Indian Institute of Technology Kanpur

## NP-TEL National Programme on Technology Enhanced Learning

<u>Course Title</u> Environmental Degradation of Materials

Module 01 Lecture 17 Broad Subject: Explanation of corrosion events on the basis of Mixed potential theory, Effect of area factor, Concentration polarization, Passivation

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So we have seen that if we have a different area fraction, when you couple galvanically couple copper and steel, you see a different behavior in both the cases.

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For example, in one case, you have copper area which is to be more and the rivet portion is still rivet, this is riveted area, which is still -- now I have said that the steel goes away quickly, because of corrosion and then copper plates, which are riveted with steel rivet, those two plates will get loosened. But instead of steel rivet, if we use copper rivet and in order to fasten steel plate, so that case the steel plate, the strength of the rivet can remain for a little longer period.

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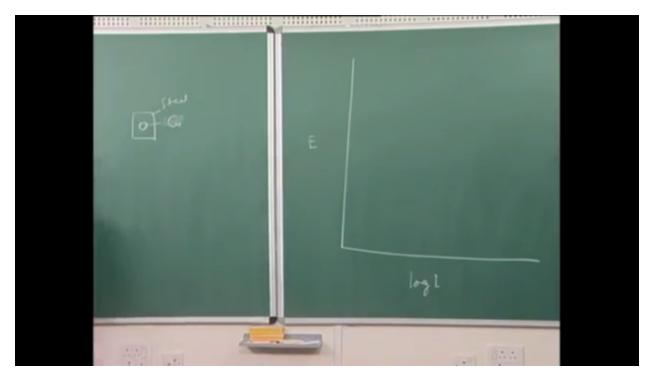


So this reason is basically we have already explained that reason is nothing but the differential area fraction. Okay. In one case, for example, the case one where steel is the rivet and copper plate are to be fastened by steel rivet, that case because you have a larger cathodic area and a very small anodic area, so the current density at those anodic areas are becoming very, very large and current density corresponding to -- corresponding to anodic dissolution is nothing but the corrosion.

So as the current density is increasing to a large extent, so the rate at which steel will corrode or the steel rivet will corrode will lead to the loosening of copper plates. But in case of copper rivet, which are used to fasten steel plate, steel, two steel plates that can maintain its strength because the copper, now it's cathodic and there is huge anodic area. So the anodic current density over the anodic area will be very less because of larger area of steel or anodic surface.

Now this can be explained with Mixed potential theory. So let me again draw the same plot, which is log I potential. Now I have changed it to capital I, which is nothing but the current, not the current density. This is to be -- this is very, very important part.

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Now if we see the relation because we are always trying to see the activation polarization on the anodic side as well as cathodic side, so activation polarization can be related to which is cathodic or anodic. This is beta c or anodic log i cathode or anodic and  $i_0$ . This is a small i, which is the current density.

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Now if you multiply area, you can write it as  $i_{c/a}$  into area of c/a divided by  $i_0$  into  $A_{c/a}$ , c by small a. The small a means anodic, small c means cathodic, and this capital A is nothing but the area of that anodic or cathodic region.

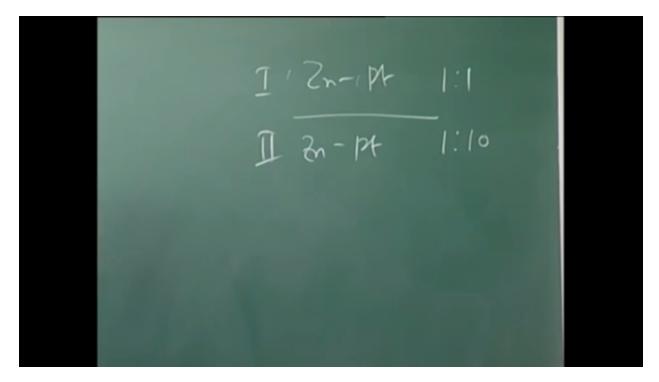
Now once you have -- you can write it as  $\beta_c$  that means for cathodic or for anodic into log I, capital I catholic or anodic capital I<sub>0</sub> of cathodic or anodic. Sorry, in this case, there will not be anything because this only gives you the idea when the system is in reversible non-corroding system.

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So when there is no corrosion, the rate at which cathodic reaction is taking place, at the same rate, anodic reaction is taking place, but at the same time there is no corrosion, so that is at equilibrium. So that means this  $I_0$  now we can express in terms of current from current density. Now this equation would be our reference.

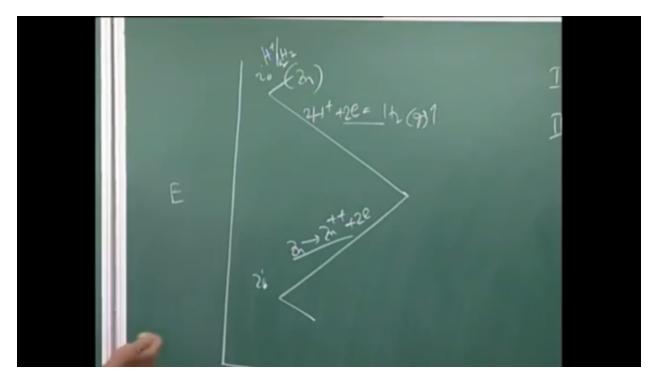
Now that case, let's say I am having a couple between zinc and platinum where the area fraction between zinc area and platinum area is 1:1 and another case where I have zinc and platinum where area fraction is 1:10. So platinum area has 10 times more area than the zinc area. So this is the two cases, case 1, case 2.

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Now what would be the situation in these two cases? Okay. Then we can definitely understand what is happening here. Now if it is only zinc, only zinc, let's say zinc and zinc just to have a sort of easiness in understanding, I have a zinc plate. I connect it to zinc plate with the same area. Okay. So that case my situation would be simple like this, and if hydrogen evolution is my cathodic reaction, so this is my zinc going to  $zinc^{++}$  plus 2e and this area is  $2H^+$  plus 2e equal to  $H_2$  gas which is evolving and this is my cathodic reaction. This is my anodic reaction and this is my  $i_0$ , and this is my  $i_0$  of  $H^+/(1/2)H_2$  on zinc surface.

