**Corrosion – Part I**
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Lecture - 41
Understanding of mixed potential theory through the case studies and events of corrosion-III

So, we have come to the concluding lecture of this particular course which is Corrosion I; today we have a lecture 41.

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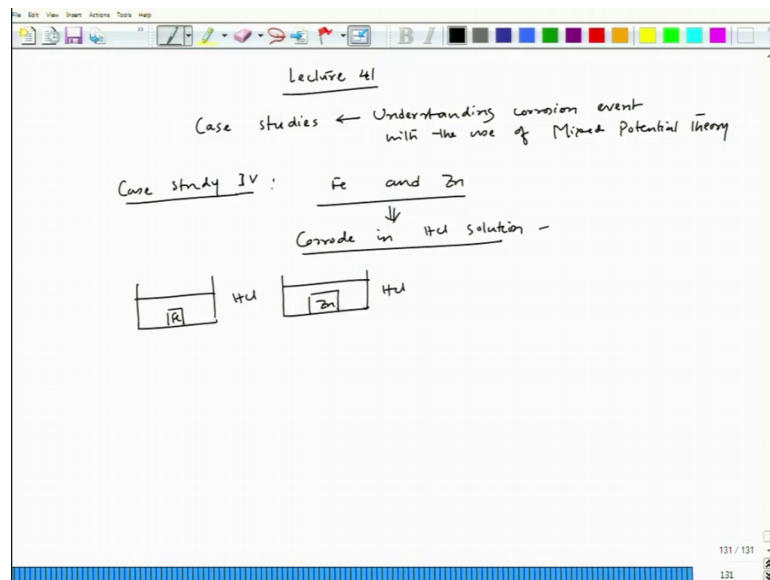
And till now what we have done in a last couple of lectures, we have try to understand corrosion events of metals from consideration of by the by considering mixed potential theory. And we have taken three examples, today we are have two three more examples and then we will conclude our session and the rest of this there will be more on this corrosion which will be covered in corrosion II later on.

Now, coming to this lecture 41, we will continue our discussion on case studies and understanding the corrosion event with the use of. So, what we have done before? We have one of the case studies that a noble metal is galvanically coupled to an active metal. And we saw that the because of the noble nature of that galvanic coupled material the corrosion rate of active component increases. And then if the area of the noble metal increases without increasing the area of the active component, the corrosion rate further

increases because of this enhancement in the cathodic area as compared to the anodic area.

So, now in this case studies, the case studies I case study I today's case study rather I would say a case study IV, here we will try to see the corrosion event when two active components are coupled. And when they are coupled one of the components will become cathode and another component will become anode and then the anodic component will corrode and the cathodic component after joining this two active metals, the cathodic part will get protected because of this enhance corrosion of the anodic part.

Now, let us say what I am pointing is, let us say iron and zinc they are both are both corrode in Hcl solution or rather they corrode heavily when they are not joined together. Now in case of separate situation for example, in one beaker you have Hcl where you have a Fe and other beaker you have Hcl and you have zinc rod zinc block. Both the metals will corrode as per the explanation given with reference to mix potential theory. If I try to draw Evans diagram for both the metals in Hcl, will have the nature of the plot will be like this.

