Indian Institute of Technology Kanpur

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On
Technology Enhanced Learning

Course Title

Environmental Degradation of Materials

Lecture – 20
Broad Subject: Different corrosion Protection mechanisms, electrochemical Ways of protection, Cathodic protection

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Today, we'll discuss protection mechanism and that to the electrochemical ways to protect metals or alloys in a corrosive medium. So today we'll start protection mechanism and that to electrochemical, electrochemical protection mechanism and two things are coming under this subject, one is cathodic protection, another one is anodic protection.

So before going to this electrochemical protection mechanism, so let us first see how many ways one metallic object or alloy object or structure can be prevented can be protected from corrosion, see in fact complete protection from corrosion is economically not preferred, so we will try to have some sort of mechanism where we can control the corrosion, rather the corrosion rate can be reduced to a great extent so that the metallic structure or the alloy structure can be used for a much longer period.

So let us first see how many ways we can have the corrosion protection, so this is different, different methods, methods of corrosion protection. Now you can have different protection mechanism, there are five broad groups, five broad groups, one is design equipment, design, second thing is change of metal, change of metal, then change of environment, then change of metal electrode potential or change of electrode potential, and then you have use of coating. Now our thing this electron, electrochemical protection mechanism is falling under this category so here we have two ways, one is cathodic protection, and second one is anodic protection.

Now in this particular lecture we'll discuss in detail about this two methods, but before that let us see how many ways we can see, what are the sub sections of this different main sections? Change of metal it can have four different sub sections, one is change of composition, second one is change of microstructure, for example change of composition one example is let's say you are considering, let's say you have the corrosion of inter granular corrosion of stainless steel 18:8 stainless steel, austenitic stainless steel, there if you reduce the carbon content below 0.03 percent with percent then we can definitely avoid the inter granular corrosion of austenitic stainless steel which is having 18:8, 18 with percent of chromium and 8 with percent of nickel, so change in composition can lead to have a bitter protection against the corrosion.

Change of microstructure, austenitic, ferritic, both have a different micro structural level, okay, so you can also have a different, for example if you have a quality structure, if you have a medium, let say mild steel with a carbon content of 0.4 where you have the mixture of ferrite and pearlite, so if you reduce the pearlite content then we are going to increase the corrosion resistance, so change in microstructure also helps.

And third one is elimination of, elimination of stress, let's say your material, the material under operation is having residual stress into it, inside the material then the most possible susceptibility, most possible cause of failure would be a stress corrosion cracking. So if we can remove that internal stress then we can avoid the stress corrosion cracking, so again a sort of protection.

And then we have introduction of surface compressive stress. So this is one more way, so if we introduce surface compressive stress then it would have inherent resistance against fatigue, so there is one more ways, there is one more way the material can fail if there is some tensile component that is the fatigue corrosion, so if we have this surface compressive stress we can reduce the tensile component part, so we can have little extra protection against the fatigue corrosion, fatigue corrosion or fatigue corrosion failure.

Now coming to this change of environment, it has also different parts, so let me put this change of environment singular here, change of, so by changing the environment where the material or the alloy system or the structure is exposed to, if we can change that environment by some external means we can avoid corrosion related problem. So there are different subsections, one is a removal of corrosion, we have seen that in case of zinc corrosion in HCL, if we have impurity then the corrosion rate of zinc increases, so if you can get rid of the impurity. Another case is if you can get rid of oxygen, dissolve oxygen, if you don’t have dissolve oxygen, then the corrosion rate automatically goes down, so like that so it can be either oxygen removal, second is moisture removal or it can be purification, let say that HCL doesn’t contain any ferric iron then the corrosion rate of zinc will reduce.

And then you can also have one more way, if you can remove the salt purification, under this purification you can have salt removal, so if you can get rid of ferric chloride percentage or ferric chloride presence in HCL so zinc corrosion rate will reduce.

And moisture, let say in a dry place or in wet place wherever you have moisture, so once you have moisture, if you have oxygen then this reaction can happen, and this is a cathodic reaction, once you have a cathodic reaction so you have to supply electron for this cathodic reaction, so electron will come from the corrosion of the metal object. So if you don’t have moisture even if you have oxygen then the corrosion problem, aqueous corrosion problem can be stopped, can be greatly avoided. So these are three ways where you can have a removal of corrosive. Second case is inhibitors, inhibitors some external agent can be added into the medium which will take care of those corrosives and this part will be taken, I will just consider this change of an electrode potential part, the other parts will be taken care of by Dr. Chaudhary.