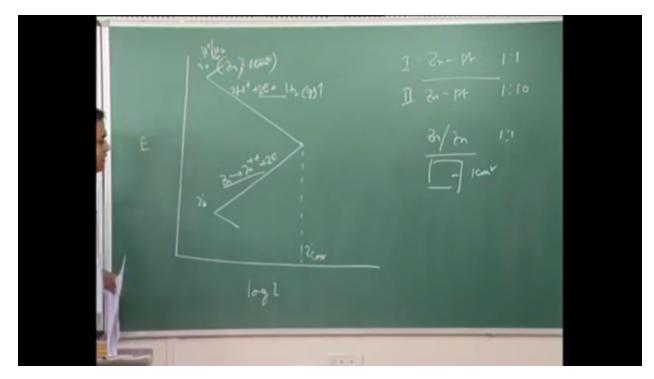
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Now it's not complete yet because I have to mention because since we are considering differential area and here also the area fraction is 1:1 because it's -- it doesn't matter because whether it's 1:1 or 1:2 because if you combine them, it's becoming a single zinc piece.

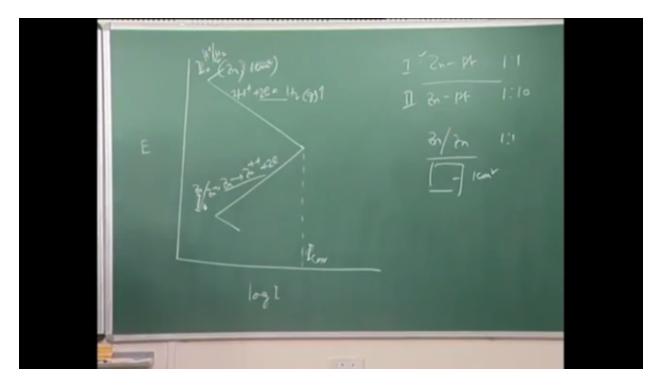
Now that case you have to mention one important parameter, that is it is basically 1 -- let's say if the total area becomes 1 centimeter square, 1 centimeter square, so I will just write 1 centimeter square. So that means this current density is nothing but the current density of hydrogen evolution reaction or hydrogen -- hydrogen reduction or oxidation reaction, that case it's happening on zinc and the zinc area is 1 centimeter square.

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Now this is my corrosion current,  $i_{corr}$ . Now since I have taken in -- in terms of log I, capital I, so I can also take it as capital  $I_{corr}$  and now instead of  $i_0$ , I can mention it as capital  $I_0$ , and instead of  $i_0$  zinc, I can mention that capital  $I_0$  zinc, which is zinc/zinc<sup>++</sup>. Fine, no problem.

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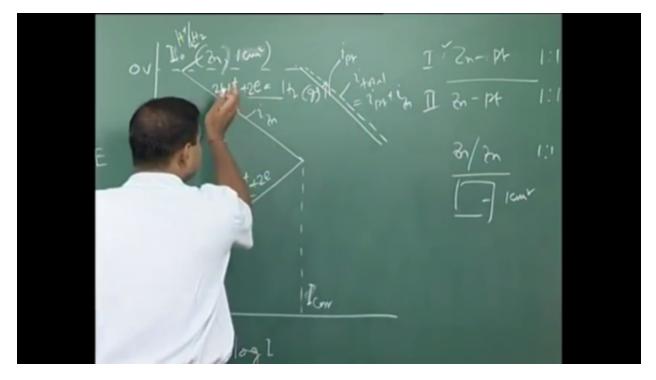


Now if we consider this, now that case we have already seen that on platinum, this hydrogen evolution reaction, the  $I_0$  or exchange current density on platinum is very, very high compared to the exchange current density for this on zinc surface. So that case my  $I_0$  value will shift to this point, but the my potential value would remain at the same value because for this reaction at -- if you consider standard reduction potential for hydrogen evolution, that case it will always remain as zero volt. Only thing is it will shift to this point because of current density change.

So, again, you will have another plot like this and we have already seen that we have to add two cathodic reactions because this hydrogen evolution is also taking place on zinc surface. This hydrogen evolution reaction is also taking place on platinum surface. So you have two cathodic reactions. It's a singular reactions, but it's happening on two different surfaces.

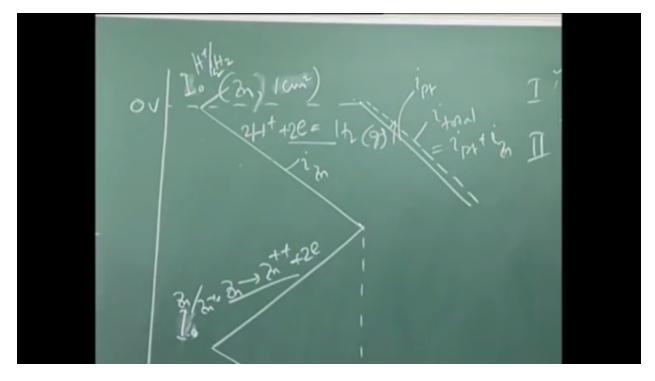
So what would be the total cathodic reaction? Total cathodic reaction would be you have to find out a dotted line, which is nothing but -- this dotted line nothing but let's say this is  $i_{platinum}$ , let's say this is  $i_{zinc}$  of hydrogen evolution reaction, so this is the total  $i_{total}$  equal to  $i_{platinum}$  plus  $i_{zinc}$ .

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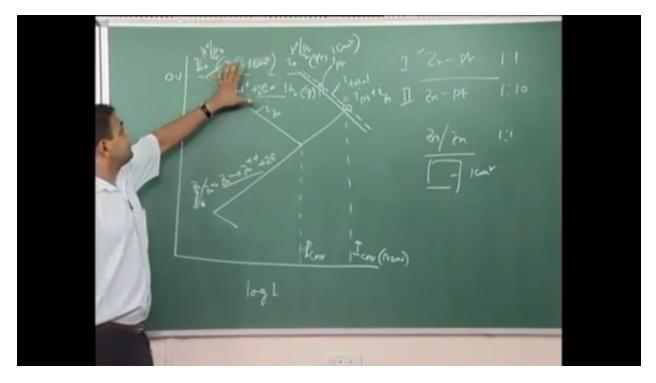
So hydrogen evolution current density during cathodic polarization, this is my total cathodic current density and these two are the contributions from the current densities for the cathodic reaction on zinc surface and platinum surface. This is clear.

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Now, similarly, we will have -- we have to extend this line and we have to find out where are my cathodic current density, total cathodic current density is going to be equal to the current density corresponds to the total anodic current density. This is my point and this is my  $I_{corr(new)}$ , and when -- and this is also  $i_0 H^+/H_2$  on platinum surface, and now it's 1:1 ratio. If you take 1 centimeter square zinc surface, so platinum surface also we have 1 centimeter square area. So you can write it as 1 centimeter square. No problem up to this. Fine.

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And up to this whether you are using capital I or small I, it doesn't matter because, finally, you are going to have 1 centimeter square area, so the current density would be -- the value of current density would be equal to the value of total current because if you consider I, that means capital I by area, and this area is unity, unit area. So i mod if you take would be equal to capital I mod if you are taking one centimeter square in both the cases.

