Corrosion - Part I
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Lecture - 25
Inferences from Pourbaix Diagrams of Ni-H2O and Al-H2O system, Pourbaix Diagram of Fe-H2O system, and Advantages and Limitations of Pourbaix Diagram

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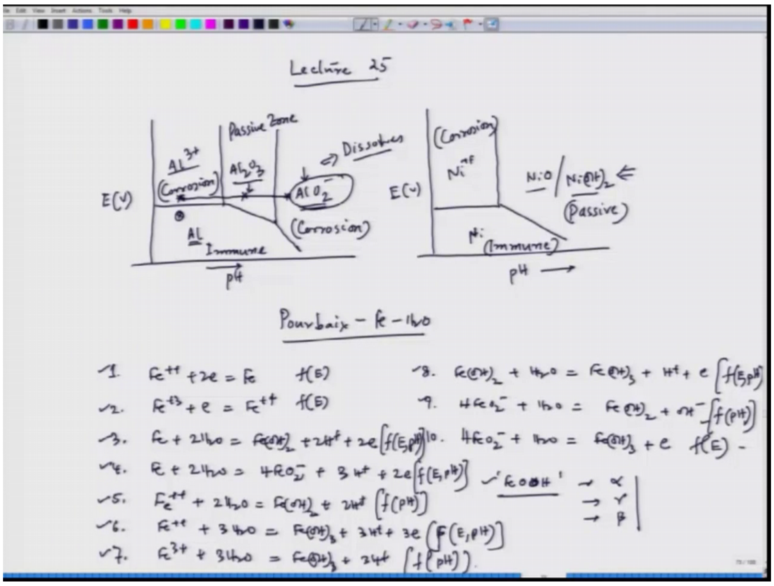

Let us start lecture 25 so, today we will finish our discussion on Pourbaix Diagram and then we will get to the kinetics of corrosion. In the last lecture we ended with schematic phase diagram for aluminium. We have given all the reactions as well as standard chemical potential for all the species active in the in those reactions. And from that you need to calculate that phase diagram, but the schematic will be the like what we have shown in the previous lecture.

The schematic phase diagram for aluminium would be this one where this is AL plus 3 this is AL AL 2 O 3 and then this becomes ALO 2 minus and this is potential axis, pH axis. Now, if we recall a Pourbaix diagram for nickel diagram was like this, this is pH, E volt. This is also schematic where this region was nickel, this is nickel plus plus and here either nickel oxide or NiOH whole 2 [vocalised-noise] that time we indicated this region to be immune zone. This region was passive and this region was corrosion. Since, nickel ion is forming and whenever ion forms nickel dissolves that is what we are talking about the corrosion region.

Now, here nickel remains as nickel and that is what this zone is immune zone and then we have a passive zone. Considering the fact that these products are forming on top of nickel surface and they are actually giving a protective nature for further corrosion of nickel. And the nickel corrosion is still there, but there the amount of corrosion is less because, the amount of corrosion of nickel would be decided by the solubility product of these 2 products. We call it as passive zone because, the corrosion of nickel is limited because of the formation of this passive layer on top the of the nickel.

But, similar comparison can be drawn in case of aluminium only at one place we will have little difference [vocalised-noise]. Now, aluminium this zone is aluminium so, definitely this is immune zone this is AL plus 3 so, this is corrosion zone and of course, here we are forming AL 2 O 3 that is what this is passive zone. Where aluminium oxide form some on top of aluminium and then it actually gives protection to the aluminium and aluminium corrosion is limited.

Now, there is one more phase or one may one more stability zone which is decided by this particular phase which is ALO 2 minus. So, this is a complex aluminium ion which is in the form of ALO 2 minus so, these dissolves easily in water. So, when it dissolves; that means, it is also taking away aluminium from the aluminium substrate. So in fact, it is corrosion it is corroding this aluminium is corroding in the form of ALO 2 minus so, this is also a corrosion zone.