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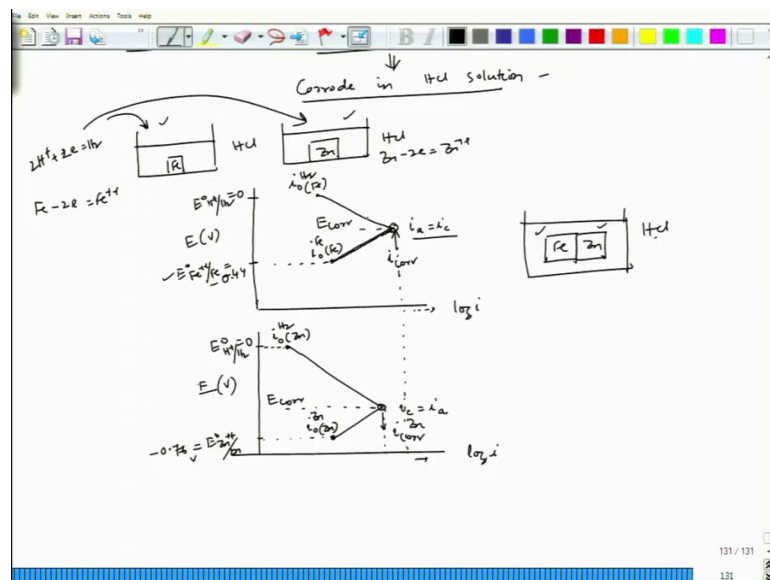
I am just drawing one after another and this is one below another. So, log i this is also log i this is E this is E volt, volt let say this is E 0, hydrogen equal to 0 and let say this is E 0 zinc plus plus zinc which is equal to 0.76 volt.

This is in case of zinc and let say this is for E_0 H plus H 2 equal to 0 in case of iron and here it is E_0 Fe plus plus Fe equal to minus minus 0.44 volt; i_0 of H simply I am writing H plus because H 2 simply writing H 2 because this is I do exchange current density of hydrogen reaction on zinc surface is a here. And then i_0 zinc on zinc surface at this point, now they will have their mix potential this is E corr and this is i corr of zinc and at this point i c equal to i a.

Similarly in case of iron generally the exchange current density of hydrogen evolution reaction is higher. So, this is i_0 of hydrogen reaction on iron surface and it is almost on the similar level this is i_0 iron on iron surface they will have their own mix potential when they are kept separately this case and this case. So, this is in case of this at this point this is the point up i corr this is E corr and here we have i c equal to i a or i equal to i c. So, at this point we have no net current, but the iron corrodes at a rate of i a which is equal to i corr.

Now, interestingly if you see generally if you are plotting it on the same marking or the same values I see that this corrosion rate of iron in Hcl is little more than the zinc, but zinc E_0 is lower than E_0 of iron now we have to joined them. So, now, this is iron, this is zinc, now we had putting it in Hcl for the same concentration, now what happens? That case you see in separately this is also active, this is also active and the cathodic reactions here is H 2 and similar reaction cathode reaction is happening here.

So, both the cathodic reactions are here and here the anodic reaction is and here it is zinc plus plus. But when they are connected galvanically, then what happens to this Evans diagram? That will tell us which one would corrode more and which one would corrode less. Now, if I combined them.
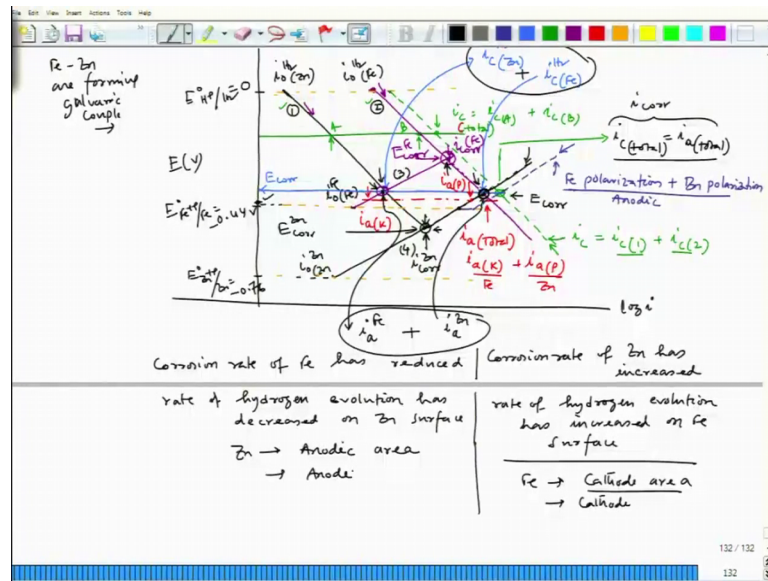
This is E 0 zinc minus 0.76 volt this is E volt let say this is E 0 plus plus Fe equal to my 0.44 which is minus volt and this where point is E 0 H plus H 2 equal to 0. Now this point lies here, this point lies here. So, now, if I i 0 H 2 on zinc this is i 0 zinc on zinc, I will shift this point little bit so that this is the point. Now, if this is my point for iron which is basically the E 0 point, let us say it is this is i 0 H 2 on iron surface, this is i 0 F e on F e surface. So, they met at this point so I put it in a different colour, this is the point which is i 0 for hydrogen reaction on iron surface.