Now situation will be little complicated because you have now the area fractions are changing. The area fractions would be here one centimeter square is to 10 centimeter square. If we are taking zinc surface to be one centimeter square, then platinum surface should be taken as 10 centimeter square, and now you see the direct correlation between this steel rivet and copper plate. So here the copper is noble metal, but here platinum is noble metal, and since it's a noble metal so -- or this will act as cathodic surface and the cathodic reaction will entirely take place on platinum surface and zinc surface will have more and more progressive corrosion or anodic reaction.

So that case let's say my -- if the platinum quality is not changing, if the same sort of platinum plate you are using, same quality and also the solution is same, so more or less this exchange current density on platinum doesn't change. But if you consider let's say this is 1 centimeter square area platinum and this is 10 centimeter square area platinum, now both the cases exchange current densities would be same if the quality is not changing, but the only one thing will change, total exchange current.

So  $i_0$ ,  $i_0$  of hydrogen,  $i_0$  of hydrogen, these will be almost same, but if you consider  $I_0$ , the capital I, the total current corresponds to the exchange current density, that would be less than  $I_0$  in this case. So this, let's say this is case 1, this is case 2. So this is case 1, this is case 2 because here you have to once you know the  $i_0$ , then in order to find out the total current corresponds to the exchange current density would be  $i_0$  multiplied -- multiplied by area.

Now since we have taken log I, which is capital I, the total current, so now situation would be the second case, let me remove this part, second case, since I have a greater capital I corresponds to

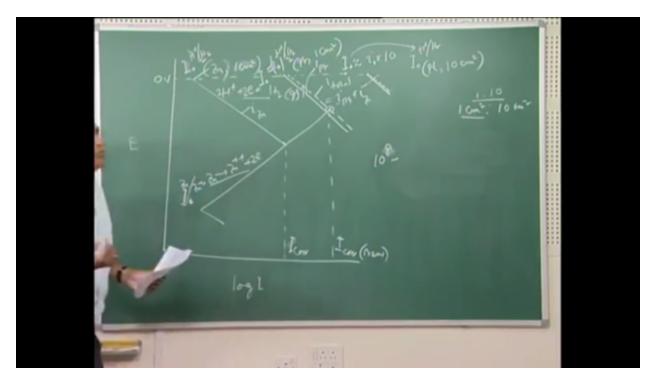
 $I_0$ , I have to go to the right side because now it would be mod if you take would be equal to  $I_0$ , which is capital  $I_0$ .

Now in this case where 1:10 centimeter square, 1:10 is the area fraction between zinc and platinum, so my  $I_0$  row would be lying here. So this is capital  $I_0$ , which is nothing but  $i_0$ , small  $i_0$  into 10, and this case I can express it as  $I_0$  H<sup>+</sup>/H<sub>2</sub> on platinum. Now here I have written 1 centimeter square. Here I have written 1 centimeter square. Here it would be 10 centimeter square.

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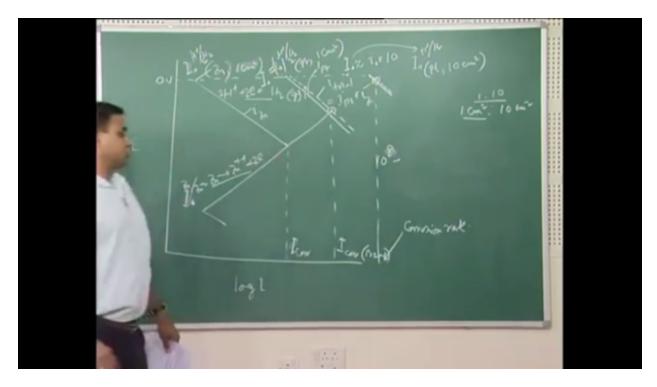
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Now I have to start my polarization, cathodic polarization from this. Fine, and it will go and meet here. Is this okay? Now still it's not okay because we have now this and this. So this is also to be combined with this cathodic reaction, but now that see the difference between the these two current and it's in log scale. So once you are taking it in log scale, now as you go to the right side, this difference would be around of the order of  $10^{10}$  or  $10^8$  let's say something like that. So if this much difference in the order of values, so whether you add it or not add it, it will not have any change in the total current density, total current because finally, you have to add these two current.



So if for sake of understanding we can put a dotted line very close to this. So now what would be my new current density where I have -- where I have cathodic current density, total cathodic current or cathodic current would be equal to the total cathodic -- anodic current density?

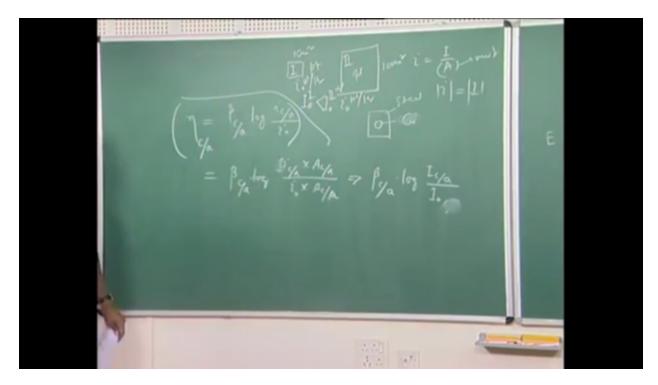
So, finally, at this point, I see another equilibrium between the rate of corrosion and the rate of cathodic reaction. So this is my new corrosion rate -- new corrosion rate.



So now you see why, when you are using steel as a rivet, why this steel is dissolving at a much faster rate because we are going to have more and more anodic -- cathodic reactions on the larger cathodic areas. In order to meet that electron balance, I have to supply more and more electrons from the small anodic -- small anodic areas. So more and more electron supply means more and more dissolution, and that's why we are going to have much higher dissolution if you combine it with a platinum, which has 10 times more area than the noble active metal which is zinc. So this is one more example.

Whatever examples we have seen which are the practical examples, we are considering within the activation polarization side because here also it's straight line. This is also straight line, and these are all activation polarization and the equation for this is this.

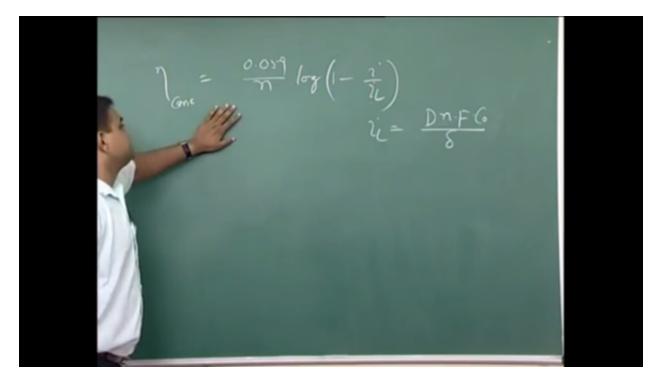
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Now if we consider concentration polarization, what would happen? Let us also have one or two examples.

