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Lecture – 06 Can we calculate the corrosion rate of metals: Mixed potential theory and passivity?

Welcome to the lecture 6. In the previous class, we discussed the application of electro chemical kinetic concepts to corrosion. The basis for application of the electro chemical concepts to corrosion is the Mixed Potential Theory right.

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Mixed Patential is the basis electrochemical concepts CDEEP IIT Bom MM 713 L 6 / Slide 1 EQA Diagram Fuans

The mixed potential theory is the basis for application of a electro chemical concepts corrosion and the mixed potential theory talks about freely corroding material; freely corroding say I call it as a metal.

When I say freely corroding, no external current, no external potential is applied on the metal. You just immerse it and let it corrode and, in that condition,, whatever corrosion rate that occurs given by corrosion current density and the corresponding corrosion potential they are all dictated by the mixed potential theory. So, in the freely corroding material essentially what happens $i_{ox} = i_{red}$

When I say i_{ox} means there can be more than one reaction of oxidation, there can be more than one reactions of reduction process. So, the total oxidation is equal to total reduction rate. So, that is the mixed potential theory.

We discussed this yesterday using you know a metal with an oxidiser wherein we said that, if you talk about a metal go back to your notes and see that, log(i) we have two independent equilibria in a corrosion system right. So, you represent two independent equilibria in the system for a metal, you have an equilibrium potential and you also have what you call this exchange.

Student: Current.

Current density right, we have this and the other equilibrium that we talk about let us say something like maybe hydrogen evolution reaction whatever you can talk about. Now you have $i_{0H+/H}$ on the metal that we are talking about is happening and this is what? This is E, E equilibrium potential of H⁺/ H, this is say what? E equilibrium potential of what? It is M^{n+}/M .

So, we said that they independently polarize following its own Tafel kinetics. This is a Tafel kinetics for oxidation, the Tafel kinetics for the reduction process let us say

 $M \longrightarrow M^{n+} + ne^{-}$ and in this case, you can say $M \longrightarrow M^{n+} + ne^{-}$

Similarly, you can write for the hydrogen as H + sorry, this is

 $H_2 \longrightarrow 2H^+ + 2e^-$ oxidation and you have reduction process corresponds to

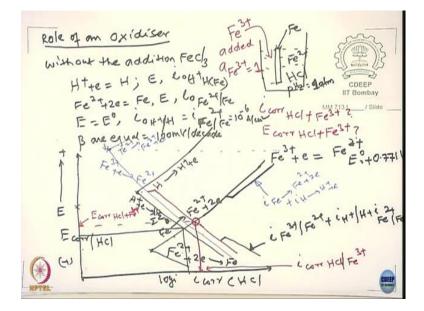
 $H^+ + e^- \longrightarrow 1/2H_2$ and you find at only one place that is, the rate of oxidation is equal to rate of reduction and corresponding to that potential, we call them as E_{corr} .

So, we are talking about the application of the electro chemical parameters such as i_0 , E equilibrium potentials, the Tafel slopes that we have here ok. How they will they govern the E_{corr} and the i_{corr} values? In the last class, we also saw two examples of iron and zinc and we said that in acid solution, zinc will corrode at a lower rate compared to iron right the reason was what was the reason for that?

Student: (Refer Time: 06:30).

The exchange current density is different ok. The exchange current density in this case differs very significantly and so despite zinc having relatively negative equilibrium potential, it will show a lower corrosion rate compared to iron the reason was the exchange current density we saw in the last class, I hope you have seen the notes. Let us move further in understanding the corrosion of metals.

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Now, we look at the role of an oxidiser. Let me give you the picture. I take a beaker and I take let us say hydrochloric acid take that and I immerse an iron piece. Now assuming that they are in the standard state ok, iron is in equilibrium with let us say Fe^{2+} of unit activity and the hydrogen gas here is 1 is equal to 1 atmosphere ok. It is possible for you to calculate the corrosion rate right.

If you are given exchange current density, Tafel slopes you can compute the equilibrium potential all you can do that right can you graphically as well as solving equation can you find out i_{corr} value in this? Can you or can you not?

Student: Yes.

Is it possible or not?

Student: Yes.

Yeah.

