Indian Institute of Technology Kanpur

NP-TEL
National Programme
On
Technology Enhanced Learning

Course Title

Environmental Degradation of Materials

Lecture – 24
Broad Subject: Galvanic corrosion

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So you see there are two factors, one is environment, another one is distance, these two factors we have discussed. Now let us get in to another important factor which guides galvanic corrosion that is area factor. So area factor is one of the most important issues in galvanic corrosion and we have already cited three examples, one is monel hull and steel rivet or copper plate and steel rivet, or a tank with a bottom of the tank is made of stainless steel 18:8 stainless steel, and the joint part which is the joint part between the mild steel and stainless steel that section will be very, very vulnerable to galvanic attack because of this differential area effect. So why area effect is important, when we discussed about the mixed potential theory we have seen that if zinc is coupled with platinum and if zinc and platinum couple is placed in acid solution then we see that if the area of zinc and platinum they are same then the corrosion rate, let's say if corrosion rate is C1 and if we have a platinum area which is more than the zinc area then the corrosion rate of zinc will of course will enhance.

Now the point is here on the platinum surface we have cathodic reaction which is hydrogen evolution since its acid solution but in on zinc surface is a zinc dissolution and let us again see that particular diagram that is when we consider both mixed potential theory which is E versus log capital I, please remember this, this is not current density this is rather total current. Now that time if we plot mixed potential theory we will see that if zinc and platinum they have the same area, now this is basically I0 or I0 hydrogen on zinc surface and this is I0 Zn++ on zinc surface this point and this is let's say E reversible of zinc, this is E reversible of hydrogen, then we have on zinc surface one cathodic reaction which is the hydrogen evolution. Another cathodic reaction which is actually the same cathodic reaction which is hydrogen evolution which is happening on platinum surface and we all know that on the platinum surface hydrogen exchange current density would be much higher than the exchange current density of hydrogen on zinc surface, so this is hydrogen exchange current density on platinum surface and if it is the same area let's say 1:1, area of ratio is 1:1 then we have corrosion current density, this is my I Corr and the dotted line actually indicates that this dotted line combines the hydrogen evolution reaction current density on platinum and hydrogen evolution reaction rate on zinc both these rates are combined on this dotted line.

Now if we increase the platinum area let’s see initially it was same area ratio this is platinum, this is zinc 1:1 area ratio, now if we increase this platinum area by threefold or fivefold then platinum, this is let's say this is 1:3 the area ratio would become 1:3, then the total number of hydrogen reaction on the platinum surface would increase, now if the total number of hydrogen reaction on platinum surface increases then the total current would increase, current density, exchange current density would not change, but the total current density total current would increase on the platinum surface for the hydrogen reaction, now instead of I0 since this is on the scale of current we can also indicate as capital I0 for hydrogen evolution on platinum surface this is capital I0 of hydrogen evolution reaction exchange current rather exchange current density we use exchange current of hydrogen on zinc surface, so if we see that the number of reactions are increasing on the platinum surface though the exchange current density will not change, but the total current density, total current corresponding to the exchange rate of hydrogen evolution reaction on this higher platinum area would increase, so that time this would be my I0 dashed hydrogen evolution on platinum this indicates the exchange current on the platinum surface if we increase the area then I'll see that the rate would increase.

Now the situation is the current density is here and this dotted line combines this the reaction rate of hydrogen on this platinum surface with higher area and this line, so this dotted line indicates combination of this and this, and this line indicates the combination of this and this. So now we see that the total current or the total current corresponding to the corrosion point increases with respect to this, so if we increase the area of the cathodic part we see that the corrosion rate on the zinc part would increase, why? The same current will be felt by the small area zinc, so if we increase the current, total current on the small area of zinc then my current density corresponding to the corrosion rate which is proportional to the corrosion rate on zinc surface would be then this I Corr divided by small area zinc, now if it is a small area zinc then the current density at this point for zinc would be much higher compared to the current density of zinc dissolution on zinc at this point this is much higher than this, so the corrosion rate of zinc would increase if we increase the cathodic area, so this is the area effect.