Now whenever we consider concentration polarization, let us only take the polarization factor, which is coming from cathodic concentration polarization. Now whenever we try to see the polarization effect, this is my concentration would be equal to 0.059 by n into log  $i/i_L$ . Let me check. I think this would be, yes, this should be one minus -- 1 minus  $i/i_L$  where  $i_L$  equal to limiting current density, which is nothing but diffusivity of that ionic species in the solution, n is the number of electrons that are involved for the reduction of one mole of ions, F is 1 Faraday and C<sub>0</sub> is basically the concentration in the bulk, bulk of the solution divided by delta, which is the boundary layer thickness.

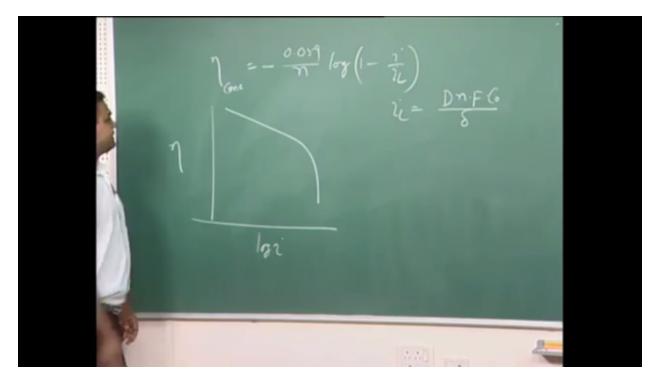
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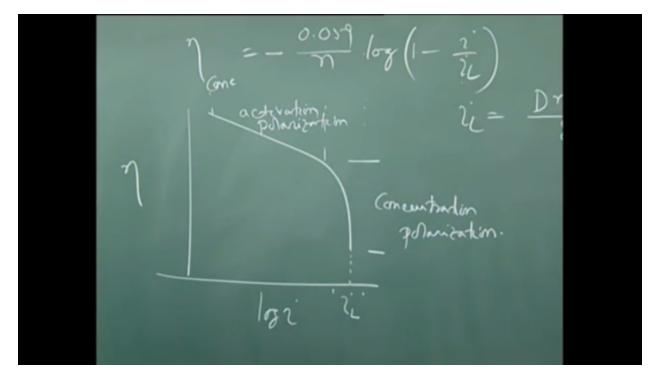
Now this is my concentration polarization and we are considering cathodic concentration polarization. We have to put a negative sign because we know that cathodic polarization means the lowering in potential from the equilibrium potential. So it will have a negative value.

Now for that case, what happens? Let's say hydrogen, let's say hydrogen -- hydrogen reaction which has reached to the level of that current density where i will experience  $i_L$ . So that case my plot would look like this and this is  $\eta$ . This is log. Again, I am coming back reverting back to small i, which is the current density.

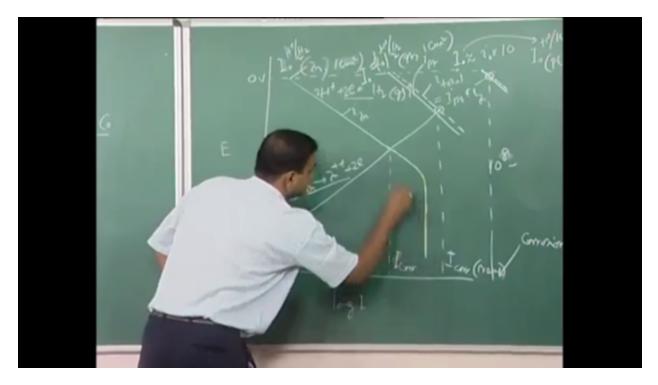
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Now that case this is my activation part, activation polarization and this is my -- this part is concentration polarization -- concentration polarization, and this is corresponding to  $i_L$ , which is limiting exchange current density, sorry, limiting current density, not exchange current density. Now this is my polarization.



Now that case this is now we can also instead of  $\eta$ , I can also express it in terms of absolute potential. So in that case I will put E and depending on what reference electrode you are using, accordingly, this value would change. So that case this is situation up to this you can relate to this. Up to this you can relate to this and then there after it is coming like this.



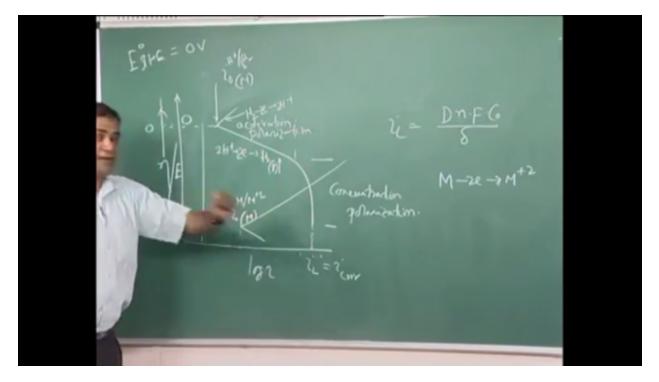
So here also you can experience concentration polarization. Yet you go to a very, very large current density. So that means this is my activation which is  $H^+$  plus  $e \rightarrow H_2$  gas and this is my -- this part is nothing but  $H - e \rightarrow H^+$ . So I can put 2, 2,  $2H^+$ . So this is my anodic polarization. This is my cathodic polarization, and we are considering only the cathodic polarization side because we have seen that concentration polarization is much more effective in case of cathodic site.

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Now that case, in this case, let's say we are using two scale. In this case this should be taken overvoltage that gives this value would be zero, and if you are measuring this potential with respect to standard hydrogen electrode, standard hydrogen electrode, and if you would like to plot with respect to potential, only absolute potential, that case also it would be 0 because standard hydrogen electrode potential is nothing but 0, 0 volt. So this will not change.

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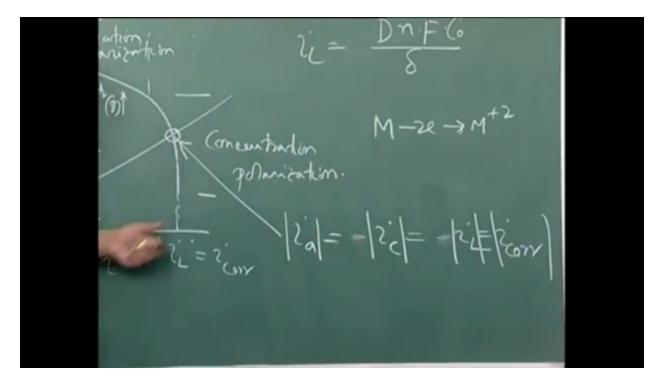
Now this is my situation. Now let's say I am having another metal dissolution in the system. Let's say some metal M which is dissolving. This is my dissolution reaction. So I have cathodic polarization. I have metal dissolution. Now let's say the situation is like this. Situation is like this. So this is my  $i_0$  for metal on metal surface, on the same metal surface and this is my -- let me remove this part. This is nothing but  $i_0$  of hydrogen on metal surface.