Now I am just marking those potential points or the E 0 points, for individual half cells reaction. As we have known from mixed potential theory that during polarization whenever a reaction whether its a cathodic or anodic polarization experiences another reduction reaction or oxidation reaction, they should be clubbed or they should be joined or they should be added. In order to reach to the mixed potential where the net current density should be 0 or total cathodic current density is equal to the total anodic current density.

Now, this is one, this is hydrogen evolution reaction and polarization, cathodic polarization for hydrogen reaction on zinc surface and this is the second hydrogen evolution reaction on iron surface. So, these are two cathodic polarization lines and then at each potential we have to add up those two current densities corresponding to this two

polarization plots. And then we have to get a new polarization line so, this is let us say this colour I am putting blue green colour.

So, this becomes my line which corresponds to i c equal to i c 1 plus i c 2 so; that means, this is for this one and this is for this one at each potential. For example, if I consider this potential then this point indicates current density i c at this point and i c at this point. So, this i c is equal to let us say this is A this is B. So, i c A plus i c B that is what this line has been drawn; similarly when this polarization line is extending, once it reaches to this potential then again it is experiencing one more anodic reaction which is let us say this one I am putting as 3, so and this was 4.

So, 4 and 3 they are two anodic reactions and when this four is reaching to the polarized value of this potential, then it is experiencing iron oxidation reaction which is also polarizing. So, from there, if we continue this line then here we have to add that part also. So, if I add it again with a green colour or let us say blue colour so this is the added part, this line this black line is the polarization line for zinc and this blue line is the polarization line for iron polarization or anodic iron polarization plus zinc polarization and here both are anodic.

And at any point let us say if I consider this potential, at that potential let us say if I consider this potential and this value let us say i a k and this particular current density let us say i a P. So, here this is i a total and this one is i c total also, this one also i c total equal to i a i a k plus i a p this is for iron this is for zinc. So, now, now we could see that this line, this one and this one these two wherever they are meeting that point indicates the new mixed potential where i c total is equal to i a total. So, this is the point where they are meeting.

Now, at this point i c total equal to i a total when they are combined. So, this plot is basically when they are clubbed, they are joined iron and zinc are forming galvanic couple. So, at this particular point let us see what are the current densities of iron corrosion; iron current density for the anodic reaction of iron and the current density corresponding to anodic reaction for zinc that can be easily found out. Since this is my new E corr and this point is also i corr.

Now, if I draw a line, this becomes my E corr and then this point is basically i c for hydrogen evolution on iron surface and this point is equal to i c of hydrogen on zinc

surface. Similarly since this particular two points this particular point is, cutting this particular line and here it is cutting the black line corresponding to this line. So, that is what they are our two current densities for cathodic polarization and similarly this point is cuttings on the zinc anodic polarization lines. So, this is i a zinc and here also it is cutting the iron polarization line. So, this becomes i a of iron. So, now if we combine them so this combination of this and combination of this that would lead to the condition which is i c total equal to i a total.

Now interestingly in the beginning when they were not connected, they were separately immersed in H c l solution, we could see that the iron corrosion rate was this one. So, this point is E corr for iron and this point is also i corr for iron before joining. So now, after joining the corrosion rate of iron has gone to has reduced from this value to this value. So that means the corrosion rate of iron has reduced when they are joined together.