So this is inhibitors, in the inhibitor part you can have, one is chemical passivator, chemical passivator, then you can have absorption passivator, adsorption, adsorpotion passivator, you can also have film forming passivator, even you can have vapor-phase passivator. So four ways you can have some external inhibitors which can introduce passivation on the material, so that the corrosion rate will be reduced.

Then you have change in operating variables, what are those? Operating variables, let say temperature. In general, if you reduce the temperature, if temperature was reduced corrosion rate will be reduced. Then second case is pH, as we have seen in case of Pourbaix diagram if pH is increased any potential also can be taken to the level of region to the level of formation of passive film, then increasing pH generally helps, so this is one and then you have velocity of liquid. So we have also seen from mixed potential theory, that if we increase the velocity generally the corrosion rate increases, but in case of active passive metal, after some critical velocity the corrosion rate suddenly drops. Now these are the three ways, so this is a change of environment. Then you have use of coating, so use of coating it can have two subsections, one is, the coating means application of some external agent or external film on the metallic object to have protection from corrosives, from corrosion, so one is metallic coating, then it can also have two subcategory one is cathodic, cathodic coating, and another one is anodic coating. So one case it will act as cathodic coating and another case it will act as anodic coating.

And then you have nonmetallic coating, non-metallic coating there you have different subcategories, one is a vitreous coating, vitreous coating a sort of amorphous coating on the material, and since amorphous material does not have any grain boundary, so it gives automatic protection against corrosion, because the grain boundary regions are the regions which are vulnerable to corrosion attack. Then you have cement, then you have paints, organic paints, in case of car bodies we generally put organic paints. Then you have chemical conversion, so this is the entire picture of corrosion protection methods.

So now let us concentrate on this particular part, particular part will concentrate. So let us start with the cathodic protection, so let us start with cathodic protection and this electrochemical protection mechanism is nothing but the change of electrochemical, electrode potential, so in case of cathodic protection before we start let us see what is cathodic reaction, so let say this is my, this is my cathodic reaction MN + ion is taking Ne numbers of electrons and going to M, this is a cathodic reaction. Now in this reaction let say if we supply electron and before supplying let's say this has reached equilibrium, let us say this is a equilibrium reaction where cathodic reaction is the forward reaction and anodic reaction is the backward reaction and that is basically let us say T and P, constant temperature and pressure this reaction is taking place, so we write without changing the temperature and pressure, if we supply extra electron from outside extra, extra electron from outside to this system to the left hand side of this reaction so equilibrium will be broken and it will reach to a different equilibrium state so in order to reach that since we have extra electron so this forward reaction will happen at much faster rate, if forward reaction happens it means that the metal ion has higher tendency to go into the metallic elemental metal so when this elemental metal formation is taking place it means that the reverse reaction is taking place at a much slower rate, and this is faster rate this forward reaction which is the cathodic reaction, so that means if we can supply electron from external source to this left hand side we see that there is a sort of deposition rather than corrosion or dissolution, so this is exactly the basic basis of cathodic protection. The basis of cathodic protection is, one is supplying electron, supply electron from external source. And supply electron from external source means if you consider with respect to current, because we can supply electron by applying the negative current. And here if you consider this way is basically ia small ia which is anodic current density and this reaction is basically IC, so that means if we can supply negative current to this system, so I will have more and more cathodic reaction, anodic reaction which is basically nothing but the corrosion reaction reduce, the rate of that reaction will be reduced to a great extent, so this is supply of electron or negative current, supply of negative current to the system or supply of IC or cathodic current this small ic is basically cathodic current density we are supplying some cathodic current and which is divided by the area of the cathode region that means it is basically converting to cathodic current density.

Now another thing is if you see the protection principle we are actually trying to make the metal object which is to be protected a cathode, so making the metal object a cathode, so if you have a metal which is to be protected it has to be made cathode, so how can we make cathode? So one way is we can connect it to a negative terminal of a power source, DC power source and the other positive terminal is connected to an auxiliary electrode AE, AE means auxiliary electrode. So since we have connected into the cathode part and we are concerned with the protection of this metallic object M, so since we have corrected to cathode part so it has become cathode, so once it has become cathode, the cathodic reaction will occur on this surface and anodic reaction will occur on this surface, so the cathodic reaction happens on a particular object metallic object so that part is cathodically protected, so this is cathodically protected, because of cathodic reaction on cathode surface.