I want a clear you know response. I just take iron piece and put it in hydrochloric acid and I say that activity of Fe^{2+} here is unit activity and I also say that the hydrochloric acid is of unit activity, the $P_{H2} = 1$ atm and I will give you exchange current density values, I give you Tafel slope. Is it possible for you to determine the E_{corr} and i_{corr} ? Is it possible or not?

Student: Yes sir.

Yes. Now what I am going to do is, at to this I am going to add to this; to this I am going to add Fe³⁺ added to this and the Fe³⁺ concentration, $a_{Fe3+} = 1$.

Now, I need to know what happens to the corrosion rate of iron and I like to calculate what is the corresponding corrosion potentials right. So, we need to calculate

 $i_{corr(HCl+Fe3+)}$. I need to calculate $E_{(corr HCl+Fe3+)}$ additions here. Is it possible to calculate or can you able to visualize how to get this based on what is called as the mixed potential theory right?

Student: Hm.

Now how to proceed, what to proceed here, how to proceed here? First of all, we need to identify the equilibrium first how many equilibria are present in this system right? So, without let us say without the addition of say ferric iron means I had ferries ferric chloride, without the addition of FeCl₂ what is the equilibrium we will have start with? One will be $H^+ +e^- \longrightarrow H$ what will be the other equilibria?

Student: Fe.

 $Fe^{2+} + 2e^{-} \longrightarrow Fe$. Now for this, I can calculate E, I can calculate E if I know the activity of the irons. I can also know maybe experimentally otherwise the $i_{0Fe^{2+/Fe}}$ and here i_{0H+H} on iron right. So, now, I can able to first of all determine the corrosion rate of iron in hydrochloric acid can I do this graphically with Evan's diagram?

Student: Yes.

So, how to do that? Can you please try yourself first? Give the Tafel slopes right, you just draw the Evan's diagram so that, you can obtain E_{corr} and i_{corr} right. You assume make a standard state, the standard state here you can assume E equals to E 0.

You can also assume $i_{0H+H} = i_{0Fe2+/Fe} = 10^{-6} \text{ A/Cm}^2$ and you can also assume that β are equal for assumption is equal to you can assume let us say about 100 millivolts per decade. You can compute right? Can you draw it yourself and get E_{corr} and i_{corr} values?

I suppose you have drawn a similar diagram like this ok. So, what is the additional equilibria now I have? Suppose I add to this ferric irons, I would have another equilibria $Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$ right.

Would I have this or not? When I add $FeCl_2$ to this solution, I already have Fe^{2+} ions it can establish one more equilibrium which is $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ right. I have given you a handout, if you take the handout there and see what the corresponding standard potential for this is.

Student: 0.7.

It is E_0 for this is equal to?

Student: 0.7.

+0.7?

7?

Student: 0.71.

 E_0 =+0.71 volt right. So, what I do? I represent the same equilibrium I mean in the same diagram, I represent this equilibrium in this diagram. So, represent the diagram equilibrium there can you put this in here so, the value comes somewhere here, I can of course, I can have a diagram going like this. What is this? This one corresponds to? What will be this line correspond to? What reaction?

Student: Reduction.

Reduction right this will be $Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$ correct and what will be this one?

 Fe^{2+} \longrightarrow $Fe + e^{-}$ here and this corresponds to your exchange current density anyhow.

Now there are 3 equilibria in the system; 1, 2 and 3 having different equilibrium potentials and maybe different exchange current densities you can also use the different

Tafel slopes you want, it is not necessarily the same slope is easier to operate here so, I have assumed the Tafel slopes are going to be same, it's not necessary at all.

Now what does the mixed potential theory say. It says total amount of oxidation is equal to total amount of?

Student: Reduction.

Reduction now. So, what I do now? I need to find out what are the corresponding oxidation reactions and the reduction reactions now. Let us take this, let us take the. Now let us take let us start from here, at any given potential this is the reduction reaction reduction. When you cross this potential, please notice let us say you are going somewhere here suppose you are coming to this particular potentials, the total amount of cathodic reaction is given by the summation of this current and this current.

If I take this metal and hold this metal at this particular potential, what are the reaction will occur reduction of hydrogen gas I mean hydrogen ions into gas and reduction of Fe^{3+} into Fe^{2+} both will happen on this metal surface when you start moving below this potentials. So, the total current will be is equal to sum of this current right and when you cross; when you cross this; when you cross these potentials how many reduction reactions will occur?