See if the situation is like this, which one is my corrosion rate? Corrosion rate is nothing but  $i_{corr}$ .  $i_L$  becomes equal to  $i_{corr}$  because this is almost straight line. Once we reach to  $i_0$  because from this reaction, from this polarization, now in this case it would be 2 because I have taken 2 electron, n to be 2,  $log(1-(i/i_L))$ .



Now if i equal to  $i_L$ , so this becomes infinite. This becomes infinite. So once i become the current density become equal to -- becomes equal to  $i_L$ , so this concentration polarization becomes infinite. At any point it can exist, but the actual existence will be decided by the cathodic -- anodic polarization line and this is my anodic polarization line, and here it cuts, and the corresponding current, if you see the current density here, this point  $i_a$  would be equal to minus  $i_c$ . And what is  $i_c$ ?  $i_c$  is nothing but  $-i_L$  because this  $i_c$  is equal to  $i_L$  and what is  $i_a$  is nothing but  $i_{corr}$ , and this negative sign I am bringing in just to include that these two current densities are flowing in opposite directions, but magnitude wise if you see all are same.



So this is my corrosion, new corrosion current density or new corrosion rate.

Now let's say I increase the velocity. In a solution one case let's say I have two situations, let's say 3, 3, 4 situations. I have in one case stagnant solution. Okay. Let me put it here. One is stagnant solution. Second is velocity Vi. Gradually, if you churn the solution, your velocity increases. Velocity of the solution increases. So Vi means let's say I have three situations  $v_1$ ,  $v_2$ ,  $v_3$  and then my relation would be  $v_1$  is less than  $v_2$  less than  $v_3$ . So, gradually, you are increasing the velocity in the solution.

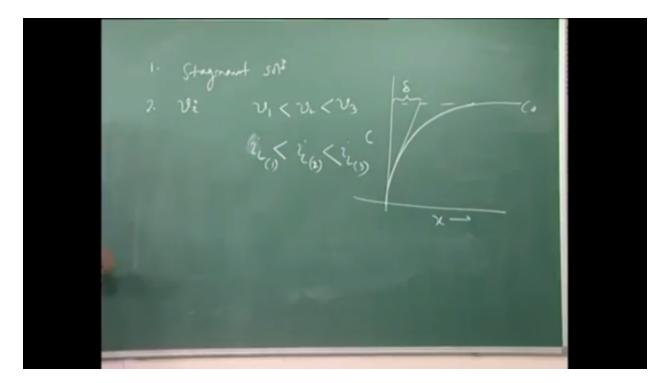
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Stagnant SAR Vi VI < VL < V3

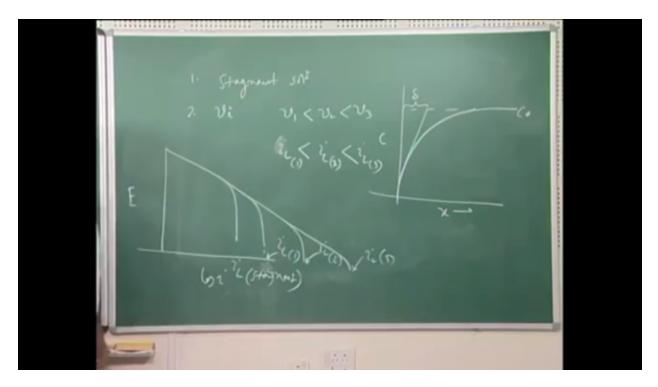
Once you increase the velocity in the solution, you are going to affect. If you see this equation, if you increase the velocity and if you see the concentration distribution, concentration distribution is like this. This is my bulk concentration and this is my boundary layer thickness, delta and this is my C axis and this is my x distance from the anodic -- from the cathodic electrode surface.

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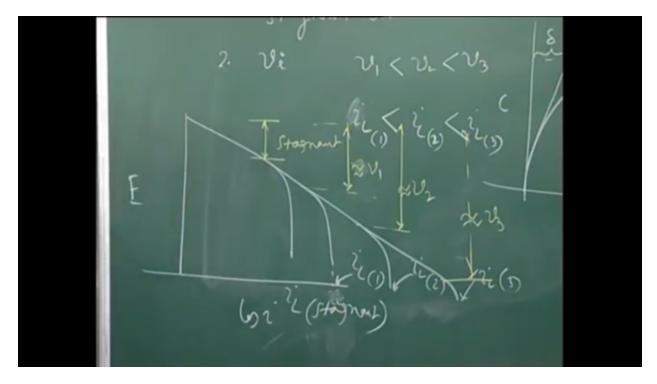
So now if you increase the velocity what would happen? This part will decrease. Yes. If this part decreases, if this part decreases, now delta is decreasing which is the boundary layer thickness. What would happen to  $i_L$ ? If nothing changes, then  $i_L$  will gradually increase. Okay. So corresponding  $i_L$  relation if you would like to see,  $i_{L(1)}$ ,  $i_{L(2)}$ , and  $i_{L(3)}$ , if you consider, if you see the relations between  $i_L$  values at three different velocities, the relation would be at  $v_3$ , which is the higher velocity,  $i_{L(1)}$  will also be very high. So, again, the relation would be like this. Fine.



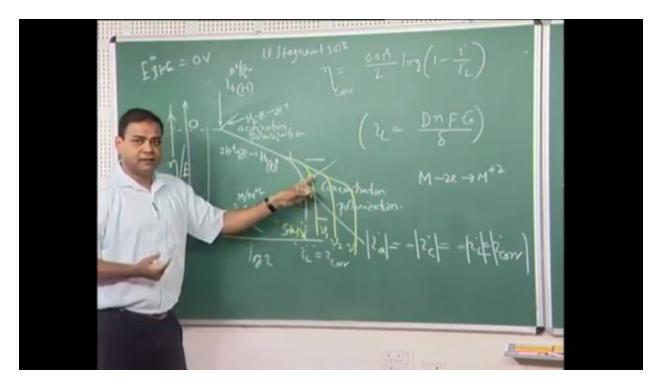
Now if you would like to see what would happen to this if  $i_L$  increases, so my -- if you would like to see the plot log i and potential, so, initially, this is my let's say at stagnant condition,  $i_L$  stagnant. Now I increase it -- increase the velocity to  $v_2$ ,  $v_1$ . I will increase the  $i_L$ . Okay. So this is my  $i_L$ . This corresponds to  $i_{L(1)}$ . Again, I increase the velocity to  $v_2$ . This is my  $i_{L(2)}$ . Again, I increase the velocity. This is my  $i_{L(3)}$ .



