Indian Institute of Technology Kanpur

NP-TEL
National Programme
On
Technology Enhanced Learning

Course Title

Environmental Degradation of Materials

Lecture – 01
Broad Subject: Introduction, Basic Definition of Corrosion

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We start a course on Degradation of Materials. The course name is Environmental Degradation of Materials. So series of lectures will be taken on this topic. And I am K. Mondal, I am an faculty at Material Science and Engineering Department, IIT Kanpur. And this course is under National Programme on Technology Enhanced Learning, which is in short called NPTEL.

And in this course we'll be concentrating on the degradation mechanism of materials when the material is exposed to environment and also we would be looking at the characteristics of the degradation of materials, and we would like to see their different forms of degradation as well as their implication on economics as well as economy, on the economy on the safety of the equipment or the process when the material is undergoing degradation. And when the processes that would be involved will be physical in nature or chemical in nature or there could be a combination of mechanical effect or there could be mechanical effect as well as chemical effect, so all those things will be covered.

And we will also try to cover all sort of materials because we know that there are four major varieties of materials, metals and nonmetals are the major groups, and then we have, in the nonmetal we have polymers, we have ceramic, and also we will be considering composite which is mixture of two or more phases and those phases consist of metal nonmetal, or metal-metal, and the kind of effect would be considering which will lead to degradation, which could be a mechanical, heat, or radiation or chemical action of chemical reagents like oxygen or moisture or acid all those things will try to cover in this particular course.

And so, what would be the broad essence of this course that would try to see a mechanism of material degradation. Then we would like to consider characteristics of material degradation. Then try to find out what are the different forms of degradation. Then we'd also try to find out what are the reasons, reason means we would like to see that what are the factors, that factors guiding degradation. Now in this also would like to once we know the mechanism

characteristics forms and reasons, finally we would like to try, we would like to see what are the control mechanism, control processes, control processes so that any degradation will not be good for practical application, so we would like to see that how we can control that degradation so that the material can function for a longer period of time.

Now before we come to little more about degradation, let us see what are the things will be covered in this particular course, mainly the corrosion and oxidation of metals and alloys, those are actually example of material degradation, those part would be covered in detail. And the other things by which degradation can happen that is one is wear or radiation those things will touch up just, but we will just see in brief, but the main consideration in this course would be corrosion and oxidation of metals and alloys and the prevention mechanism.

Now if we see the course content, now in the course content it will start with the definition, introduction, where we would consider definition, then we would like to see the need for studying this particular course, introduction. In the introduction we will see definition, different forms, then would like to see cost of corrosion, and then would like to briefly see the electro chemical nature of degradation, which are basically mainly corrosion and oxidation. And then what would be our aim for this particular course.

Then secondly, we'll start with thermodynamics of degradation. So in the thermodynamics we'd cover what are the processes that will be happening at the interface, so processes at interface, then we would see free energy consideration to understand the degradation, rather to understand whether a material would like to go for degradation or not? What is the driving force? Then we would like to consider EMF series, because in corrosion, EMF series would be very crucial. Then we would like to see important reactions which could be in aqueous medium or in gaseous medium. For example in case of oxidation, we would discuss what would be the reaction of the metal with oxygen or gaseous oxygen. And in case of aqueous solution, would like to see what could be the reactions that would be happening at the interface between the metal and the environmental species. For example, hydrogen, ion or dissolve oxygen or moisture or it could be a different metal caton if those are present in the solution what could be the effect of those different metal catons on the degradation effect of, or the corrosion effect of the metals and alloys.

Then we would see a reference electrode cell potential a reference electrode, and then would also try to see pourbaix diagram to see that at particular pH level, and potential level what could be the phases that would form on the surface of the metal in contact with the environment and this is nothing but E versus pH diagram potential versus pH diagram. And this is mainly considered in case of aqueous corrosion.

Then we would see the kinetic of corrosion, we would see then kinetics of degradation, it could be oxidation, kinetics of oxidation, or the kinetics of corrosion. And there we would like to discuss mainly the current density, then we would like to discuss the rates. Then one important issue in corrosion is exchange current density. We would like to discuss the polarization. And finally we would like to see what are the experimental techniques, so the experimental techniques would allow us to find out what would be the extent of polarization, what could be the current density of different polarization, for example cathodic, or anodic polarization.