Student: (Refer Time: 21:13).

Below this potential how many reduction reactions will occur?

Student: 3 time.

3 right. So, you have one more current adding to this, this understood. So, this corresponds to what? This corresponds to i of what? $i_{Fe3+/Fe2+} + i_{H+/H2+} + i_{Fe2+/Fe}$.

Student: Here all the three-reaction taken part simultaneously with the same diving force. Since Fe^{3+}/Fe^{2+} have high potential and are also noble the H^+/H_2 what will happen in every cases?

So, we are coming to that we are coming to that we are coming to what will happen to Fe^{3+} , Fe^{2+} , hydrogen gas evolution that is what we are going to arriving at actually. So, this is the one step towards learning what would happen ultimately you got it? We are

reaching that point, but we are trying to go step by step to show how that point is reached. So, that you have clarity in terms of the electrochemical kinetics ok. I hope this question is clear and I hope.

Student: Hm.

You are clear as to what we are doing. We are simply trying to relate the current versus potential if you have multiple reactions actually right. So, please notice every case, the equilibrium will behave its own manner.

This one this is not going to change; this is not going to change, nor this is going to change. But what will happen is the total amount of reaction that are occurring are going to be changing depending upon the potentials you got it or not ok? So, you find that the number of reaction that will happen will increase it becomes 2 here, it becomes 3 here.

Similarly, you can also consider what will happen to the anodic reaction right. Let us look at the anodic reaction, this you can extrapolate this, you can extrapolate this. Where will the anodic reaction start be increasing? It starts increasing on this point got it. So, you will find the anodic reaction for this is going to be this.

So, what is this one corresponds to? This corresponds to both i $_{Fe/Fe2+}$ + i $_{H/H+}$. Am I right? Correct or not correct?

If I go to this potential, if I cross somewhere here suppose I draw a line here and beyond this point what happens? You have one more what reaction

Student: Oxidation.

Oxidation reaction will take place. So, this is very simple way of putting things here. Now look at this diagram, only one place the mixed potential theory is valid tell me where it is? All other places the mixed potential theory is not valid. For the mixed potential theory to be valid, the rate of oxidation is equal to?

Student: Rate of reduction.

Reaction, I mean total oxidation rate is equal to total reduction rate. So, tell me where in this diagram the mixed potential theory is applied.

Student: (Refer Time: 26:08).

Can you tell me that you have red colour and you have blue colour and you have black colour?

Student: Red colour.

Red colour intersecting with the?

Student: Black line.

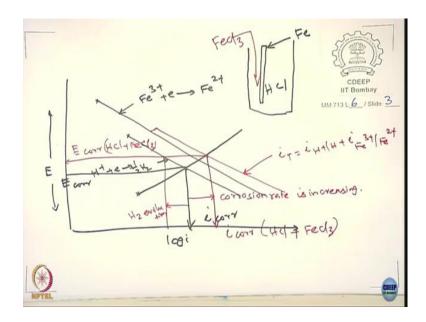
Black line here ok. So, only here you find the mixed potential theory is valid here only. In all other places, if you just; if you just hold you know at any given suppose you take this potential here right what happens? The rate of oxidation is more than the rate of reduction all will happen here, only here the rate of oxidation is equal to rate of reduction.

So, that is going to be your changed what? Changed i_{corr} values. So, this is going to be your $i_{corrHCl+Fe3+}$ and $E_{corr HCl + Fe3+}$ I hope you are not simply taking down the notes, I hope you are following whatever I am discussing here.

We are simply applying the mixed potential theory right. An any given potential, you find out you take any potential you want right maybe you take this particular potential you find out what are the reactions are occurring there is only one reaction occurring here. So, there is only one current no anodic kinetic is consumes only one current, but you have how many you have? Two cathodic currents here so, sum it up.

So, you just have to find out at any given potential, how many reactions are occurring and add up that current that gives you total current, total anodic current and total cathodic current or the total oxidation current and total reduction current right. Are you clear about this? Can I move? So, I am going to read out this for your clarity so that, we can understand this diagram a bit better.

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Let me draw only the relevant portion of the Evan's diagram ok. This corresponds to hydrogen ok. Drawn this diagram, this is your i_{corr} in the absence of ferric chloride so, E_{corr} ok. Let me now tell you what happens. Let us visualize this diagram again we have a beaker, hydrochloric acid and you have put the steel here put an ion for simplicity ok.