Now, the only interesting fact is in case of nickel system if you increase the pH; that means, if you increase the basicity of the aqueous medium we get to achieve passivity. But in case of aluminium system of course, if you increase the pH level or basicity [vocalised-noise] you for example, you are here or you are if you are here let us say this zone. And now if you increase the pH level you reach to this zone so, you are going to get passivity, but if you increase the pH farther once it come to this zone, you are going to achieve no passivity rather corrosion will again start.

So, that is what this Pourbaix diagram it is actually giving an idea that what could be the stability of the reaction products and what could be the spontaneity of corrosion. So, here corrosion is spontaneous, in this zone corrosion is limited, in this zone again the corrosion becomes spontaneous. And if we are here let us say then of course, where the corrosion becomes very limited because, it is actually remaining as aluminium immune zone. Now, these information is very critical.

For example, in case of aluminium we know that it is a very passive metal because in aqueous system it gets to the passivity. Now, if we increase pH level the passivity will be broken and then it will form ALO 2 minus ion if we increase pH level to certain extent and if we reach to the stability zone of ALO 2 minus the corrosion will further start. This similar situation arises in case of iron and we need to talk about iron because iron constitutes almost about 80 percent of our structural bodies rather.

So, now we talk about iron Pourbaix diagram little bit, here also we will give some equations and those equations if you follow if you see the book by Pourbaix there is a famous book on Pourbaix diagram. I will give the data later on my ts will give you the data for those chemical potentials as well as chemical potential of the all the of all the species which are taking part in different reactions. In order to understand the stability zone of different phases in iron H 2 O system and you can construct that iron Pourbaix diagram.

So, let us talk about Pourbaix diagram of iron. Now, here also we can have several such reactions, [vocalised-noise] reactions patterns are let by let us keep in keeps seeing that reactions, this is 1 reaction, 2nd Fe, 3rd, 4rth. So, I am just writing down all the possible reaction that could take place when iron is exposed to aqueous medium Fe plus I am just writing down all the reactions.

So, let us get to these equations there are such equations available and another equation which is HFe O 2 minus plus H 2 O equal to [vocalised-noise]. So, these are the reactions I have noted, there are other reactions possible for example, one important phase in case of iron system, this could be available in the form of alpha or in the form of gamma, in the form of beta. So, these 3 have allotropes are possible for this particular phase and these phrases are important in the sense that they give a different levels of passivity of iron surface [vocalised-noise].

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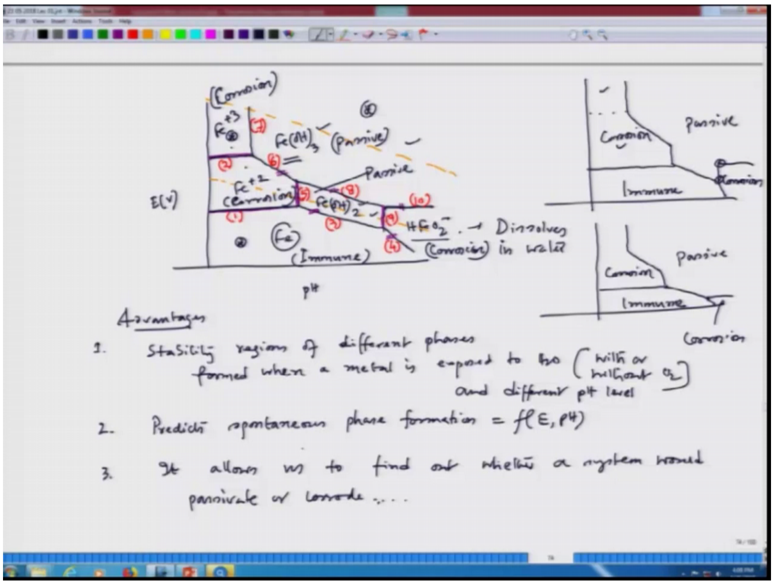

Now, if I try to see the schematic diagram of iron system, let us get to the schematic diagram would look like. So, this is the diagram what it looks like if this is Fe, Fe plus 2, this is Fe plus 3, Fe OH whole 2 and this region is Fe OH this is Fe OH whole 3 whole 2 and this is HFe O 2 minus. Now, here also this phase and this phase they are insoluble phase with a very low solubility product, rather this is very this has very low solubility product.