And then once we understand these issues we can get to the mixed potential theory. Mixed potential theory, which actually binds kinetics of degradation and thermodynamics of degradation, and this is the advanced theory in order to understand the corrosion of metals and alloys.

Then we would also see whenever and then once we know the mixed potential theory we can understand many of those corrosion effects from that mixed potential advanced theory and then would go to passivation. Since we know that many metals when it reacts with the environment it forms a surface film, for example iron, it forms ferric oxide on the surface, if we come to chromium, chromium forms chromium oxide on the surface, and that chromium oxide gives a protection to the metal, because the film which is actually a passive film that is forming on the surface, and that demarcates, or that prevents that environment to further react with the metal. The one particular example is stainless steel, 18/8 stainless steel where we have 18 percent chromium, and a 8 percent nickel, and in that since we have 18/8 percent chromium that chromium forms a chromium oxide surface and that passive hits the iron or stainless, that gives the stainless property of the steel. Then once we understand these issues then we will discuss different forms of corrosion.

And in the different forms of corrosion, we would also discuss a major discuss, what are the different factors, those will affect corrosion. For example, we can think of factors like the stress factor, we can think of the impurity factor, we can think of the presence of oxygen in the environment, we can think of presence of impurity in the environment, or conductivity, or the salt content in the environment, those factors will definitely guide or definitely affect the corrosion of metals and alloys.

And then we'll talk about, and in the different part we will talk about corrosion measurement. Corrosion measurement and failure analysis, since once we know different forms of corrosion and different factors then we can come to this corrosion measurement and failure analysis. So the corrosion measurement and failure analysis, in this case we would discuss different test methods, different test methods and of course we would also try to see the test methods are either field exposure test or electrochemical test, so it could be field exposure test or plant test or it could be electrochemical test.

Now once we know the corrosion measurement and failure analysis then we can go for protection mechanism or control mechanism. In the corrosion control, then corrosion controlled will be discussed that actually gives the idea that how to go for protection of metals and alloys in a particular environment for a particular specific use, and this has five different segments, one is it could be materials, material selection, then we have design of equipment, then we can have change in environment. For example change in environment means, environment we have dissolve oxygen so if somehow we can think of some mechanism by which we can get rid of that oxygen then corrosion rate can be reduced to a great extent, so that kind of change in the environment, in the change in the environment we can also think of adding some external agent, reagents, for example inhibitor which will take care of the corrosion, which will reduce the corrosion rate to a great extent. Then we can think of electrochemical ways of protection which

are mainly cathodic or anodic protection then we can also think of coating, so we'll discuss coating.

Now once we have this all the topics till now and those topics we'll be covering metals and alloys, but at the same time we would briefly discuss the corrosion of or the degradation of the other materials like polymer, composite or a ceramic material, but that would be very brief, but mainly the discussion will be concentrating on the corrosion of metals and alloys.

Now once we have this things, then we'll discuss oxidation or high temperature oxidation, high temperature degradation. In the high-temperature degradation the main discussion would be on oxidation. Then we would also discuss liquid metal corrosion, and then of course hot corrosion. In the oxidation, we would like to see again the thermodynamics as well as kinetics of oxidation will be studied, will be discussed and there also we will see the what are the protection mechanism or the protection routes we can employ in order to reduce the oxidation rate of a particular metal and metal or alloy in a particular high temperature application, so that the operation can be carried out for a longer duration.