So now you see whether we are satisfying these two things or not, first thing is supplying electron from external source and in fact we are supplying, we have connected it to negative terminal, so the positive current which is I is actually flowing from positive to negative side and the negative current is basically, or the electron is flowing the other side from negative to a positive terminal, like this it will move, electron will move like this, current will move like this, so that means we are supplying electron to the metalic object, first thing is done. And second thing is making the metal object a cathode, since we have connected this metal object to a negative terminal we have made it cathode, so cathodically protected because of cathodic reactions on the cathode surface, so this is nothing but cathodic protection.

Now let's see what are the, some of the points associated with cathodic protection. First point is this method is widely used to protect steel structures or any structure such as pipeline buried in soil or immersed in water tank, so protection to pipeline and that too immersed in water or what? In water, then water tank like that where you have intimate contact between the metallic object and the electrolyte. This intimate contact is essential to have a cathodic protection to go for cathodic protection. And second thing is, this method is very, very useful if you have a barrier coating on that metal object, so that case let's say you have a barrier coating so many times it happens because of transportation and other things, some of the parts of the barrier coated part can be exposed, let say this is my metallic object and this is my barrier coating. Now let say the small part is exposed because of some damage, so that damaged part will have very good protection if we have a cathodic protection given to this system, so it means that the coating, in presence of coating this method is very useful, this is cathodic protection.

Now it can prevent both general corrosion or localized corrosion let say pitting or crevice, so it can give import protection towards general or localized, protection to localized general or localized corrosion, then as I have mentioned that intimate contact between the metal object which is under corrosion protection by cathodic means and the electrolyte if you don't have that contact then that part cannot be protected, so that is to be taken into consideration, so intimate contact is very important. And then there could be a problem of shielded, there could be a problem of shielding, let say the shielded region or let say the inner member, example is inner member, inner member of, in a bundle of inner member, in a bundle of pipes.

So for example you have let's say this is a bundle of pipe, so this pipe is moving like this, so this if you have a cathodic protection then this inside part will not have any protection, because this inside part is getting shielded by the outside region, outside pipes. The shielding pipes, see what is actually shielding, let's say we have, we are going for a protection of water tank, we are going to have the protection of this water tank, this is electrolyte, now that protection is done from external power source, external DC power source, so that means if we would like to have this metallic object which is to be protected from cotton, so we will connect this metallic object to the negative terminal of the power source, so we will connect it to a negative terminal of the power source and we will also have inert auxiliary electrode, positive terminal is connected to inner auxiliary electrode, so I have negative current is going through, this electron is going there and the circuit is like this the current is flowing like this, this is current and that current is going all direction to all the parts of this metallic object but here we have a pipeline, so now in order to stop that water flowing out which only put a stopper, metallic stopper. Now current is flowing all the direction and the external circuit is completed through this way it will, current will go like this and then flow back like this, but the thing is when the electron is flowing like this if we don't have this, electron can flow out like this and it can have entire system, entire system together with this pipeline will be part of cathode and then it can have a cathodic protection, but since we have put a metallic stopper it means that we are basically short-circuiting these two parts and metallic stopper is giving a very less resistance for electron flow, so instead of taking this path which has a higher resistance this electron will take the least resistance path which is nothing but the stopper. So electron instead of going like this, electron will flow like this, so electron will come to this other section through this stopper, so what happens? Wherever electron flows that part will be cathode, wherever electron doesn't flow that part cannot be part of the cathode.

So now you see initially if you don't have this stopper, metallic stopper you can have the entire system under the cathodic protection, but once you have this stopper, this lower part, this part is coming under cathodic protection. So this part is basically getting shielded by this stopper, so that is the entire mechanism of shielding, so the shielding is basically trying to prevent that electron to flow out into the system and this part will not be under cathodic protection, but initially the design, this power source is designed such a manner that the lower part is also will be protected but actually we are not saying any protection to the lower part, only this part is getting protected. So the actual function what we have thought of having that is not met, so this is a case of shielding, here also if you have connected it to negative terminal, if you have connected it to negative terminal auxiliary electrode, and in an electrolyte so electron will flow from the outside, outside section electron will flow the inner part is not getting any benefit, so inner part is basically getting shielded by the outside part, so we have to take care of the shielding in order to have the proper protection due to cathodic, this cathodic mechanism, this proper cathodic protection.