Now, when they form they try to form [vocalised-noise] on iron surface and they try to passive it, but here this is remaining as iron. So, this region is definitely immune zone this is Fe plus 2 so, this is corrosion. This is also Fe plus 3 so, this is also corrosion; that means, whenever we have iron, iron formation in the stability this diagram this Pourbaix diagram we have to say that metal iron is forming. So, corrosion is taking place, this is passive, this is also passive zone.

Now, interestingly just like in case of aluminium we have one complex iron ion which is HFe O 2 minus this also dissolves in water easily. So, again these zone definitely will be corrosion zone.

And then if I try to indicate with schematic for example, here also I can note down those reactions. For example, this is if I note down with different colour red colour let us say this is reaction 1, I simply right with the bracket 1, this is reaction 2, this is this line is

FeOH whole 2. So, this is 3, this is 4, this is 5, this is 6, this one is 7, this one is 8, this reaction is 9 and this one we can write it as 10.

So, if you go back and see all those reactions if you see 1, 2, 3, 4, 1 to 10 we have indicated those for example, this line if I see that this line is basically pH independent, this is also pH independent, this is potential independent, pH dependant, this is also pH dependent. This line and this 3 lines are all pH as well as potential dependent and of course, this one also pH independent.

And if we see those reactions definitely I can simply write in this fashion function of E, function of E I can write function of E and pH. This is also function of E on pH, this is function of pH, function of E and pH, this is function of pH because here no electron is involved. If you follow the Pourbaix diagram for nickel you can easily understand this is function of E and pH, this is definitely a function of pH this is function of potential.

So, it is very clear that this will be parallel to x axis, this will be vertical to x axis, this would be at an angle to the x axis, this will be [vocalised-noise] parallel to x axis, this is at an angle to x axis. That means, pH axis, this is at an angle to pH axis, this is perpendicular to potential axis, this is at an angle to pH axis, this is also this is perpendicular to pH axis or parallel to pH E axis, potential axis. So, we are very clear and that is what our diagrams also confirming to that.

Now, here also we are saying that there is an immune zone there are 2 corrosion zones rather 3 corrosion zones 1, 2, 3, 3, corrosion zones and this is passive zone, this is also passive zone. Now, if I try see schematically how it looks it will look like this ok. So, both the zones are this zone and this zone both the zones are corrosion and then now here we have this one and then this is passive this is corrosion immune and corrosion.

So, this is [vocalised-noise] a typical diagram, some book you might looks like this type, where this is passive, this is corrosion, this is immune and this is of course, corrosion. Now, these 2 lines this 2 lines merge together depending on the phases what where we are considering [vocalised-noise]. So, this is about Pourbaix diagram for iron schematic drawing, then aluminium we have also given the reactions as well as chemical potential data, in case of iron we have just given reactions chemical potential will be provided to you. And then in case of nickel we have complete formation of Pourbaix diagram.

Now, here one thing is you have to do that is we have to also indicate your water reactions, water, this is hydrogen reaction and this is let us say oxygen reaction lines so, then it becomes complete. At the end we would like to see the advantages and disadvantages or the limitations of Pourbaix diagram. So, we have done a quite detailed analysis on Pourbaix diagrams so; first see what are the advantages.

The advantages first thing, it indicates without going for detailed calculation it indicates the stability region of different phases forms different phases formed when a metal is exposed to H 2 O with or without oxygen and different pH level [vocalised-noise]. So, that is what we are saying that we are finding corrosion zone, we are finding immune zone, passive zone and corrosion zone further on the right side of on the on the higher pH side. This is one important information we do get once we do this thermodynamic calculations [vocalised-noise] and find out this diagram.

2d part it somehow predicts spontaneity spontaneous phase formation as a function of E and pH. Definitely, it can predict for example, if I am here it will be iron if I am here it will be a Fe plus here it will be FeOH whole 3 like that way we can decide what could be the spontaneous phase, when a metal is exposed to the water system.