And finally we would definitely conclude by seeing what could be the effect of this material degradation on the society or on the industry, so this are the course content in brief. Now let us get into the first part which is the introduction. Now when we start talking about material degradation, we need to define it, and we need to also know why do you want to study that, this two things are to be needed first. First, let us start with why do you want to study? So why to study degradation and what to study, and then of course how to study? So if we answer that then we would have the purpose of this course, or purpose of studying this particular analyzing the degradation of materials. Now if we come to see the cost that is incurred by any country towards the protection or prevention of material degradation we have some number and that time we would be able to see, we would be like, we would appreciate that it involves lot of money. For example, few data if we see the cost of corrosion in India is about 5% of total GDPA of our country. So the 5% is, I have one rough data, the cost of corrosion that means the corrosion related effect like the prevention route, prevention mechanism or prevention of ways we think of to operate that particular material for a longer period or there could be loss of material or there could be replacement of the material due to the degradation, so that is around 2 lakhs crore. So 2 lakh crore money, rupees 2 lakh crore is the expenditure of India towards corrosion control, or towards the loss that we, or loss or protection route we employ for protecting for this, towards this degradation of materials.

Now in case of US, one data it says that in US it's the cost is about, cost of corrosion is about $260 billion, now if we see this number that means we need to worry about it, and if we consider by different segments where we have say this corrosion problem, in case of US data it says that a drinking water and sewer system that involves maximum cost which is around $36 billion, so that means it is actually, involves lot of money and then forget about money we have, if we have money then we can take care of it but it also involves lot of damage.

Now if we come to see damage, for example if a person has gone for prostate replacement, let's say bone is broken and there somebody replaces and that bone is replaced with a biomaterial, let us say the titanium alloy and that rod is fitted in order to give strength to the, rod is fitted in

the place of that break or the dislocation of the fracture and if that rod prematurely fails then that person can even die, okay, there could be failure of bridges, there could be failure of airplanes, because of corrosion, so that is the loss of human life which is more important than the loss of money.

Now if we come to see what could be the direct cost and indirect cost. Then in case of direct cost we can see that in US data 98, and the data is taken from www.corrosiondoctors.org, so source is this website and that data shows that in infrastructure, infrastructure it involves around $22.6 billion. And then in case of utilities, utilities it is around $47.9 billion, and then transportation it is around $29.7 billion, like that we have in case of production or manufacturing it is about $17.6 billion and in government thing and then total is coming about around $137.9 billion. Now this direct cost involves it could be what are involved in that expensive materials which can Katter corrosion for a longer duration and which can be operated for a longer duration.

And then we have over design, let say one particular metal object is going through a continuous or uniform corrosion that means all throughout the sections we have uniform dissolution, so that time in order to operate that material for a longer duration generally the design criteria that is taken that increase in thickness of that material, so that increasing thickness of the material would also involve a lot of money.

Then third is cost of repair, or cost of, or replacement, cost of repair or replacement of material. Then fourth is employment of anti-corrosion means. So anti-corrosion methods or means, so these are the main part which would lead to the direct cost in corrosion. Then we can also think of indirect cost, in case of indirect cost and that time it also, it's around close to around $275.5 billion so it also involves lot of money and what are the issues that involve, that are involved in the direct cost, one is cost of labor, then we have loss of productivity, let say one particular material needs to be replaced because it has gone through a lot of corrosion, so that replacement time in the replacement time, the production needs to be stopped, so there is a gap, there is a loss of productivity. And then this is because of delays happening due to replacement, due to failure, so those are coming up under this particular, but these are basically the direct reason. And now this delay is leading to loss of productivity, then it also involves cost of equipments which will be used for corrosion related activities, so those are coming under indirect cost, so we see that, if we don't understand this environmental degradation materials we cannot think of some sort of protection mechanism or protection methods to have a control or to reduce this amount of money that is spent on corrosion, so we need to study this.

Now coming to the definition part, if we come to see the definition of degradation, in general it says that the loss of performance, loss of performance of an engineering system, and this loss of performance can be related to these parameters, one is there could be loss of strength, loss of mechanical strength, then loss of efficiency, then loss of lifetime, then loss of appearance. Loss of appearance means for example if we go for ornaments if that is corroded that the ornament becomes very dull looking, so that is actually, that means the loss of appearance, then it will also involve a wear and then there could be expensive control system, expensive control, and there could be a routine checkup, so those involve the loss of performance, and that is actually

by the loss of performance of an engineering system, and engineering system it practically involves materials, so that is the definition, the general definition.