And what happens to the corrosion rate of zinc? The corrosion rate of zinc has actually increased when they are combined, the corrosion rate of zinc was at this point this is i corr zinc when they were uncoupled and this was the value E corr when they were uncoupled, but after coupling I could see that the corrosion rate of zinc has gone to. So, the corrosion rate and this value at this point the i a is much higher than the i a what used to be here before coupling. So, the corrosion rate of zinc has increased.

So, now interestingly one more information before coupling the corrosion rate that i c of hydrogen evolution reaction on zinc surface was at this point and after coupling I could see that hydrogen evolution reaction rate or i c on zinc surface has gone to this at this point. So, I could see that corrosion rate of the sorry, not corrosion rate the cathodic current density for the hydrogen evolution reaction has moved from this point to this point.

So, the rate of hydrogen evolution has gone down, has decrease rather on zinc surface whereas, if I could see the, what happens to the corrosion, what happens to the rate of hydrogen evolution on iron surface. The iron surface it is here the hydrogen evolution rate or i c on iron surface is at this point and before coupling hydrogen evolution rate or i c on iron surface was at this point. So, I could see that the rate of hydrogen evolution has increased on iron surface.

This is important observation; that means, the hydrogen evolution and hydrogen reaction on zinc surface has gone down or has decrease has decreased whereas; hydrogen evolution on the iron surface has increased. Or in other ways since hydrogen evolution is the cathodic reaction that is taking place on both the surfaces I could see that the hydrogen evolution of the cathode reaction is preferably taking place on iron surface rather than zinc surface. And from the zinc surface I could see that the corrosion rate of zinc has increased whereas, the corrosion rate of iron has decrease because of this coupling.

So, as we have understood before that if we have preferable cathodic reaction on a surface that surface becomes cathode and if we have preferably anodic reaction on some surface that surface becomes cathode. So, here iron turns out to be cathode area since preferably hydrogen evolution takes place on that an iron dissolution or iron dissolution or the anodic reaction for iron has decreased to a great extent.

Remember this is in log scale log i scale; that means, that that decreases quite a lot because it could be a of the order of 10 to the power 2 to 3 order scale so the cathode area. So, iron becomes cathode and since zinc surface rate of hydrogen evolution has decreased; that means the cathodic reaction is less on zinc surface so and zinc dissolution has increased on the zinc surface. So, this becomes i zinc becomes anodic area or it will act as anode.

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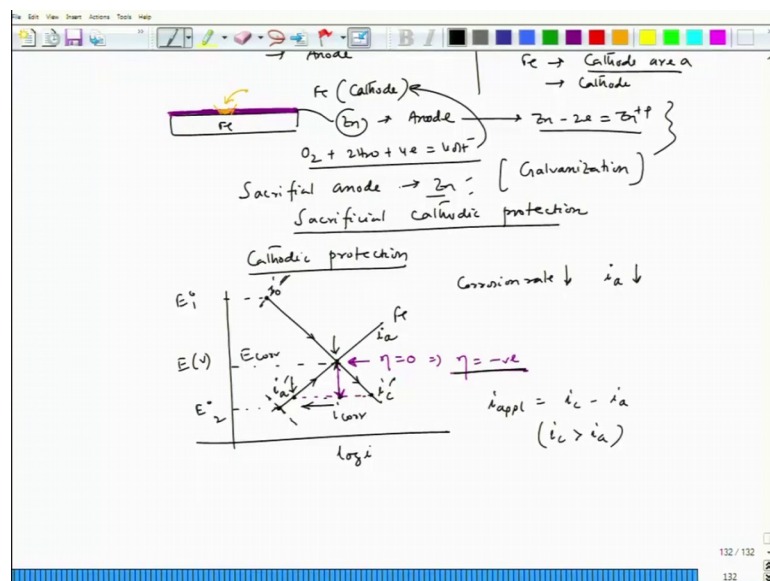
Exactly this similar situation happens when we have iron phase, this is iron and on top of it if I put a zinc layer zinc layer, this is the red colour is the zinc layer. So, until and unless zinc is covering iron surface we have one single reaction which is zinc dissolution. But the effect of zinc on the iron corrosion will take place whenever there is a opening. Let us say this is the opening part, now this opening region is basically iron this is iron and rest of this case is zinc.