Now, 3rd point if I see the 3rd point indicates that it allows us to find out whether a system would passivate or not or corrode that information would definitely get, we definitely get. Now, interestingly in order to do that we need to just see the iron see in case of iron and aluminium system if I see the aluminium Pourbaix diagram.

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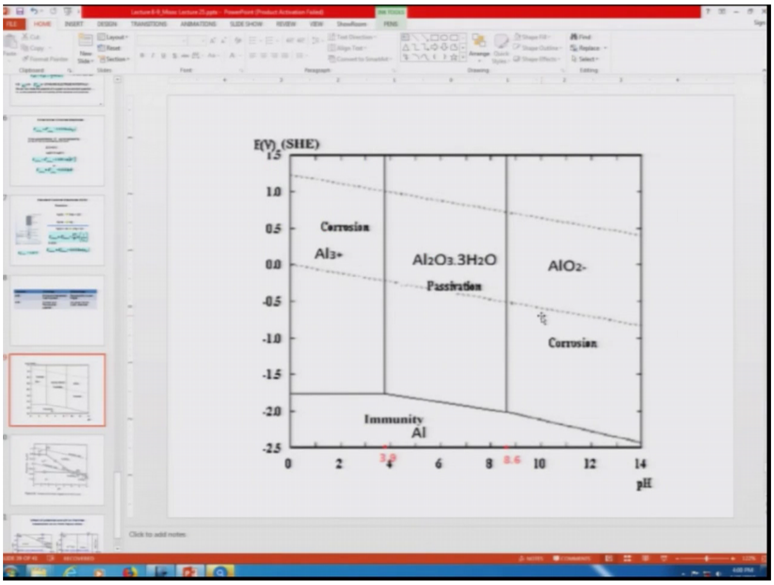

This is aluminium Pourbaix diagram, if we see that when the pH level is 8.6 this is [vocalised-noise] if I do see the cursor. So, this 8.6 beyond that we do get Al O 2 minus and then it would corrode, but when the pH is between 3.9 to 8.6 and if the potential is within this region Al 2 O 3 region we do get a passivity.

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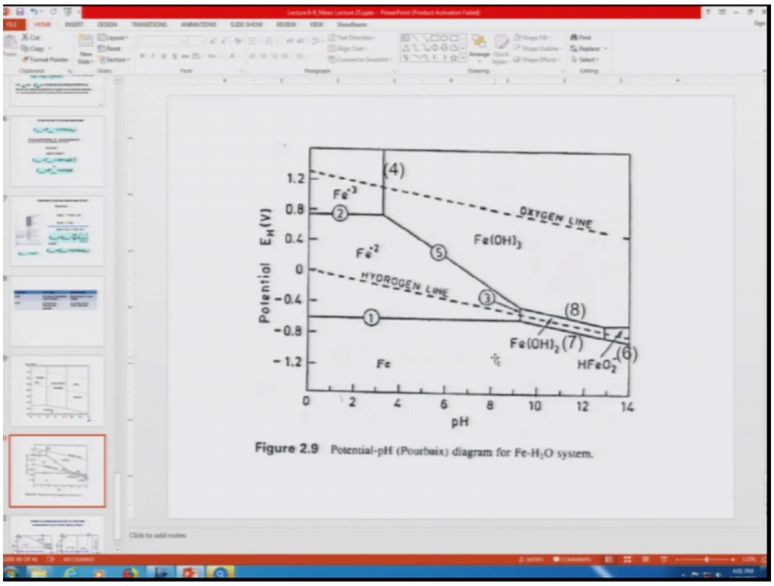

But, in case of iron situation is different, so, this is iron Pourbaix diagram what we have shown in the schematic this is the exactly the same and here if you see that this particular zone this FeOH whole 2 as well Fe OH whole 3 these zones we do get passivity. And if you see the pH level varies from 9 to almost about 13 [vocalised-noise]. So, generally in case of rebar we maintained atmosphere. So, pH is maintained at around 12.5 to around close to 12 and 12.5. So, at that high pH the iron passivates within in that concrete system, rebar when the rebar is placed in a concrete medium.