If I measure the E_{corr} of this, that corresponds to this one, am I right? If you can know the i_{corr} of that, that should correspond to this agree? Now, the rate of hydrogen evolution on the surface please notice the rate of hydrogen evolution of the surface is given by this point corresponding to this current, the hydrogen evolution occurs. The same point also corresponds to the i_{corr} I mean high dissolution of the metal right.

If FeCl₂ is added, if I add FeCl₂ to this so, what do you observe on the metal surface will there be increase in hydrogen evolution, decrease in hydrogen evolution, increase in the corrosion current or decrease in the corrosion current, increase in the E_{corr} or decrease in the E_{corr} . Please note down, I would like to know the following what happens to the hydrogen evolution rate on the metal surface? What happens to the E_{corr} ? What happens to i_{corr} ?

Now, let us go to the question number 1 what will happen to hydrogen evolution on the metal surface? Can you look at the diagram and tell?

Student: Yes sir.

Please look at the diagram, you know what is the corresponding E_{corr} right what is the corresponding E_{corr} for that? If the E_{corr} remain the same when I add FeCl₂ solution to what will happen to E_{corr} ?

Student: Potential (Refer Time: 34:03).

So, potential move up.

So, then what happens? Then what will happen to hydrogen evolution? Please see there.

Student: Decreases.

No, you please look at the diagram.

Student: It increases.

Student: It decreases.

It decreases right.

Student: Decrease.

At this particular potential, the hydrogen evolution on the metal surface is decreases, it is decreases from where? It deceases from the hydrogen evolution rate is decreasing what happens to the corrosion rate is it decreasing? No, it is increasing right.

Student: Increasing.

The corrosion rate is increasing ok. So, please follow the diagram you if you follow the diagram, you will not go wrong. Why does it decrease? It decreases because the over voltage for hydrogen evolution reaction what is the over voltage for hydrogen evolution reaction in this case can you how do you find out? Without FeCl₂, this is my E_{corr} right?

Student: Yes.

Can I find out the over voltage for hydrogen evolution? What is the

over voltage= E_{corr} - E_0 ?

Student: (Refer Time: 35:52).

Student: Ecorr -E₀

E equilibrium right. Now when you applied, when you add FeCl₂ what is happening to more voltage? It is?

Student: Decreases.

Decreasing.

Student: Decreasing.

So, the hydrogen evolution reaction rate has to be decreasing, it should be consistent. Then, I increased the corrosion rate of iron, hydrogen evolution is decreasing how is possible?

Student: Oxidizing.

Because the ferric ions are getting reduced to ferrous ions. The electrons are now taken by the other species to look at it actually here. Of course, law of consideration of charges have to be there, it cannot happen you go on increase your corrosion rate and there is no corresponding cathodic reaction, it will not happen.

It only says, the hydrogen evolution rate is decreasing, but the Fe^{3+} to Fe^{2+} is increasing it is going to increase from here to this, the over voltage for that is increasing from here to this is happening around right. So, that is the important thing you should understand in the electro chemical concepts ok.

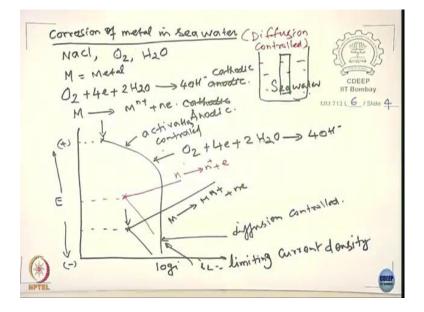
Any questions here? Is it looking confusion ok? So, this is a an important and the most one of the most difficult Evan's diagrams that you can think of ok. You will see one more complex Evan's diagram later, but this is one of the most complex Evan's diagrams. It is very simple, what have you done here? When I said corrosion, I identified what are the possible equilibria all right you started from there.

So, identify the equilibria right, you identify the equilibria first of all. If you identify the equilibria, then you should have an electro chemical parameters for that equilibrium potentials, exchange current density, Tafel slopes all that required. Use that parameters to draw Evan's diagram.