Now the same thing would be true if we have copper plate, this is the two copper plate now if we, this is, these two copper plates are fastened with steel rivet, this is the steel rivet, this is my iron steel is nothing but iron so the iron rivet is fastening copper plate. Now the same situation will prevail there, now here what is cathode here? Let's say this entire stuff is put it in seawater, now in this situation we go to galvanic series, and in the galvanic series copper is noble and iron is active, since copper is above iron in the galvanic series in seawater solution so copper will act as cathode, so what would be my cathodic reaction in seawater? The possible cathodic reaction is, this is my cathodic reaction and if this is my cathodic reaction so the anodic reaction would be since iron is active here, so iron will dissolve, this is my anodic reaction. Now if that, and here we see that the copper area is much higher than the anodic area or the cathodic area is much higher than the anodic area, so the same situation will prevail, what would happen? The rate at which the iron will dissolve will be much higher since the area of the cathodic part is much higher compared to the area of the anodic part, so in this situation the dissolution of this steel rivet will happen very quickly and this entire stuff will become very loose, now how to, so we see one particular phenomena that if area of cathode is greater than area of anode in a particular solution that situation is very bad then that time the anodic dissolution would be much faster compared to the situation where area of cathode and area of anode both are same.

Now the favorable situation where my control would be better on the corrosion rate, area of the anode if it is less than the, if it is more than the area of cathode, so this is one important observation, another observation is small area of anode and large, small area of cathode and large area of anode this is unfavorable and this is favorable. Now let's say I reverse the material if this is my copper rivet and this is my steel the plates become steel and the rivet become copper that time situation would be much better, why? Steel in the sea water iron will act as anode, copper will act as cathode but the area of the anode is much higher compared to the area of the cathode so the number of anodic reaction would be less since the area available for cathodic reaction is less and the consequence would be the corrosion of the iron plate would be much slower, still the corrosion of iron plate would occur but at a much slower rate compared to the situation where we have this, so the main point is we have to have a situation where the area of the cathode should not be more than the area of the anode, this is one situation, the same happens if we have the monel hull with a steel rivet there also the hull strength would decrease because there would be aggravated corrosion on the steel rivet because of this unfavorable area factor.

Now we have one more classical example let us discuss that part let's say we have a water tank, this is my water tank and the roof is also made of steel and this is mild steel, this is mild steel water tank and let's say we have water which is industrial water and that is let's say mildly corrosive to the system, now this tank can operate for a very long period even maybe more than 10 years or so and there would be definitely some corrosion effect because there is dirt of, there are dirts in the solution and all other affect and more importantly generally if we put a phenolic coating on the mild steel this coating, damage of the coating could be possible because always there are dirts and other things so there could be damage of the coating, and there could be the possibility of contamination of the stored water. Now if we think that let us make the bottom of this section, bottom of this tank with stainless steel in order to have less corrosion and so that we can have less contamination as well as very small corrosion rate or very low corrosion rate of the bottom, because the bottom part is always exposed to corrosive so let us change the bottom part, let us change the bottom part with stainless steel, this bottom part is made of stainless steel now, this bottom part is made of stainless steel and this is a basically stainless steel clad and here we have rest of the thing is mild steel and we see that, and since this is basically a contact between stainless steel with mild steel so we extend this phenolic coating up to certain distance and the bottom of this and here also we extend this phenolic coating just to avoid this galvanic effect at this zone since this is mild steel is anodic and stainless steel is cathodic as well as noble in the galvanic couple.