Now zinc would act as anode and iron would act as cathode and in the environment this reaction would take place since the environment is nearly neutral and this reaction would take place on cathode since iron act as cathode and the anodic reaction would take place on zinc so where zinc.

So, zinc dissolves and iron is protected because of this mechanism and that mechanism can be easily understood from this diagram which is the Evans diagram for the combined situation. This particular method of protecting iron surface we call it sacrificial anode in the zinc becomes sacrificial anode and this is called sacrificial cathodic protection. So, as by using sacrificial anode we are creating that iron surfaces cathode and then it is basically that zinc is sacrificing itself in order to protect iron; we call this particular method as galvanization. Galvanization is nothing, but the putting zinc plating or zinc coating on iron surface, this since we have talked about sacrificial protection method. So, there are cathodic protection, we call it cathodic protection.

And this cathodic protection works on the basis of sending negative current to the cathode let us say if we have this E verses log i and if this is i 0 for cathodic reaction. Let us say this is the cathodic polarization this is anodic polarization, this is iron and this is the potential which is the new potential or new mix potential and this is the i corr and these are corresponding E 0 values of 1 and 2.

Now, how can I decrease decrease in corrosion rate if I need to decrease I need to decrease i a and this particular line is i a and this is i c. Now in order to do that if I go downwards, now this is my new starting point corresponding to over voltage is 0. Now as we go down; that means, if I put eta to be negative then I will go down, let us see if I reach to this potential I could see and let me draw the corresponding two other lines.

For this case it is cathodic polarization, this case it is anodic depolarization, but since this potentials are extreme. So, this new potential will arrive in between two potentials. So,

now, this particular point is let us say i c prime and this particular point is i a prime and I if I keep this potential at this potential with this over negative overvoltage or the cathodic overvoltage I could see that the corrosion rate, which was initially here before polarization I can reach to the new current density of that iron dissolution at this point ok.

So, it is decreasing corrosion rate of iron and interestingly during that I am sending this extra negative current and then i applied is nothing, but i c minus i a and here i c is greater than i a. So, that is the philosophy of cathodic protection and you can do it by using sacrificial anode by zinc or you can have it by sending negative current to the iron structure, which is to be protected cathodically from a DC power source, it is d c because we have to keep this iron surface to be cathode all the time now in case of this in case of sacrificial anode case.

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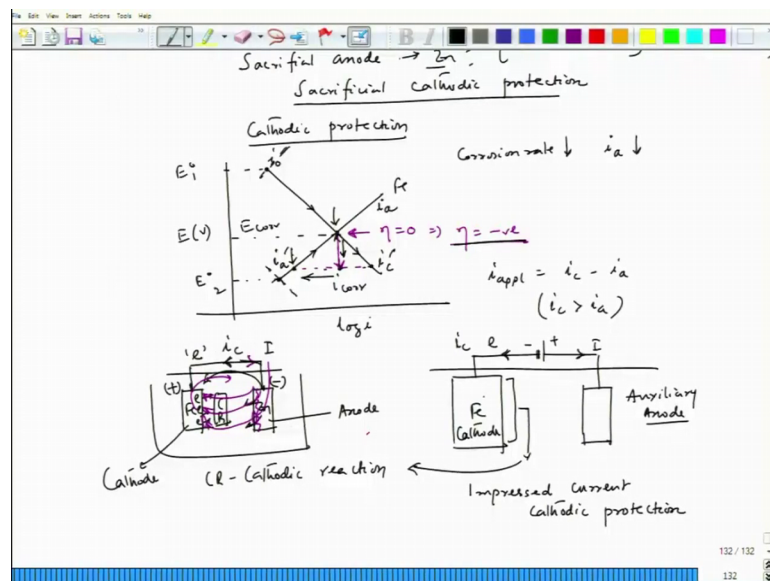
So, if we have this is a soil this is a soil below the soil we have iron piece and zinc piece they need to be connected, I can connect them I can connect them and then leave it like this. So, in that case in this becomes my electrolyte this becomes my anode this becomes my cathode as discussed before and the current i c will go from this to this, because if it becomes cathode in case of galvanic corrosion this becomes positive terminal this becomes negative terminal so the current which is i flows negative to the electron flow. So, i c is going this way it means electron is coming from this end to this end electron

