

Corrosion Failures and Analysis
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 12
Factors associated with galvanic corrosion: Case study 2

Welcome to the course Corrosion Failures and Analysis, today we have lecture 12 and the topic we will continue Galvanic Corrosion. What we will do, we will try to see different factors associated with galvanic corrosion and some case studies and then we will try to say protections what we can think of to prevent galvanic corrosion. Now the topic ok, so, this is the course on corrosion.

(Refer Slide Time: 00:49)

Lecture 12

Topic: Galvanic Corrosion

Area ratio: Cathodic area < Anodic area
 $\frac{\text{Cathodic area}}{\text{Anodic area}} < 1$

Galvanic effect is felt around the joining/coupling of two different metals/regions on a same metal

Resistance offered by the electrolyte & conductor

(NaCl) ↓ Ladakh (Dry area)
 H₂O content ↓
 T ↓
 Zn | Fe
 Overall corrosion of this couple ↓
 Fe will be protected
 Zn dissolution rate ↓

Chennai - Wet area
 NaCl ↑
 H₂O ↑
 25°C ↑
 Zn | Fe
 Overall corrosion of this couple ↑
 Zn dissolution rate ↑

36/43

Now if you recall last lecture, we saw two factors one is area ratio it means that cathodic area should be less than anodic area or if we consider the ratio the cathodic area divided by anodic area should be less than 1. It means that in any joining wherever in the structure you have such kind of situations that anode and cathode materials are different of course, different because you sometimes you cannot avoid using different materials.

For example, in case of riveting, in case of joining, in case of fastening nuts and bolts there you have to use different materials and that time you have to make sure that the cathodic area should be less than anodic area this is the design criteria.

Now, second part what we have seen that galvanic effect is felt around the joining or coupling of two different metals or we will see later when we talk about inter granular corrosion, but you have already seen in case of rain water droplet so the different metals or two different regions on a same metal.

We have seen the effect of coupling of two different metals in case of zinc and iron that was the kind of situation like this if this is zinc this is zinc, this is steel, if the area exposed to the environment is less for the cathode area we do not have much of dissolution of zinc, but still it gets protected, but if the area is exposed is large. So, the galvanic effect it will be felt around this zone and around this zone it will be more or less uniform corrosion.

And in fact, that time you will see that the steel is protected around these areas, but this area we see lot of rust. So, this is the very concept and that relates to the resistance offered by the electrolyte as well as conductor fine and if it is away from for example, in this case resistance offered the distance travelled by the electron or ions will be shorter compared to this region and this region.

So, the between these two there is a huge path large path that electron needs to migrate. So, that time electron will feel resistance and that resistance would avoid this galvanic effect or minimize galvanic effect. Now, another factor we would like to consider so that is before coming to the factor let us see one example.

Let us say I have one particular metal object let us say two metal object let us say this is zinc, this is iron, this kind of couple is kept in Ladakh area and another near Chennai area or any seaside cities in India we will see in this case the overall corrosion of this total couple will be less would be less.

Now in this case iron will be protected and a situation like this a sheet metal of steel where we have thin layer of thin layer of zinc layer ok and this is the situation and that time you have some portion which is exposed to the environment because of mechanical erosion or mechanical damage other kind of situation what you see here it will get protected, but the overall weight loss of that component would be less.

But if we consider the Chennai area overall corrosion of this couple would be very high and here it will be less, here also same situation happen same situation what we see here

it will happen, but overall corrosion as well as zinc dissolution rate also would be very high and in this case would be less the possible reason being if all the things remain same we have to look at the environment.

Now the Ladakh being a dry area as well as it does not have salt much of salt there. So, if it is a dry area. So, H₂O content would be less at the same time NaCl content would be also less, but in the Chennai area NaCl as well as H₂O both would be high.

Another part is this is temperature is less average temperature of Ladakh could be around 10 degree Celsius, but even low the lower than that in Chennai average temperature over the entire year could be around 25 degree Celsius, you have to check you just go to the internet and you can check, but of course, the average temperature in Chennai area would be high.

(Refer Slide Time: 09:51)

The slide contains handwritten notes comparing corrosion in Ladakh and Chennai. At the top, it states "Resistance offered by the electrolyte & conductor".

Ladakh (Dry area): (NaCl) ↓, H₂O content ↓, T ↓, overall corrosion of this couple ↓, Fe will be protected, Zn dissolution rate ↓.

Chennai: NaCl ↑, H₂O ↑, T ↑, overall corrosion of this couple ↑, Zn dissolution rate ↑.

Environment: Electronic item ↓, P_{oxy} - airtight, O₂, Silicon gel → Moisture.

Environment

Polarity: Zn coating on Fe: Galvanic Protection of steel.

Galvanic Series: Zn⁰, Fe, Zn.

Chemical Equations:

$$O_2 + 2H_2O + 4e = 4OH^- (R)$$

$$Zn - 2e = Zn^{2+}$$

$$Zn(OH)_2$$

Diagram: A Zn-Fe couple is shown with Zn on the left and Fe on the right. A red arrow labeled "Anode" points to Zn, and a red arrow labeled "Cathode" points to Fe. Below the couple, it says "Dis-solution of steel will be very fast".