If there are more than one oxidation or more than one reduction equilibria possible represent them in the Evan's diagram, follow the mixed potential theory what does that mean? You can also find out any given potential what is the total amount of oxidation and what is the total amount of reduction right.

You construct Evan's diagram for that and then at one point, you will see that the mixed potential theory is valid wherein the rate of total oxidation is equal to the rate of total reduction. So, that is the place the metal will corrode and that is a corrosion rate that will be the corrosion potentials. So, it is a very simple concept. It is only thing is you need to go systematically to get this particular you know the E_{corr} value and i_{corr} values. Let me go further into the system.

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Let me take another example of corrosion of metal say in seawater. It is an example; it is only an example here. What does the sea water consist of?

Student: Salt.

Salt solution NaCl solution. What is the cathodic reaction here predominant cathodic reaction? It has got what oxygen; it has got water. Suppose I take a metal say I am having M, M metal immersed. So, the picture is that I have a seawater and I am immersing a metal in this. Why did i take seawater? What is the cathodic reaction here in

this case? What is the likely cathodic reaction in this case? Anybody recollects. The cathodic reaction here is $O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$

Student: (Refer Time: 40:53).

What is the anodic reaction you can say? $M \longrightarrow M^{n+} + ne^{-}$. This is your cathodic, your anodic reaction right. I am sorry this is the cathodic and this is anodic reaction. Why did I give this system because we remember that we talked about oxygen reduction reaction is diffusion controlled right? So, when is diffusion control, we will see how the corrosion rate changes or what are the factors that control the corrosion rate of metal when the system is under diffusion controlled ok?

Before I go into that, it is very interesting to see we talked about sodium chloride here. Sodium chloride does not figure out anywhere here. Can sodium chloride directly take part in corrosion process in oxidation reduction? Can it take place? It cannot take place; chloride cannot take an electron.

Sodium ions are you know they are so electro negative it cannot happen. So, NaCl directly does not take part in the corrosion process, we will see later how the NaCl (Refer Time: 42:58) corrosion you wait for some time, it is indirectly affecting the corrosion process.

No electro chemical reactions are possible with sodium chloride dissolved in water. Neither it can take electron, nor it can accept the electron because of the electro chemical potential, this particular equilibrium will have. Let us come to this. Now where is a diffusion-controlled process

ok, how I represent this? I have two equilibrium: one for oxygen other for the metal ok. For a metal, it is oxygen that I had here, this is activation controlled here and what is this?

This is diffusion controlled. And you can also know what the equilibrium potential is, it is in current density, equilibrium potential for that, exchange current density for this all you can represent in the Evan's diagram. What does i_{corr} depend on? What is this current called by the way what is this current called?

Student: iL.

 i_L right, this is called as i_L is called as limiting.

Student: Current.

Limiting Current density. So, i_{corr} depends on what? Depends upon diffusion current density or limiting current density i_L . For arguments sake, if I change a metal another metal n let us say with this is let us say n \longrightarrow n⁺ + e⁻ ok.

So, what happens? This is the other metal so what happens here? It has got a different equilibrium potential, it may have a different exchange current density, what happens to corrosion rate? What do you see? So, limiting current so, the corrosion rate does not change as long as the corrosion is controlled by?

Student: Diffusion.

You know diffusion process. There is a cathodic reaction here. So, you may have a relatively noble metal relatively active metal for example, I take stainless steel, a technical carbon steel may all corrode at the same rate if it is a diffusion-controlled corrosion process. Can you make this statement? Is it correct? Not correct. I want response is it correct or not correct? You have any convection or not?

Student: No sir.

No. What will happen now? You please tell me in this case, if I change the equilibrium potential of the metal or exchange current density may change, will the corrosion rate of the metal change or not?

Student: No.

It would not change ok. So, it would not change. You do not see that things are happening at all ok. So, this is what is important, and this is we call them as diffusion-controlled process.

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Passivity Michael Faraday (1840) Reactivity J. falk, under certain **IIT Bombay** cir cumstom ces MM 713 L 6 / Slide Test Test-3 HNOZ C. HNOZ HNOZ , olutio Corresion. from test-1 bservable bservable rosion crotch

We have seen so far, the metals which are actively corroding. There are some metals there is so passivity ok. So, you should understand the concept of passivity and it was Michael Faraday. I suppose all of you will know him right.