Now once we have this knowledge, let's see where we cannot use cathodic protection, once this is known, we can easily consider those cases where cathodic protection cannot be employed, so this is the sort of cathodic protection where we can apply cathodic protection and now where we cannot apply cathodic protection, cannot apply cathodic protection, so once we have this general knowledge then we can decide, first is location above water line or the part which is not in the electrolyte which is not in contact with electrolyte so that location above water line because there we are losing intimate contact between electrolyte and the metallic object.

Second thing is where we have non-conducting electrolyte, non-conducting liquid not electrolyte, non conducting oil or liquid, so since here we cannot have any charge transfer reaction because in this case the intimate thing is the circuit should complete a current should come like this and flow out like this, so we see that conducting oil or liquid this cathodic protection cannot be applied. Now one small point here, with respect to the first point we have to have cathodic protection where we have intimate contact between the electrolyte and the metallic object which was under protection. Now if you see this picture, here we have connected this metallic object to the negative terminal so we have made it cathode and this is auxiliary electrode is the anode. Now you see the current is flowing through this, through this external circuit and coming like this, now this is under protection, the another way to understand that which part of the metallic object is protected we have to see that where the current is entering into the metallic object, here the current is entering into the metallic object at this position, this position, this position, all the surface, outer surface is getting this current which is entering into the system, so that external current we have to always see another way to see whether that part is protected or not, that is where, which the part of that object let say this is a big object, so this is a big object which is to be protected or cathodic protection we have to see where the current is entering, external current. Now we have to see that current is entering like this, now if current is entering throughout the outer surface but not entering into this part so this part will not be under cathodic protection, so this part can have still the corrosion can continue on this part and the other part where the current is entering will be protected, so this thing will come into picture when you will see, that’s why we need to have a sort of enclosure by some metallic anodes to protect the metallic object, and this is to be taken care of, this is very important because we have to see the main thing what we are trying to say that we have to see that where the current enters into the metallic object that part will be protected.

If we have the screen area or shielded area, like in case of example that have given in case of water tank with a pipe line attached to that water tank, the pipe line will be not under protection because of that shielding or because of that small metallic stopper what we are using just to stop water flowing out through the pipe line.

Now the shielded part, we have to check the shielded part if we have some part which is shielded that section we should not go for any cathodic protection. And then fourth one is though we are basically having cathodic protection to protect the object from corrosion, but if the corrosive media is very strong or extremely corrosive environment, we should not go for this cathodic protection, because that case cathodic protection will not be economically viable process or economically, it will not be economically cheaper process, so we have to go for something else. So these are the four sections where we cannot go for any cathodic protection we have to think of some different ways to protect those substructures under these conditions.

Now let us come to the principle, though we have talked about the principles, I've talked about in this section but let us explain this part with respect to the mixed potential theory, since we know right now, by the time we know the mixed potential theory.

Now coming to again this E versus log I diagram where let say this is my I0 for that metal and this is my I0 for the cathodic reaction, let's say the cathodic reaction is hydrogen evolution so we have to find out the new point where I see that the rate at which electrons are generated because of anodic reaction will be equal to the rate at which those electrons are getting consumed because of cathodic reaction happening on that metal surface, so this is let say M N+ + NE, M going to M+ +NE and this is H + E going to 1/2 H2, so this is cathodic polarization, this is anodic depolarization. And we have also learned that cathodic polarization corresponds to IC and anodic polarization corresponds to IA, and at this point IA = IC with a negative sign because this two currents are having the opposite direction, here this is IC direction and this is IA direction, so that's what at this point the magnitude of these two currents value, current will be same with an opposite sign and this is = I Corr, so i small ia is nothing but I corrosion at this point.