So, if it passivates dissolution becomes very limited in when we have this 12.5, but 12.5 is not suitable for aluminium. Because, when we go for 12.5 we might get to the corrosion zone which is Al O 2 minus. So, these information definitely we can gather from Pourbaix diagram.

If I get to another important information for example, when we have a metal mixtures for example, let us say a particular system particular potential and pH level, we need to see that which metal would corrode and which metal would not corrode, that information can also be obtained let us see it one such example.

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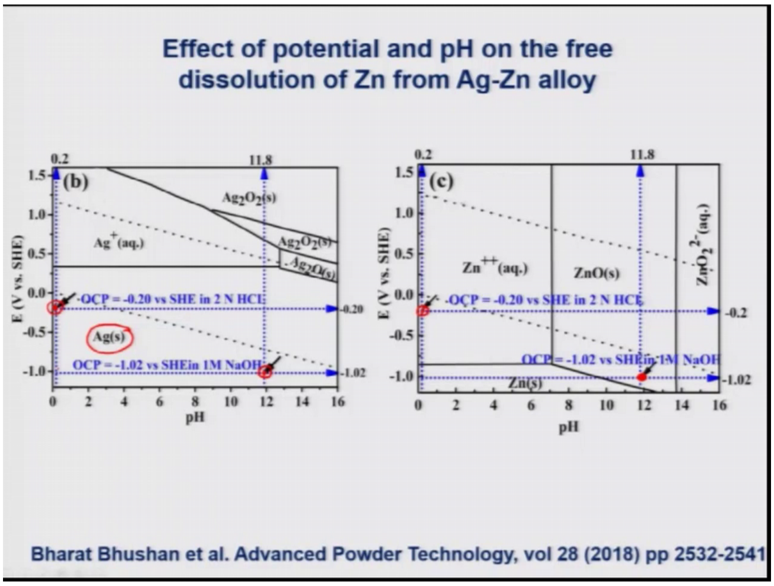

If I try to see this diagram so, this diagram is Pourbaix diagram for aluminium and this diagram is for silver and zinc system separately they are drawn. And if I try to see the 2 potential values and pH value this is one and this is this is one point and this is another point ok.

So, now, if I am here, that time silver is in immune zone because it is maintained in the Ags which is solid silver; that means, the potential and very low pH; that means, very acidic medium; that means, this is 2 normal HCL. So, the silver would not like to come out as a in the form of ions in the in the aqueous medium, which is of course, very acidic.

But, if I try to push the pH to 12 and the potential if we try to get it here there also I could see that silver is maintaining immunity. But, when I look at the silver zinc system when I am looking at the pH and potential of this particular section which is this one here in case of zinc system it is in the zinc plus plus which is corrosion zone.

So, if we maintain the pH and potential at this point silver would not corrode, but zinc would definitely corrode, but when I go to this point where silver is not corroding as well as it is maintaining immunity, but when I look at this point in case of zinc Pourbaix diagram it is in the zinc oxide region. So, if it is in zinc oxide region then it of course, it would like to passivate. So, these information we would definitely get if I try to carefully analyse our Pourbaix diagrams.

Now, these are some of the advantages what are the information what we get, but there are many things what we do not get from Pourbaix diagram. Now, what are the limitations?

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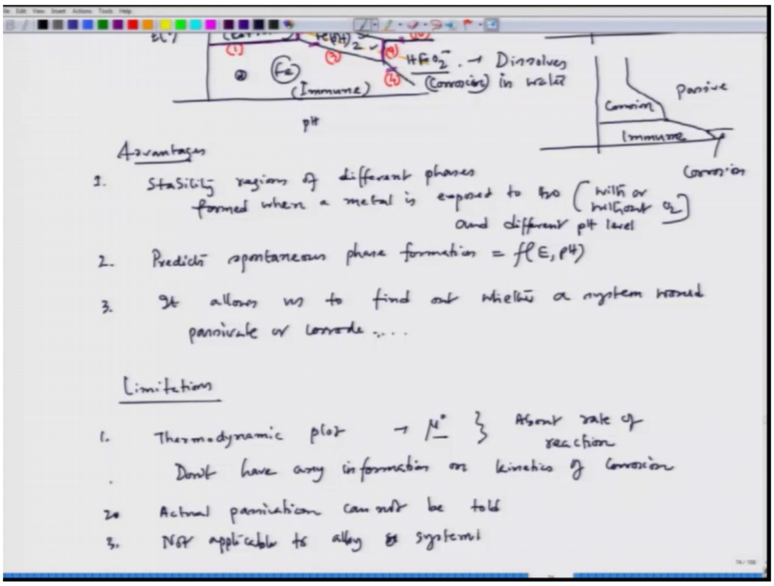