Equation: $R_{-Zn} = R_{+Fe}$

37/43

All these factors would lead to this high corrosion rate in case of this kind of couple in Chennai area because moisture of course, here also you will find oxygen, but oxygen percentage would be less because the pressure is also low because it is on the hill here the oxygen there are lot of oxygens.

So, for corrosion to happen all the ingredients are highly present in case of Chennai and NaCl in fact, NaCl does not take part in corrosion reaction, but for example, any system let us say some passivating one if that is there in Chennai still it corrodes because NaCl

hinders passivation, we will see later how it hinders passivation we will talk about inter granular corrosion.

So; that means, if we can control these corrosives ok, this is temperature is also a kind of corrosive factor the temperature increases the reaction rate, if we drop the temperature corrosion rate would generally drop, it is not likes all the time because provided there is no polarity change remember this is important there is polarity of metals is also important oxygen.

So, if we have all those cases are taken care of or removed you will have overall control over the corrosion. So, environment is a factor. So, that is why the third factor which is coming environment.

Now one practical example let me just give you that when whenever you open any electronic item box when it is coming to your house you have ordered online and it comes to you electronic products, you would generally see that inside that you will it the box it comes it is airtight item the boxes airtight as well as there is a small silicon gel a pack where silicon gel is kept, silicon gel takes care of moisture and air tight means oxygen level oxygen cannot ingress into the system where the packing is done.

In fact, many a times big items like transformer cold rolled grain oriented sheets which are used for transformer making when it is packed that packing is actually a done when packing is done there is a small evacuating system it takes out moisture as well as air from it.

So, the partial pressure of oxygen as well as moisture drops and it is also air tight so that air does not increase during transportation, because the corrosion of those sheets will also affect the magnetic properties because that is important for development of making of transformer.

So, there also we do take care of those moisture as well as a oxygen so; that means, you could see that if we can take care of oxygen and moisture we would have lowering of corrosion rate. So, my environment is also very important factor. Now I talked about polarity, now in case of zinc coating on iron for the protection of which is the galvanic protection of galvanic protection of steel that is never used beyond temperature 70

degree around 60 to 70 to 80 degree Celsius ok or even you can say around 65 degree Celsius.

So what happens you have this two iron zinc at that temperature we have generally the reactions are $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- = 4\text{OH}^-$ and $\text{Zn} + 2\text{e}^- = \text{Zn}^{2+}$ and that form zinc OH whole 2.

Now below that temperature this phase forms now beyond that temperature the product becomes ZnO zinc oxide and interestingly when zinc oxide forms on top of it, this is a zinc oxide let us say the zinc oxide and iron that time if we see galvanic series zinc oxide stays on top of iron, but zinc remains below iron.

Now this zinc oxide; that means, over the entire area zinc oxides which is forming and a situation like this so, this is zinc this is zinc, this is steel and zinc oxide is forming on top of it. Now zinc oxide is here cathode and that time this become anode. So, the cathodic reaction that was happening on iron surface now it will happen on zinc oxide surface.

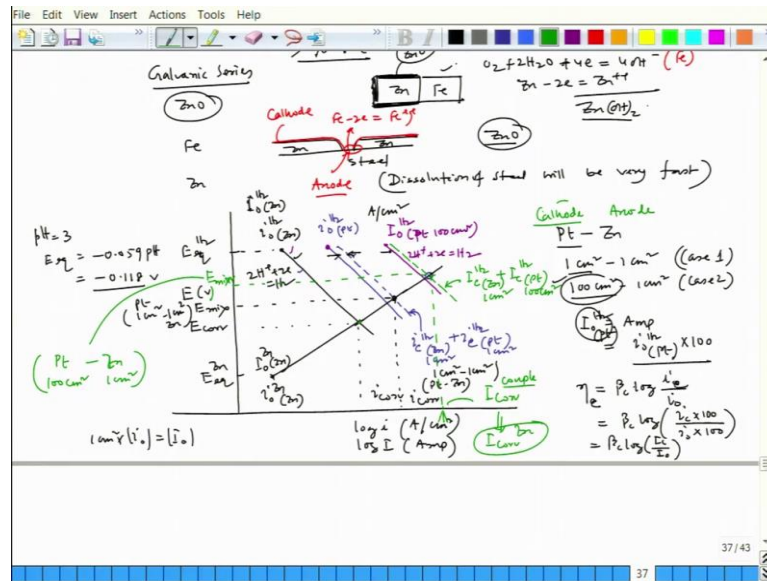
So, once zinc oxide becomes cathode. So, this would become anode. So, instead of protection of iron we have iron dissolution iron dissolution would take place and in the addition to that since there is a huge area of cathode and there is a small area of anode the dissolution of steel would be very fast very fast ok.

So; that means, you could see that we have to also be careful about the polarity change during operation we should see that if something is used for cathodic protection of iron or any component that particular component or metal should not form some component some oxides or hydroxide that should not act as a cathodic to iron ok.

