on both side of that line, for example this line indicates the equilibrium between Ni and Ni++, this line indicates the equilibrium between Ni++ and Ni(OH)2 and this line indicates the equilibrium between Ni and Ni(OH)2.

So now we see the position of different species, for a system where nickel is reacting with H2o and forming different species, for example nickel can form Ni++, from nickel it can go to Ni(OH)2 even Ni++ it can go to Ni(OH)2. Now this three lines we can now remove all those things, let me put all the three lines, this is line number 4, now this is let say I am putting Starbucks, star then Ni++ +2e going to Ni, this is line number 1, corresponding to the equation 1, then third one which is Ni(OH)2 + 2H + 2e going to Ni + 2H2o, this is line number 3 corresponding to the equation number 3. Now we can see the equilibrium, when we plot this equation in the form of line on E versus pH diagram then that line indicates the equilibrium between Ni(OH)2 and Ni, so this is that line, the rest of the line which is going into Ni++ that would be invisible, I am putting it a dotted line just to indicate the reference from where it has originated, if it is 1 then it should origin it from, if the pH is 0 or the activity of Ni H+ is 1, H+ concentration is 1, then this it should origin it from 0.11 volt, similarly this line indicates the equilibrium between this Ni(OH)2 Ni++, and this line indicates the equilibrium between Ni++ and Ni.

Now also we have seen another reaction which is NiO + H2o = Ni(OH)2, and if you see this, this is not a potential dependent reaction because this reaction you cannot express in the form of Nernst equation, similarly here we don't have any H+ ion, so if there is no H+ ion this is also potential pH independent. So pH as well as potential independent reaction, now from this we can have a very, the major outcome, what is that? Let me see this reaction, this reaction also we can have all those chemical potential data for NiO H2o and Ni(OH)2 then we can have the K value, the K value also we can calculate, so K value we can calculate from this relation Del G0/RT exponential minus, this way we can find out the K value, this is nothing but the K value and if you put all the values of this, I think I have not given this potential chemical potential data for NiO, the chemical potential data for NiO is Mu0 NiO = - 216762 Joule per Kelvin, the other data I have provided then you will see that this key is becoming 1, so if K becomes 1 then K you can express in the form of concentration of Ni(OH)2 concentration of NiO and H2o = 1, this is of course 1 because this is pure element, so if we have a little bit of concentration and these are the precipitating phase, but we can always have little bit of dissolution of this phase and which is the dissolution of this phase in the solution H2o that can be dictated in the form of solubility data, so then it tells you the concentration of Ni(OH)2 would be equal to concentration of NiO, so this is one information.

Similarly I can also write this equation in this form NiO + 2H + +2e = Ni + 2H2o, so I can also write in this form. Now for this reaction if I would like to find out what is my relation between potential and pH you will see that the relation would become E = 0.11 - 0.059 pH, you just put all those values of Mu0, you will see the same sort of reaction, this is sorry, here 1H2o, so if you calculate what is my standard reduction potential for this reaction, since this is a reduction process, I will see that this value becomes 0.11, similarly it would be related to pH of the solution and the slope of that line would be 0.05 net, so this equation let me put it as 5, this equation and for this reaction I know what is my relation E = 0.11 + let me put it in white color for this equation E = 0.11 - 0.059 pH, so it actually whether you write this equation or this equation, this indicates the same line because the equations are same this equation was number

3, it was given the number 3. So this is equation number 5 and equation number 3 both are exactly same, so the line for this reaction or this reaction would be always same.

Similarly I know this relation, so actually you can also write / NiO / NiO because this is equivalent to NiO as well as this reaction and this reaction both are almost equivalent, because the equation from the Nernst equation you can see the both equations are same. So you can have either NiOH or NiO and then have this potential pH diagram or Pourbaix diagram for nickel system. So this is, I can have this relation, this relation, this relation, this as well as this, so from that 5 relations I can have the complete Pourbaix diagram for nickel system Ni H2o system, this is as Ni H2o system. There could be some complex ion formation at some different pH or potential values but with the available equations what we have in our hand, we can plot this.

Now once this is over, then we are not, this is not complete this Pourbaix diagram it just is telling you the different equilibrium between different ions or species, but this is not complete because we can also have another 4 different types of reactions, which involve H+ OH - and H2o and also it involves dissolved oxygen, if it is not deaerated, if it is aerated, so let me put all other reactions now which involve only H2o O2 H+ and OH – ions.