The if I try to see the limitation a first limitation is this is definitely a thermodynamic plot. So, you need to have only [vocalised-noise] chemical potential ok. So, whenever a thermodynamic plot is given it cannot give you any information about rate of reaction.

So, now, you will not be able to tell what could be the corrosion rate if I am in the corrosion zone. So, the corrosion zone can tell me yes, there will be corrosion, but we will not be able to tell what is the rate at which the corrosion is taking place and many a times the rate becomes crucial even if there is a spontaneity. So, we have spontaneity because it is in the corrosion zone, but the rate may be very slow. So, we might say that the corrosion is very low.

Now, 2nd part so, we do not have any information on kinetics of corrosion and 2nd part if I try to look at so, if I look at the passivity region. So, whenever we are looking at the passivity zone so, we are saying that we are assuming that particular phase would form on top of it. So, but it is not guaranteed why it is not guaranteed because, sometimes those phases may not form on the surface of the metal rather they might be very loose, they might contain lot of porosities and they would not give much of protection. So, that time it may not be the actual passivation though the Pourbaix diagram predicts that it is passivation.

So, actual passivation cannot be told [vocalised-noise]. 3rd point is for example, this is only for metal pure metal system; we are not looking at the alloy system. So, in case of alloy system predicting the phases and predicting what sort of regions we will choose would be difficult. So, this is not applicable to alloy system [vocalised-noise].

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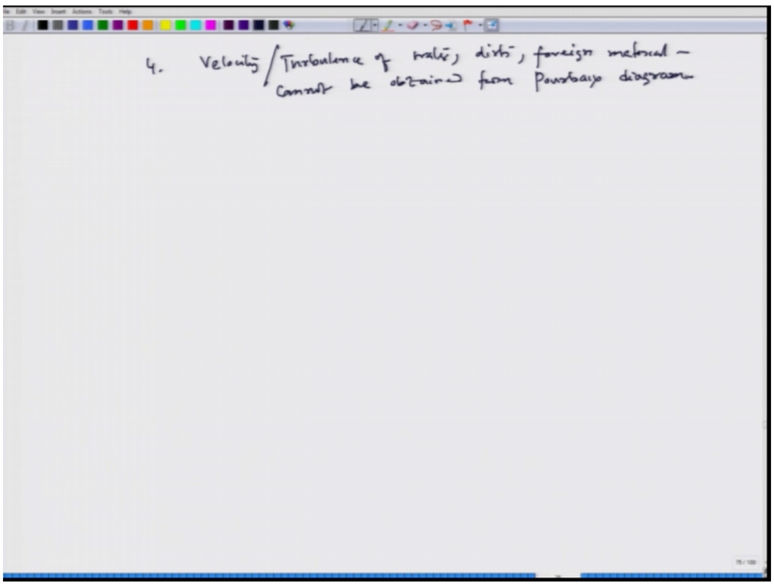

Now, 4rth, now another point what we can indicate is what is not possible from Pourbaix diagram is other conditions like; velocity of the velocity or the turbulence of the medium [vocalised-noise], velocity or turbulence of water. Then, if there are other things like dirts, foreign material those informations cannot be obtained from Pourbaix diagram. So; that means, it is very clear that though Pourbaix diagram gives lot of information about the possibilities, but it cannot give us any information about the actual happening.

So, in order to know the actual happening we need to understand the kinetics of corrosion. So, now, we end our Pourbaix diagram now we would shift to kinetics of corrosion from the next lecture onwards, let me stop here.

Thank you very much.