flow and once electron comes here. So, these electrons will be consumed for cathodic reaction.

So, CR is cathodic reaction and the electron would be supplied by dissolution of zinc and the current this current will flow from this direction. So, it will flow through this to this and then coming back like this. So, whenever the current enters into electrolyte from a metal that zone is the corrosion from zone and whenever current enters into a metal object that part is protected. So, that is what this part is protected like that way current will flow like this all the time and then the entire surface of the metal is protected and by that time during that time zinc surface is actually corroding.

So, this is sacrificial anode. So, another situation I could have where I have an iron piece and this is a auxiliary anode, this is auxiliary anode which does not take part in any reaction rather the anodic reactions take place on this auxiliary anode. So, now, if I connected to external this is in below the soil and if I connect this end with a DC power source. So, and this is the negative terminal this is positive terminal. So, electron is going to iron and current is flowing to this auxiliary anode.

Now, since electron is coming here so; that means, I am sending preferably i c to the iron surface. So, if I send i c to the preferably i c to the iron surface; that means, I am going towards this; that means, I am going towards the anodic cathodic polarization on the iron surface. So, this becomes cathode. So, cathodic reaction happens on those surface and iron is protected.

So, this particular process is called impressed current cathodic protection. So, now, it would see there are two ways to protect the method one by using sacrificial anode and other by using auxiliary anode by using a DC power source, and why DC power source? All the time with this iron should be maintained as cathode. So, that is what it is DC power source.

In case of AC power source this terminal polarization changes. So, one time it becomes negative another time it becomes positive. So, that time iron also become vulnerable to dissolution. Now finally, I would just explain one more example and then will rapid off for this particular session.
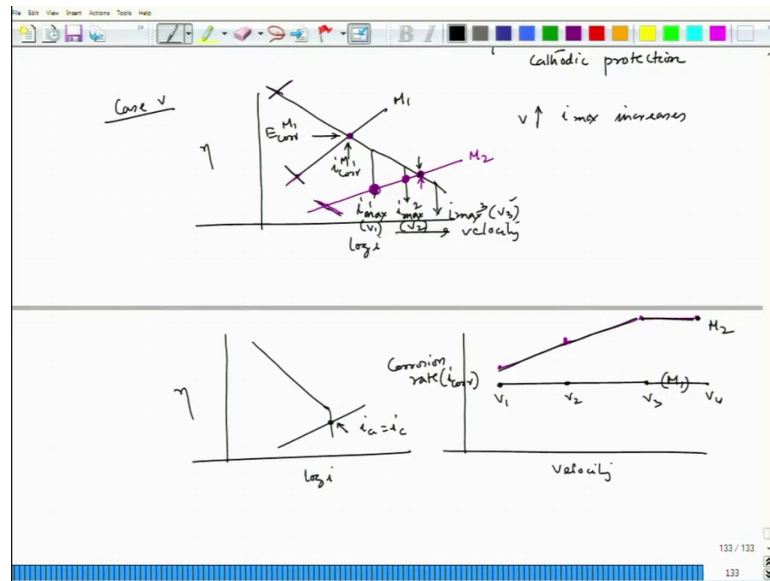
Now as we have informed that this is case 5 let us say, previously we could see that if we have concentration polarization let us say. So, these are basically i max value i max 1, i max 2, i max 3 and we have seen that with increase in velocity. So, this is if I increase velocity, I could see that the i max increases, velocity increases i max increases. Now, if we have two metals in one metal we have the polarization behavior is like this another case the polarization behavior is like this. So; that means, in two cases I would have different corrosion rate situation corrosion rate variation with velocity.