He did it in 1840. He did some nice experiments to show that, the metals undergo passivity all of us know about that I think, you know I do not think that any of you guys who are not aware of passivity you know stainless steel and the carbon steel the difference is in the corrosion rate and that corrosion rate is achieved because of stainless steels showing passivity.

So, let us try to understand systematically what is mean by passivity. Passivity means the reactivity comes down, reactivity falls that means, the corrosion rate of the metal drops under certain circumstances, under certain circumstances. So, that we should know how what kind of circumstances we are talking about. He did it some nice experiments Michael Faraday.

You people know that nitric acid right it is a very highly oxidising acid what he did was, he took a beaker and he fill that with concentrated HNO₃ and he dropped a steel piece. It is not highly oxidising solution it should corrode very heavily ok, observed no corrosion.

No, I may say no corrosion, I may say no observable corrosion ok; no observable corrosion right you can see that surface looks reasonably you know un corroded

somewhat shiny you can say. Then, he did another experiment he took in this case dilute nitric acid, steel you found lot of hydrogen gas coming process so there is hydrogen evolution. So, you see corrosion process, corrosion is visible.

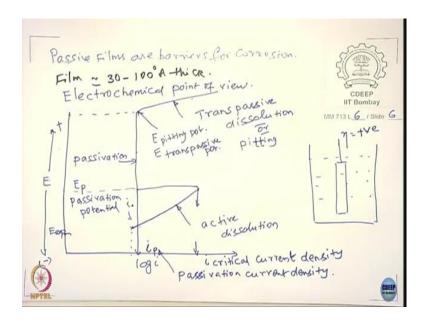
Then, he is wondering what is happening and all. He made a scratch here, he took a glass rod, he made a scratch here like that ok, then he found corrosion occurred, but again stopped; again stopped.

Then, he did another experiment, wherein you have beaker, dilute nitric acid, he put a steel here steel; steel from test 1. This is test 1, test 2 and test 3 and he transferred this one ok; that means, he transferred sample here found no corrosion, no observable corrosion, then he made a scratch corrosion occurred.

So, when there is a scratch here, he had a scratch here the corrosion start occurring lot of hydrogen starts evolving from that. When he made a scratch here, it did not happen corrosion occurred, but again stopped. In this case, it is happening, in this case it is continues to happen from the beginning. So, he concluded that, film forms in test 1 he called as passive film.

So, that was an experiment and he showed that steel will corrode less in concentrated nitric acid, it will corrode more the dilute nitric acid there is in unusual right. When increase the oxidized concentration, the corrosion rate should increase only, but does not happen. So, you called this as a passivity.

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Now passivity is the big subject and I will just give a brief account of that. You form a film, passive films or barriers, barriers for what barriers for corrosion. They form an electrical barrier for corrosion right it is happening and this film, say about 30 to 100 angstroms thick. You know what angstrom is it is 10^{-10} m

Student: Meter sir.

Meter.

Student: Yes sir.

A sorry 10^{10} angstrom = 1 meter. Now what does this passivity really means, what does it mean from electro chemical point of view. What happens?

Now, I consider a metal in a solution and I apply this potential, I apply η = negative sorry positive. If I apply a positive η , what is eta? It is a?

Student: Over voltage.

Over voltage. Now I follow the current and you will see so, I start with an equilibrium potential and I have a corresponding exchange, current density right, this is the equilibrium potential for the until here. When I apply a over voltage, it is positive what will happen to current? Current is supposed to increase like that, and this behaviour is called what? What relation does it follow here?

Student: Tafel.

Tafel relations right it is a Tafel behaviour it increases. At some time, the current drops then again it goes like that, again goes like this. See there is an active dissolution, the dissolution rate decreases and what happens here? Here it is a passivation call it and again what happens here? Here again dissolution this is called as trans passive dissolution or we will see later, it is also called as pitting.

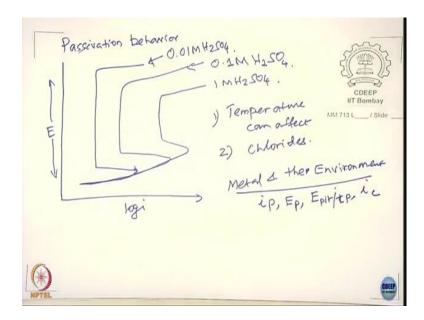
The metal undergoes active, passive, trans passive transition right as a transition, active, passive, trans passive transitions this is how the current is moving. This is a schematic of a metal exhibiting passivity. As you raise the potential, you see the driving force of a corrosion increases, but then again decreases and again increases and this metal is supposed to be showing active, passive, trans passive transitions. They are all very important for us.