Now we think that this will function better because we have stainless steel at the bottom and this stainless steel corrosion rate is very small, very low in this mildly corrosive water solution but the situation is entirely different, after some day maybe after few months previously this used to operate for more than 10 years, now after a few months this section the joint section where we have mild steel and stainless steel joint, okay, that section there is a possibility of leakage, there is a possibility of leakage, why it should happen, and every time we have this situation, now the main point is we can see that whether the situation is due to some corrosive or oxygen, dissolved oxygen level or something or heavily corrosive action so we can do one experiment we can put mild steel, stainless steel and in stainless steel the same stainless steel we put water same water and then boil it, so we see the corrosion rate we don't see much of corrosion rate, okay, it's a very low corrosion rate, the main thing is since we are boiling it that time and we have we are basically taking care of oxygen, dissolved oxygen, dissolved oxygen will go out and there would be very less corrosion effect. Now, why this is happening? Now this phenolic coating always, there could be some a minut pores in the coating, very small pore, let's say very small pore, a very small pore which is there in the coating, this part let's say a very small pore, very small pore, or there could be a small crack due to operation, now if there is a small pore water or the corrosive can seep in and if water seeps in now we have, we are at the solution of the corrosive is seeing mild steel, if it sees mild steel and now the bottom part is exposed to the solution since there is no phenolic coating at the bottom and this section is having huge area and we know that if mild steel and stainless steel these are clubbed then mild steel will be active and stainless steel will be noble in the system, so the mild steel corrosion would happen and stainless steel corrosion would not happen. Now the, what would be the rate of mild steel? Since we have large area then of the cathodic area and a very small area which is exposed to the corrosive then this situation will prevail there again, so the rate of corrosion at this zone would be mini fold and gradually this will dissolve and there will be leakage, and this is also happening because we have large exposed cathodic area and a very small anodic area, now how would we protect it? The simple protection would be if we can extend this phenolic coating even and cover up the entire stainless steel bottom, see if we cover up the entire stainless steel bottom then we don't experience this phenomena of large cathodic area and small anodic area which is very unfavorable with respect to this galvanic corrosion, so the protection would be like this, so there are three examples we have discussed, and in case of unfavorable area ratios the corrosion rate of the anodic zone would be very, very high and then finally there could be failure in a very short duration.

Now we see that galvanic corrosion is definitely bad and we have to control it we have to protect system from galvanic corrosion we can have different mechanisms, okay, so what are those mechanisms or what are the ways we can protect corrosion rate or galvanic corrosion? One is let us see different ways of corrosion protection or the galvanic corrosion protection, one is choice of metals and alloys, we have to choose metals and alloys for a particular structure in such a fashion that they are very close in the galvanic series so that we don't have much of potential difference between this, between different metals and subsequently we don't have much of problem with the galvanic corrosion.

Now second is unfavorable area that means large cathode and small anode, this part unfavorable area that is to be avoided, that is to be avoided. Then third is use of coating, and in the use of coating if we simply quote the cathodic area exposing the anode surface we can have a very good protection, so coating, use of coating and always try to cover cathodic area even you can expose the anodic area if we can cover the cathodic area, so if we don't have cathodic area we don't have the problem of, we don't have the more of cathodic reaction that could have happen on the cathodic surface. Now fourth is we can have inhibitors which take care of corrosives or some ions, we can have cathodic protection, we can have cathodic protection. Now another position where we can experience galvanic corrosion, let's say we have a threaded joint these plates are, this is basically the threaded joint, now we have, this is the let’s say a screw or bolt, now in that case most of the cases the bolt material would have higher strength compared to the material which is being fastened. Now and the bolt material of course would be a different material compared to the material which is basically, which is threaded, which is fastened.

Now in this case how to avoid galvanic corrosion, because these two materials this material and this material would have a different compositions and there could be a possibility that this material is cathode or this material is anode, if this material is anode then the problem was much higher we have seen that steel rivet and copper plate so that case one possibility is we can use some nonmetallic sleeve in this zone to avoid galvanic contact, so if we use nonmetallic sleeve then we cannot have much of contact, electrical contact between the material between this bolt and the base material which are basically getting fastened. Now another thing is here also we can put rubber gasket, rubber gasket we can put so this way also we can protect so these are some of the protection mechanism or protection ways where we can avoid galvanic corrosion to a great extent.

Now we have been discussing about the problems with galvanic corrosion, now galvanic corrosion may be advantageous, let us see what are the advantage, the one major advantage is if we don't have galvanic corrosion then we cannot make dry cell battery, since we have this galvanic effect that's what we are going to have the benefit of battery, so battery one is cathode one is anode and that's what this potential difference between cathode and anode in that particular electrolyte gives rise to the electrical energy or the chemical reaction that is happening and chemical energy is converting into electrical energy and that electric energy is basically happening because the galvanic potential difference between the cathode and anode.