Now, we could see in this case of metal 1, this is this is metal 1 and this is metal 2 and this is the polarization this is the corrosion potential and corrosion rate for metal 1. So, this is i corr M 1 and this is E corr metal 1 and whereas, in case of metal 2 I am just drawing the other lines, cathodic as well as anodic polarization line. In this case I could see when the velocity is this much V 1 let us say corresponding to V 1, this is V 2 this is V 3 when it is V 1 I could see that it is cutting at this point.

Since that time this is the point where i a equal to i c; now if we increase the velocity the new mixed potential is at this point where again i a equal to i c. Now, if you increase velocity further at this particular V 3, but I could see that it is not cutting in that concentration polarization region, I am cutting the potential this cathodic potential cathodic polarization line at this point where again i c equal to i a and i a is nothing, but the corrosion rate.

So, if I plot in case of two metal this is corrosion rate, let us say I plot corrosion rate in case of metal 1 whether its V 1, V 2 or V 3 does not matter because its cutting all the time on the activation polarization part of that cathodic polarization line. So, its corrosion rate with velocity will be constant one, whether it is a V 1, V 2 or V 3 now let say this is V 1 this is V 2 and this is V 3 that all the time it is the same point same corrosion rate or i corr.

Now in case of metal 2 this is metal 1; in case metal 2 situation is little different now when the velocity was V 1 the corrosion rate was at this point when the velocity is V 2 the corrosion rate was at this point. And when the velocity has become V 3 the corrosion rate has gone to this point and beyond that if I increase velocity further it will all the time cut the cathodic polarization line at this particular point. So, it will become constant. So, now, in V 1 the corrosion rate is the lowest.

And then or as per this diagram I could say that the corrosion rate is at this point now V 2 to the corrosion rate has increased and then V 3 still increased and then if we increase the velocity it will be constant. So, now, the corrosion rate plot is like this, now in this case even if you go for V 4. So, it was like this. So, this is V 1, V 2, V 3, V 4, but in case of M 2 the corrosion rate variation is like this since, they are cutting at different points depending on the velocity increment as well as change in i max.

So, this is another behavior that can be explained with the help of mixed potential theory finally, we have come to the end and as we have seen that we could understand corrosion or the fundamentals of corrosion has got two parts, one is definitely probe diagram another one is the kinetics part one is thermodynamic another kinematics.

And in case of thermodynamics we could see that we could select a areas in the potential pH access where we could get passivity and where we could [get corrosion or immune zone. We have given some examples for example in case of iron and aluminium, if we have a pH of around 9 in case of aluminium it dissolves even if aluminium is considered to be highly passivating metal.

But in case of iron if we go beyond around 13 pH again there could be a possibility of dissolution that is what in case of concrete the rebar the pH is maintain around 12.5 to 13 around that level. So, that is what the iron always remains in passivated condition, but if

we have aluminium there and if we increase that pH to 13 then aluminium definitely would corrode.

So, that was one part, another part is this mixed potential theory as well as its associated complications as well as the not complication I would say. The associated equations and then finally, how we could analyze some of the corrosion event from the basis of Evans diagram those are defected in this particular corrosion one.

So, that is it for corrosion I part and in corrosion II which will be taken up in future near future I would say where we will take a passivation, you know the passivation happens when we go for anodic polarization or either high anodic polarization. And we will try to understand corrosion events on the basis of passivation and mixed potential theory, we will also consider some of the practical events of corrosion like cavitation damage of (Refer Time: 47:00), then we would also consider a high temperature corrosion mainly oxidation part; so that is it.

Thank you.