Now you see as you increase the velocity, your activation polarization, the width of that activation polarization is increasing. When it is stagnant, my activation polarization is this much. That means this is stagnant. When I increase it to velocity  $v_1$ , my activation polarization width is this much. This is corresponds to  $v_1$ . When I increase the velocity to this, my activation polarization width is becoming this corresponds to  $v_2$ , and when I increase it to  $v_3$ , my corresponding activation polarization width is this one corresponds to  $v_3$ .



Now same thing, we are not affecting this reaction anodic side. We are only affecting this side. So, gradually, same thing I am plotting it here like this. Okay. Now that means up to this up to velocity  $v_2$ , this is  $v_1$ , this is  $v_2$ , this is  $v_3$ , and this is stagnant, this condition. So when you increase the velocity, your new equilibrium point where the rate of electron consumption and the rate of electron deposition, electron generation, both are same, and also you are seeing that that  $i_{corr}$  is increasing because  $i_a$  is also increasing. Fine. No problem.

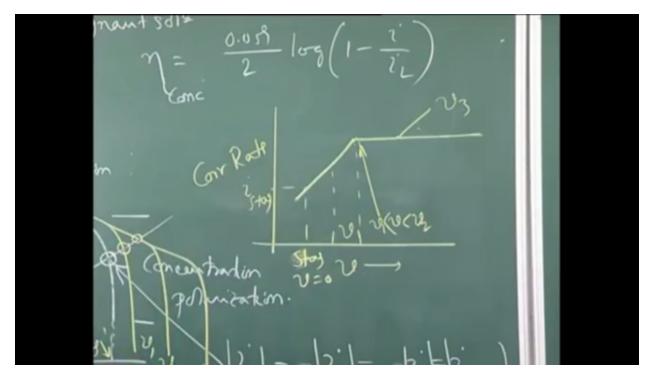


But once you go to  $v_2$ , you see, again, I am increasing this,  $i_{corrosion}$  is increasing, but after  $v_2$ , if you change the velocity to  $v_3$ , we are not going to get any change in the corrosion rate because corrosion rate always will be decided by this point. So if you go to  $v_3$ , it doesn't matter. Fine. So after that you are going to have a constant corrosion rate.

So if I would like to plot the corrosion rate versus the velocity, then we will see a plot like this. I would like to plot corrosion rate and velocity. Let's say this axis is velocity, this is corrosion rate. When it's in stagnant condition, what is my point? Corrosion rate is this point. Let's say some value which is correspond to  $i_{stagnant}$ . When I increase to  $v_1$ , corrosion rate is increasing. When I increase farther the velocity, corrosion rate is farther increasing, and then when I go to  $v_2$ ,  $v_3$ , I am not seeing any difference.

So the corrosion rate would be like this. So this is my  $v_1$ . This is my stagnant when v equal to zero. This is my  $v_1$ , and this is my velocity corresponds to this would be  $v_1$ ,  $v_2$  this point, and this point is  $v_3$  and gradually, it would be constant.

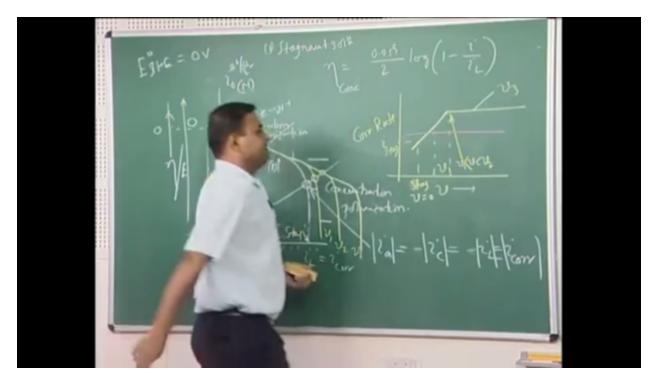
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So if I join this, this is my corrosion rate plot. Fine. So the corrosion rate plot is basically, initially, with the increase in velocity, it would increase and then finally, it would be a plateau or constant corrosion rate. So we have that notion that if we increase the velocity for an active metal, then there is a possibility that the corrosion rate would always increase, but it doesn't happen like this. Of course, there would be increase, but once you have this situation, particular situation because of concentration polarization effect from the anodic -- from the cathodic side, then you are going to have a plot like this. Fine.

Now if the situation is little different on the same plot, a plot like this, let's say another metal which is  $M_2$  is also having a polarization effect like this. In that case will the churning affect the corrosion rate? No, because I am always going to have this point as the corrosion rate with the increase in velocity because I am not getting any benefit because of the concentration polarization, which is coming in case of M.

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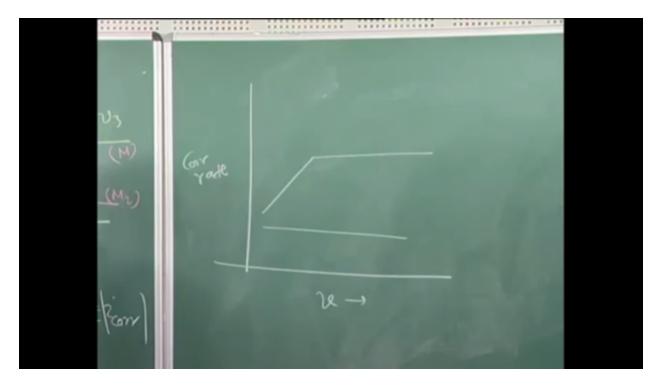
So in this case, if I would like to plot my corrosion rate, the corrosion rate plot would be, let me put it in red, corrosion rate plot would be this, which is a flat line. Fine. So if you consider the scale, actual scale as from the figure, so this point would be here. So this is my corrosion rate for this M2 case. This is M2 and this is M.

So we see that because of concentration polarization from the cathodic end and if the anodic polarization is only activation controlled, then we see that in two cases the corrosion rate has two -- has -- has different natures. For example, in case of M2, velocity doesn't have any effect, for example, the red line because always the current density corresponds to the corrosion rate point. Corrosion point is going to be this. So current density always remain constant as a function of velocity because with the velocity, of course, we are getting the change in  $i_L$ , but that is not going to affect this.