Second case as we have seen in case of electrochemical ways of protection we see that there is a route called, there is one particular route through which we can protect the material that is cathodic protection, and in cathodic protection we have two ways, one is sacrificial anode and one is ICCP which is impressed current corrosion protection or cathodic protection, so now let us see this onem, where we see most why we do galvanization of steel, in case of galvanization we put a zinc coating and the zinc access anode and steel act as cathode, cathodic reaction which is the oxygen reduction that happens on the steel surface and zinc will dissolve and by the way and when it dissolves that time it protects the steel surface, how? Let's say some part is broken if entirely this is covered no problem we have much better way of protection, but if something is disturb, some part is disturbed or broken then we have steel surface which is exposed and on the steel surface we have this reaction, we have this reaction so we know that if cathodic reaction happens on a particular metal surface that part is cathodically protected.

Now and when we have this reaction then zinc would dissolve and supply electron for this reaction, so this is my anodic reaction, so zinc is sacrificing itself and it's protecting the steel surface and this is giving rise to one particular mechanism for cathodic protection that is sacrificial anode. Now if let's say we use tin coating, this is steel and we are using tin coating SN and also in atmosphere tin is staying above steel in the galvanic series. Now if there is no damage on the tin surface this will function better than this, but if there is any damage now the situation is very different, now in this case steel will act as cathode and this part will act as anode and since we have a large area of the cathode then this part will be corroded at a very, very fast rate because of this unfavorable area ratio so the tin coating is not advisable and zinc coating is advisable, so this is one particular advantage of cathodic or galvanic corrosion since there is a galvanic couple and due to this galvanic couple zinc is corroding and protecting the steel surface. Another particular advantages cleaning of silverware, cleaning of silverware, how would we do that? Generally if we go to some person who makes ornament what he does he has one particular bowl and that bowl is nothing but the aluminum made bowl, now in that bowl what it does the silverware he puts in the solution and there is a solution which contains baking powder, and he hits it, it's basically a warm water, hot water and there he puts this silverware and the silver has a particular problem silver becomes dark or black as we use them, this black silver is nothing but the silver sulfide AG2S this looks back, now if we have this aluminum bottom and silverware now in the presence of aluminum, in the presence of aluminum this reaction happens, this reaction happens, now you see there is a galvanic contact between this and this, and this acts as anode and this acts as cathode so if this acts anode and this acts cathode so this will oxidize and this will reduce and the reduction product is AG which deposits back on the silverware, fine, so here you see this is reducing and giving rise to silver or the reduction reaction is happening that means AG+ +E going to AG this reduction reaction is happening and here aluminum releasing 3 electron going to AL+3, so due to this there is no silver loss silver again redeposits back and during this process all is there is a foul order which is just like a rotten egg, okay, because we have sulfuric H2S that evaporates because this one hydrolysis and the hydrolysis product is nothing but H2S that's what it gives a very foul order, okay, and this one will hydrolyze it will go to this H2S gas will go up and then it lead to a foul order, so this is the way silverware is cleaned and during that process we don't have any silver loss, let's say we scrap it with some scrapper, okay, that time this scrapping business would take care of this particular AG2S and we have silver loss but this method will always recover this oxidized silver and that oxidized silver will go to silver again, due to this reaction, so this is the cleaning of silverware and this is taking the advantage of galvanic corrosion.

Acknowledgement
Ministry of Human Resource and Development

Prof. Phalguni Gupta
Co-ordinator, NPTEL IIT Kanpur

Prof. Satyaki Roy
Co Co-ordinator, NPTEL IIT Kanpur

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Dilip Tripathi
Padam Shukla
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Badal Pradhan
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Shubham Rawat
Shikha Gupta
Pradeep Kumar
K.K Mishra
Jai Singh
Sweety Kanaujia
Aradhana Singh
Sweta
Preeti Sachan
Ashutosh Gairola
Dilip Katiyar
Ashutosh Kumar

Light & Sound
Sharwan
Hari Ram

Production Crew
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Puneet Kumar Bajpai
Priyanka Singh

Office
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari
Saurabh Shukla

Direction
Sanjay Pal

Production Manager
Bharat Lal

an IIT Kanpur Production