Now we have said that we have to supply extra electron from external source, this extra electron can come from one external source or it can come from another anode material which is in connection with this metal object, but if we consider this case only here we are having some external power source which is the DC source, so there if we apply this negative current or negative or the electron, electron supply means nothing but the supply of negative current or the IC. See if we increase the electron supply into this, so at this point we have equilibrium so this equilibrium will be broken and since we are supplying electron to this so we have more and more cathodic polarization, see if you have more and more cathodic polarization so this line will be extended, so if we supply some extra electron from this point it will have cathodic polarization, so I will let's say after some time I am staying here, if I stay here because of this extra current flow negative current flow or electron flow, so what would be the corresponding anodic polarization? So we have seen that if we have this is my polarization over voltage and this is my log i with respect to a singular reaction, let say this is N++ Ne M reaction if we consider this which is cathodic so this is my cathodic reaction polarization line which is nothing but this is IC this is beta C log of IC/I0 and corresponding, if we consider the reverse polarization it is my over voltage, anodic over voltage = Beta A log of IA/I0 and this is my zero over voltage and this corresponds to I0, this is with respect to this, but here we have this and another different cathodic reaction, so if I supply extra negative current, if I supply extra negative current which is IC here, so then this polarization will move to the negative side. If I move to the negative side, what would be the corresponding anodic polarization, let's say I am here, so corresponding anodic polarization would be at this point. So what would be my corresponding, IA corresponding IA would be this one. See if I stay here my IA would be equal to I0, but if I come here with a negative polarization because of negative IC, I see that IA is decreasing, if IA decreases which means that I have much lower rate of this forward reaction. So if I am here, so corresponding anodic current would be this one, so if I don't do anything the system will remain here my corrosion rate will happen at this rate, at the rate = I corrosion, now if I take the polarization to the negative side because since we are supplying extra electron to the system so automatically I will go to the negative side, so I remain here after with respect to a certain amount of electron transfer, electron supply from the external source to the metallic object, my corresponding current density for the metal dissolution is this one, so here I was, now because of this my current density for the anodic current has reduced. So if that means this is let say IA - is less than, less than I Corr because this is in log scale, so what does it mean? If this has reduced the anodic current density is reduced, hence it is clear that my corrosion rate has reduced. So this is the concept for cathodic protection, so we have to take the polarization to the negative side. So if I take the negative side polarization because this is my reference point, now from this I go when to negative, I am going to the negative direction and correspondingly I am reducing the current density corresponding to the metal dissolution reaction. Now like that I can take it to this level, further I am reducing my corrosion current, density or anodic current density I can take it to this, but if you take it to this point and this point what is the difference?

Now let me put some values here, let say this is my I0, so this correspond let say 10 to the power – 10, now gradually if you reduce 10 to the power – 9, -8, -7,-6, -5, - 4, and this let's say -4, IC is - 10 to the power – 4, and here this is let say 10 to the power – 9, so what would be my applied current? Since we have seen that I applied is nothing but IC – IA, I am putting a mode sign because we are just taking a difference between IC and IA which is nothing but I applied, so as we go down my I applied is increasing to a great extent, and then if I applied increases what does it mean? I have to supply huge current to the system, and huge current means? A lot of, it involves lot of money because we are spending lot of power.

Now like this so it's not advisable to go for a large cathodic protection so that I can have also economic part should be looked after, so that I can also have a reasonable money, spending money to the system at the same time I will have a reasonable corrosion protection, so that I can have a longer duration of operation with that metal part.

Now if you see that like that if we go along this if I can reach to this level, let me put it in red color, if I can reach to this level, so if I supply IC, if IC is to be at this point corresponding IA would be I0, so corresponding with the red one IA would be equal to I0, I0 is what? I0 is the current density corresponds to the non-corroding system, so if I can reach here I will get complete protection, so if I can reach to the level of, if I can have this much, this much, this much, if I can reach to this this much level of cathodic polarization I can take the anodic current density to this I0 level and I will get complete protection. But this is again not advisable, because you see again I have to supply huge current to have the complete protection this is also not advisable, because it involves lot of money because we are supplying huge current.

Now if I can, we can also go further below so then what I am getting if I reach there so in fact that case I will have the reverse reaction, because this side is the cathodic polarization, but this is not advisable there are one reason is huge current supply, and second reason is, in case of amphoteric metal like zinc or aluminum there will be further corrosion, because this is taking the potential below this, this is called cathodic corrosion.

Cathodic corrosion, there is no surprise because of making the metal, if the cathode, since here is the cathodic reaction is going on the reverse reaction will take place, so since we are making it cathode that time because of this amphoteric nature of this two metals complex ion can form in the system either acidic or basic medium and they can corrode instead of getting protection, so that's why it is called cathodic corrosion.

We will discuss it, let us take it to the next level of discussion and that too I will consider in the next class. Thank you.

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