So this is a flat line, corrosion rate as a function of velocity, but if you have situation in case of M, the corrosion rate is going to change as you increase the velocity, but finally, it will reach to that metal level. So that case once you reach to this, so this point is almost similar to this point because there -- there is no effect on the velocity. So it will remain like this.

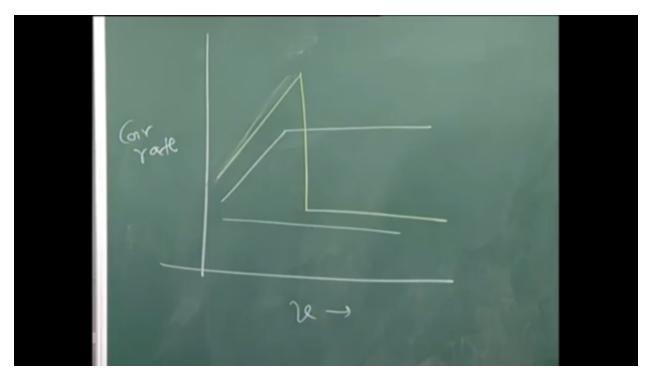
Now we are having one small variation in the corrosion rate as a function of -- a peculiar variation of corrosion rate as a function of velocity in case of some particular metal. Let me plot it there. So this is velocity, increasing velocity, and this is corrosion rate. Now in one case M2, it is like this. In case of M, it is like this as a function of velocity.

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Now we can have one small, one -- one particular situation. With the increase in velocity, my corrosion rate can vary like this. Initially, it will increase just like this. Then, suddenly, it will drop, and then it will remain constant.

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So up to this we can understand this is also behaving like this, but why there is a huge drop in current density corresponds to the corrosion point? So something different is happening here. So we have to understand that what is happening there. See in order to understand this, we need to get into another concept in corrosion that is called passivation -- passivation.

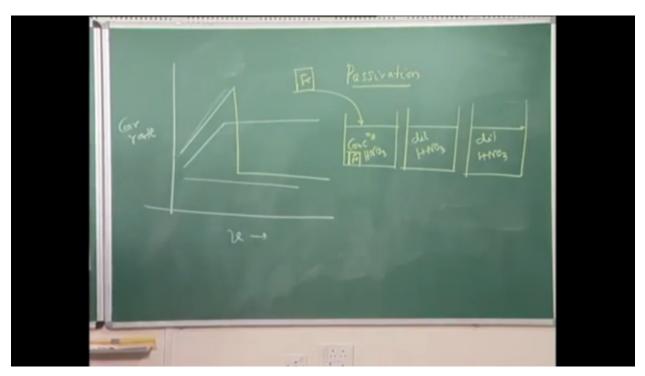
Now when you talk about passivation, before going into the definition of it, let us understand the experiment that has been carried out, that had been carried out by Faraday. The Faraday's experiment was very simple, and what he did, he took three beaker. He took three beaker, and one beaker he put concentrated -- concentrated HNO3, and this case he has put diluted HNO3. Now another case, the same concentration of diluted HNO3 he has put.



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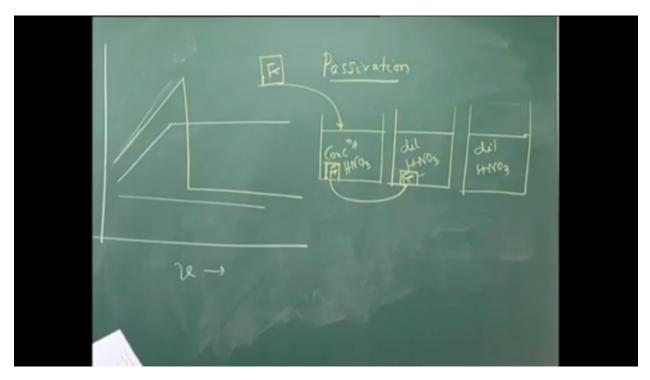
Fine. These are three beakers, and here he has put iron piece, pure iron piece. Pure iron piece he has put it here. So once he puts it inside iron piece, these iron piece, initially, for some time, few minutes, there would be vigorous bubble formation, and then there would be no bubble formation. The iron piece initially it will show some bubble formation, but after that it will not show any bubble formation. It will remain like this and as if there is no reaction happening.

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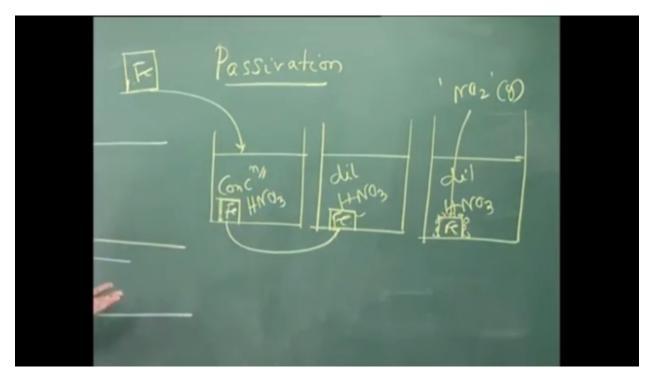
The same iron piece he has picked it up from there, this concentrated  $HNO_3$ , and put it in dilute  $HNO_3$ . The same piece he has put it here, not this one, rather the piece what he dipped in  $HNO_3$ , concentrated  $HNO_3$ . He took that piece and put it here. Again, we see that he saw that there is no reaction, no bubble formation. Fine.

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Now what happened? He has again taken it out. Again, he took it up, again, and then put it, the same piece, put it here, but here he did small change. Now this iron piece was cracked a little bit. The iron piece was taken from this and then it is -- it was little scratched with a -- with a glass pipe, so that scratch piece is put it here so that, again, there is vigorous bubbling on the surface, which is nothing but the scratch now. The scratched iron piece is showing vigorous reaction and this bubble is nothing but NO<sub>2</sub> gas.

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What's happening here? This is a simple experiment, but we have to understand what is happening there, and this gives you the idea that iron passivates in HNO<sub>3</sub>, not HNO<sub>3</sub>, rather in concentrated HNO<sub>3</sub>. That we have to mention whether it's dilute or concentrated.