Most of the engineering metals, you want to make them corrosion assistance one way to do is to make them passive or you want to reduce the corrosion rate, you have to go for a noble metal. Noble metal is not possible you cannot use copper, you cannot use silver, you cannot use gold, but if the metal can show passivity then they are very good such metals are what like stainless steels are alloy, titanium, chromium, some of these metals and alloys are very much useful because they exhibit passivity.

Now for us, from this diagram, we need to know how from this diagram we understand the corrosion of the passive metals. Before you go this, I would like to you know tell you what these parameters are really mean. This is the maximum current metal reaches right when you polarize anodically and this current density is called as i_c : critical current density.

The maximum current beyond which the metal starts passivating and this current density is called as i_p : passivation current density and this potential above which the metal starts passivating and this potential is called as passivation potentials. We can use E_p as passivation potential and this potential what you see here, where the current steeply increases this potential corresponding to this is called as pitting potential and also called as E_{tp} :trans passive potentials ok.

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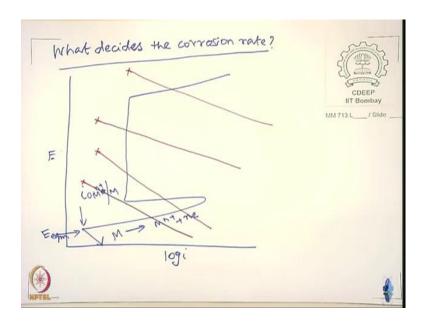


Now let us look at the behaviour of this active, passive, trans passive transition how it changes. It would change depending upon the metal, depending upon the environment right. So, passivation behaviour. Suppose I take a metal that exhibits passivation let us say I am getting this passivation in sulphuric acid ok. The concentration of sulphuric acid here is let us say 0.01 molar sulphuric acid.

If I increase the concentration, if I increase it further, so, if I can change the concentration of the environment, the passivation characteristic change. You know what are the characteristics? The critical current density, passivation current density, the trans passive potentials things will change. This could change other like even temperatures. You can also have let us say chlorides, suppose I have chlorides could change.

The passivation characteristics depend upon what? Depend upon the metal and the environment. They decide what? They decide i_p , E_p and E_{pit} are also called as E_{tp} trans passive potentials and you can also change your current density. So, the metal and the environment can influence these parameters they are not unique you know kinetic parameters.

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Now, let us go to the next question for us. In such a case, what decides the corrosion rate; what decides the corrosion rate in this system? Follow the same principle right. So, you know that the metal is passivating right.

This is an anodic reaction maybe let us say you have a M \longrightarrow Mⁿ⁺ + n e⁻, this maybe your cathodic reaction for that, this is your $i_{0Mn+/M}$

 E_{eqm} : this is the equilibrium potential. How do you get corrosion rate for this? What you need for that? You need a cathodic reaction. So, what is the corresponding cathodic reaction?

If the corresponding cathodic reaction is represented, I can get the corrosion rate. Assume that the cathodic reaction follows this, assume that I have a cathodic reaction it follows this, assume that I have a cathodic reaction follow this. Of course, I can has a cathode reaction somewhere here. You; you can imagine, I mean you have no restrictions about that ok.

Now, you can have a cathodic reaction of this kind, this kind, this kind, this kind all are possible. Then for you, now to determine E_{corr} and icorr is not difficult. What are the criteria for identifying E_{corr} and i_{corr} ? What are the criteria?

Student: Mixed potential theory.

Mixed potential theory, the rate of?

Student: (Refer Time: 71:26).

The total oxidation rate of the reaction is equal to

Student: (Refer Time: 71:32).

The rate of the total reduction rate of the system. If it is; if it is governing, you get E_{corr} and i_{corr} it is as simple as that. What would be the nature of the anodic curve and the cathodic curve, that is the criteria for you to determine the E_{corr} and i_{corr} values ok.

So, we will see this in the next class, how you can determine these values and how such diagrams are useful in real life situations ok.

So, I stop here.