So, that time this situation of reverse situation would happen that time the small cathode what we were protecting now that small cathode will go to small anode and it will corrode at a very very aggressive rate because we have a large cathode area now and small anode area ok. So, that polarity factor is also very important.

Now coming to the area factor let us understand that area factor from mixed potential theory. So, this has been done in our previous course, but still I am just bringing in so that it becomes complete.

(Refer Slide Time: 18:15)



So, if I see the mixed potential theory let us say we have dipped this particular component in HCl. So, hydrogen evolution is basically my cathodic reaction now we have ok. So, let us not take this examples instead of in order to understand the area factor ok.

So, let us take platinum or zinc and if platinum area let us say 1 centimeter square and 1 centimeter square this is case 1 and another one is 100 centimeter square and 1 centimeter square case 2. So every time both the couple we have zinc area which is maintained at 1 centimeter. So, only the platinum area is changing. Now when it is 1 centimeter square this is bold and let us say zinc this is E equilibrium instead of E not let me put equilibrium which is decided by the zinc double layer zinc concentration.

Now here this is $\log i$ instead of that we will put like this. So, we have hydrogen is here let us say this is here this is this. So, this is E equilibrium hydrogen, this E equilibrium zinc fine. So this E equilibrium hydrogen if the pH is let us say 3. So, then E equilibrium would be minus 0.059 pH which is minus 0.118 volt ok.

So, that and this is i_0 hydrogen on zinc surface and this is i_0 zinc on zinc surface, this is the E_{corr} and this is i_{corr} and now we have connected to 1 centimeter square platinum. So, this platinum has a higher exchange current density of hydrogen. So, then it will be extended and now as per the mixed potential theory where the total reduction rate should be equal to the total oxidation rate at the point of mixed potential.

So, the mixed potential would appear we have to add this current and this current. So, it will continue like this and then you extend this you get this point. So, this is my E_{mix} for this is the case 1 centimeter square platinum, 1 centimeter square zinc this is the situation and corrosion rate is this ok.

Now once we add once we connect 100 centimeter square area. So, that time if the conditions remain same the solution condition and the metal character then the exchange current density would be same which is ampere per centimeter square. So, that time this is Ampere per centimeter square, but in order to consider this area factor we have to take current which is i_0 which is ampere now.

How do we get it and this is gotten by i_0 hydrogen on platinum surface into 100 centimeter square. So, this would be my i_0 and everything would that equation the now that truffle equation would also remain same only thing is we have to multiply i_0 . So, that is basically over voltage if you consider $c_{beta} c_{log} i_c$ by i_0 ok.

And here i_c is basically so, this reaction this cathodic reaction when it is getting polarized we are putting that i_c value. Now this is small i which is current density now in if we want to convert into capital which is current that time I multiply i_c into 100 i_0 hydrogen into 100. So, it becomes I_0 . So, here it is capital I which is current density current.

Now if we convert everything for example, if we consider it to be current previously it was Ampere per centimeter square now it becomes $\log I$ when we consider this so that time it becomes Ampere fine. Now that time this particular point and this particular point will not change, because the area is always 1 centimeter square. So, that time magnitude wise I_0 ok magnitude would be same only the unit would change because I am multiplying this one with 1 centimeter square then I am getting I_0 .

So, that one I can keep I_0 cap, small i_0 or capital I_0 in this case also I can write capital I_0 hydrogen on zinc surface because area of zinc remain same and now we have to consider this I_0 for hydrogen reaction on platinum surface. So, that can only be possible if we change the scale here and that time if that value comes over here because I have multiplied this is hydrogen on platinum 100 centimeter square ok.

But if we calculate small i_0 which is current density it will be same as this. Now with this I have to add this current density because that current density or current does not change because the area remains 1 centimeter square over zinc surface. So, now, it will have its own polarization which is hydrogen and I extend this and now I have to add this one and since it is a log scale if we consider the gap here and here the gap after addition would be less because its in the log scale. So, then that would come like this ok.

So this is basically I_c hydrogen on zinc 1 centimeter square plus I_c hydrogen platinum of 100 centimeter square, but here it was this one if I consider this is nothing, but i_0 hydrogen on zinc surface 1 centimeter square plus i_0 sorry this should be i_c because cathodic current density now i_c hydrogen on platinum surface of 1 centimeter square.

So, now, new mixed potential would be this point. So, that point if I extend this is E_{corr} or rather I would say E_{mix} and that time this one is nothing, but for the couple for this couple.

And the corrosion rate so, this would be my I_{corr} couple and this I_{corr} couple is nothing, but I_{corr} zinc. And this I_{corr} zinc if we consider now you divided now if you see this I_{corr} zinc is happening over 1 centimeter square area so; that means, it will go up large factor over a large factor and the corrosion rate of zinc would increase to a great extent.

So, now, you could see that in this case this was cathode and this is anode and the cathode area if we go up in comparison to anode area you could see the consequence the anode dissolves at a much higher rate ok. So, this is the mixed potential theory to analyze to understand the effect of area ratio ok. So, let me conclude we will continue our discussion in our next lecture, but till then let us stop here.

Thank you.