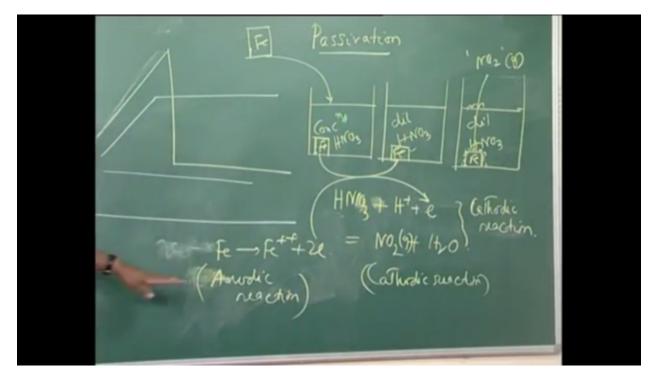
Now once we have  $HNO_2$  gas, so that means from  $HNO_3$  if you see the formation of gas,  $HNO_2$  gas can be related to this relation, this equation plus  $H_+$  plus e equal to  $NO_2$  plus  $H_2O$ . Now this reaction is nothing but -- and this is reaction which is nothing but a cathodic reaction because we have electron acceptance reaction, and this is nothing but the cathodic reaction. So due to this cathodic reaction, this gas is forming, and this gas is coming out. Initially, it's forming in the form of bubbled, and then bubble will collapse together, and form a big piece and then that would come up. Okay. So there would be a little bit of boil on this surface. So  $HNO_2$  gas is coming up.

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So if this reaction is happening and which is -- which needs electron, so who will supply electron? The only place, only thing that can supply electron is iron has to corrode. See these 2 electron will go there. So that means we have cathodic reaction. We have anodic reaction -- anodic reaction and corresponding cathodic reaction would be this, which is cathodic reaction.

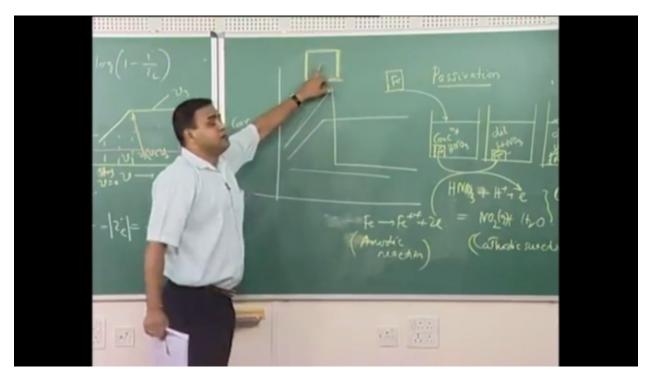
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So now we see that in this case, if this  $NO_2$  gas is coming up, this reaction is happening. In order to supply that electron, which is needed for this cathodic reaction, I need to have iron ion formation, which is nothing but the corrosion. So, actually, here we see that corrosion is taking place and that is happening because of scratching because the only difference between this and this is here we have scratch, here we don't have scratch. So if we don't have scratch that means we don't have any bubbling, so it means there is no reaction. Okay.

But here, initially, we saw a little bit of bubble formation. That means initially, when iron is nascent on the surface, okay, that means it can -- you can relate to -- related to this where here you have few scratches and in all the surface are full of scratches and it's exposed. So once it is exposed to concentrated HNO<sub>3</sub>, it will initially react, and the reaction would go like this, but finally, you will see that there would be a formation of a layer on the surface which is nothing but the oxide layer and that oxide layer is giving inherent protection to this piece, iron piece.

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So if there is inherent protection, so you have this iron piece. Fine. And on top of this, you have a small layer of oxide, which is preventing contact between  $HNO_3$  and iron surface. So it's giving sort of protection and this formation of oxide layer or sort of surface layer, which prevents further corrosion is nothing but the passivation, and that too is happening in highly corroding medium.

This part is very important. Of course, there would be oxide layer or surface layer formation for prevention of further corrosion, but that should happen in corrosive atmosphere. Okay. So this is passivated iron. Now once you have this layer, if you put it here, you don't have contacts between the HNO<sub>3</sub>, dilute HNO<sub>3</sub> and iron because it's covered with the oxide. So it will not give you any bubble formation or corrosion, but if you scratch it, so once you scratch it, that means the iron surface is exposed, that means you have scratched it. So this section is exposed to dilute HNO<sub>3</sub>. So this reaction can happen on this surface and gradually, iron will dissolve, and at the same time as this reaction iron dissolution is taking place, this will extend over the entire area, and then entire area would be susceptible to dissolution.

Fine. So here is passivating -- passivation is maintained, that iron oxide layer which is forming at the surface layer which is forming that is maintained. There is no contact between the iron surface and dilute HNO<sub>3</sub>, no bubble formation. Scratched, bubble formation and corrosion. Fine. So this is passivation. This is passivated, already passivated, and this is activation. I would say activation or breaking down of passivation. Okay.

So now this part we have to understand now, and if we understand this passivation, then we can definitely explain this curve. That explanation part will come when we see what is passivation. Now let us define passivation from that Faraday's experiment. This is Faraday's experiment.

Now let us put this passivation. Passivation is defined as the condition of corrosion resistance. Here in the first case, initially, it corroded little bit, and then there is no reaction, no further cathodic reaction, or  $NO_2$  evolution reaction. So if this is not happening, so the corresponding anodic reaction would not happen. So here once this surface layer is formed, we are getting some sort of corrosion resistance. So it's a condition of corrosion resistance due to the formation -- formation of a surface film, which can be oxide, which can be hydroxide, which can be sulphate, anything which protects the surface of the metal from the -- from the electrolyte.

Okay. If you don't have that contact between surface, metal surface and electrolyte, you are going to have less corrosion reaction. Surface film under -- now one most important parameter for this passivation is coming now. Here HNO<sub>3</sub> is a highly oxidizing acid, okay, and highly oxidizing acid. At the same time, you are getting a cathodic reaction whose potential is of the order of 0.80 volt with respect to standard hydrogen electrode. So this highly oxidizing solution or highly corrosive medium and this concentrated HNO<sub>3</sub> is a very, very high, highly corrosive medium. So that case I am getting this passivation. So under oxidizing condition -- conditions with high anodic polarization.

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Now condition of corrosion resistance, we are going to see from the Faraday's experiment, and this is happening because of formation of surface film. This is also understood, and this is also

happening under oxidizing condition, but we are yet to understand why this term is written 'with high anodic polarization' because we have seen that if you have anodic depolarization, that means log I, anodic polarization, high anodic polarization means what? This value is very high. So if this value is very high, so this is nothing but  $i_a$ , which is nothing but corrosion dissolution rate or corrosion rate.

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So this thing, this top 3 things, this condition of corrosion resistance with the formation of surface film should happen under with a very high anodic polarization, so when  $\eta$  should be very, very high or when  $i_a$  would be very, very high or not  $i_a$ , sorry, I am -- I am mistaken. You don't consider  $i_a$ . That time  $\eta$  should be very, very high.

So now from this thing, we are clearly saying that if this is high,  $i_a$  should be also high, but situation would be different when we see that what happens to this  $i_a$  as a function of increasing anodic polarization. Then you would understand that why this last thing is written.

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So we'll understand this thing in the next class. Thank you.

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