First let me put this relation, first equation let say H+ +e = H2o half H2, for this reaction again this is potential dependent as well as pH dependent, because this relation I can write it as E = E0, which is nothing but 0 for hydrogen reaction minus you can write 0.059 pH because partial pressure of hydrogen in standard state is 1, so if I consider the pressure of hydrogen is 1 atmosphere, then I can write this relation. So now you see this relation is nothing but pH dependent as well as potential dependent, because the potential is becoming 0, the standard reduction potential for E0 is 0V. This we can also plot here, now when pH = 0 or the activity of the activity of H+ ion in the solution is 1, then it should start from let say 0V, when the pH is 0 it should have the value 0V because pH then, sorry, activity pH is 0 or the activity of H+ ion is 1, then this potential becomes 0. Now as pH is increasing, it will also increase as per this relation so it will also have a slope, this is my slope let me put it in blue color, let me, so this is my, let say reaction number I have 4 that's way, let me put it as 5, so reaction number I think I have already put the number here, reaction number 5, so this is number 5. And also it has a slope which is - 0.059, now if you compare this line and this line both are parallel because here also the slope was this line, for this line slope was – 0.059. So now these indicate this reaction H+ +E half H2.

Now I can also have another reaction which is 2 H2o + 2e = H2 + 2H -, this is another reaction that is possible in a system. Now if you see this and if you see this it involves H+ ion, so that means it involves this reaction is possible in acidic medium. Now in this reaction you will see that this reaction is possible in basic medium or neutral medium depending on the pH of OH - ion, so if OH - pH is 7 or more, then this reaction is possible and this is possible when pH is equal to less than 7, so that means if this reaction is possible less than 7 so this is happening in acidic medium and if this is greater than C = 7, then this is happening in neutral or basic medium.

Now with the thermodynamic data that means chemical potential data of H_2o and OH - we can also find out what is the standard reduction potential for this reduction process. So this reduction process I can write it as ox oxidant and reductant = E0 reductant + now we involve two electron so RT 2F Ln H_2o square, now since this is in the gaseous form so pH2 OH – ion concentration square, now this is one, this is one, since this is considered to be in standard state because we would need to find out what would be the value of E0.

So then and this is one atmosphere, standard state it is one atmosphere and the pure substance the activity would be considered as 1, so this two are one. Now we can have would be equal to E0 + RT now since there are, there are used as square term, if you take this square term out so then it would become minus and if you put all those values RT as well as F this 2 and this 2 would get cancelled and if you convert in terms of log then you can see that 0.059 into log of OH -, log of OH- concentration of log of OH -, so this is my relation. Now I can replace this OH - in the form of H+ how would we do it that I would come in a while. Now I can also find out what is the value of this, so this value I can calculate from standard reduction potential, standard chemical potential data again so this would become Del G0 = - NF E0, so here n is 2, n is 2, F I know 96500 Coulomb per gram equivalent, that would be equal to so Mu0 H_2 + Mu0 OH – 2, because 2 OH - ions are involved - 2 Mu0 H_2o, fine, so this is 0, this value I know, this value is nothing but -157147.1 + 2 x 236946.2, so from that you can find out E0, E0 would be then since there is a positive sign so E0 would be minus, so -2 x 236946.2 -157147.1 = so this is 316745.2 / 2 x 96500 = 1.641, sorry there should be 2 sign here because we will involve two things, so I think I had made a mistake, so 2 x 2, just a minute, 236946.2 – 157147.1 equal to into 2 / 2 / 96500, 21., this would be 1.106, 107 let me put 107, so this is my E0.

So now once you find E0, so it would be one point, it should be minus sign because there is a minus sign – 1.1, let me put 1.1 - 0.059 log of OH -.

<u>Acknowledgement</u>
Ministry of Human Resource and Development

Prof. Phalguni Gupta
Co-ordinator, NPTEL IIT Kanpur

Prof. Satyaki Roy
Co Co-ordinator, NPTEL IIT Kanpur

<u>Camera</u>
Ram Chandra
Dilip Tripathi
Padam Shukla
Manoj Shrivastava
Sanjay Mishra

<u>Editing</u>
Ashish Singh

Badal Pradhan
Tapobrata Das
Shubham Rawat
Shikha Gupta
Pradeep Kumar
K.K Mishra
Jai Singh
Sweety Kanaujia
Aradhana Singh
Sweta
Preeti Sachan
Ashutosh Gairola
Dilip Katiyar
Ashutosh Kumar

Light & Sound
Sharwan
Hari Ram

Production Crew
Bhadra Rao
Puneet Kumar Bajpai
Priyanka Singh

Office
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari
Saurabh Shukla

Direction
Sanjay Pal

Production Manager
Bharat Lal

an IIT Kanpur Production