And when we consider degradation and there could be any natural phenomena that can be involved in the degradation. So now we see that what could be the losses, it could be mechanical strength, loss of mechanical strength, it could be appearance, it could be loss of material. Now we need to see what are the environmental, overall what are the natural things that can lead to degradation? If we see a material, if we look at this material let say this is my material, this material can be used on the surface of the earth crust or it can be used inside the soil, or it can even be used in the normal atmosphere, so if we make a segment, if we make a segment, now in this segment we have, one is soil and it can also involve aqueous environment. Aqueous environment means let say seawater application, some material used in seawater application that involves aqueous environment and let say the pipeline, let's say one pipeline is laid just below the articles in the soil that involves soil corrosion, so in that case we have several factors. Several factors for example temperature, temperature then acidity, then partial pressure of oxygen, we can also have presence of chlorine, we can also have the presence of bacteria, so in the soil due to these effects corrosion can increase, then in the aqueous environment the effects are even now temperature then pH level, we can talk about partial pressure of oxygen or we can talk about, here we talked about, here we have partial pressure of oxygen, here we talked about dissolve oxygen, then we can think of presence of chlorine or presence of any other metallic ions. For example ferric ion if it is present in HCL then the corrosion of zinc increases. Then we talked about flow velocity, then we can also talk about conductivity. So conductivity of the aqueous medium would guide the corrosion.

Then this is the surface, and in the environment we have, in the atmospheric condition we have air and gas presence, temperature, then of course humidity, partial pressure of oxygen, salt content in the environment, salt content all would definitely affect the corrosion rate or corrosion, then we can also think about the radiation effect, radiation effect or even sunlight, for example in polymer due to the effect of radiation there could be huge degradation of polymer. So these are the common effects which can affect the materials degradation.

Now if we come to see that whenever we talk about material degradation, we would see that this degradation is actually a very, very natural phenomena, because if we come to see the thermodynamics of this material degradation we would always see if the material degrades that actually decreases the energy of the system. So if anything which changes the energy towards the negative side, that means if there is any decrease in energy that process is more natural than the increase in energy. So for example one case, let us say in case of corrosion, in case of corrosion of iron if we consider, if we consider corrosion of iron the first thing if we see that what is the source of iron, source of iron in our environment natural sources iron ore, okay. So we have iron oxide, hematite, magnetite, so those are there which contains iron and that iron is taken out from that hematite or magnetite by refining route. Refining and then once we do go for refining then we can make pig iron, then we can go for steel making, so actually purification, so this purification would decrease the carbon content of pig iron and it goes to the steel production even we can go for pure iron making, pure iron we can make and this involves melting. So we see that all this process and it involves lot of energy, so energy consumption. So this energy consumption involves in this entire process from iron oxide to

pure iron, because this process actually if we see from this to this it involves change in energy in the positive side so we have to supply energy in order to make iron from my iron oxide.

Now if we have iron block in normal environment, we will again see that if we have a block like this iron block like this, we will again see that there would be gradual corrosion, so gradual loss of material, okay, so the block is, thickness is reducing and all the side the thickness would reduce. So finally from there, from that point onwards your thickness is reducing and finally if you keep it for a longer duration it will convert to, this is iron, it will convert to, again this, so we see that this process when iron is oxidized that involves lowering of energy. So actually it has a natural tendency to go to the iron oxide again and this is actually corrosion which takes the iron to iron oxide. So now we see that this is a natural process the corrosion is natural process.

Now when we talk about corrosion we need to see a proper definition of corrosion, so we have talked about the degradation, now let us see the proper definition of corrosion, so definition of corrosion there could be practical definition, practical it says that the tendency of a metal to revert back to its native state, that means iron goes for change to iron oxide.

Now if we come for the scientific definition that says that it is an electrochemical degradation, electrochemical degradation of metal, if we consider only with respective metal, metal as a result of reaction with environment. Now the key factor is electrochemical nature, so the corrosion scientific definition of corrosion involves electrochemical nature, what do you mean by electrochemical nature? Now electrochemical nature means it's actually involves the transfer of electrons, okay.

Now if we consider a zinc rod which is dipped in HCL which is acid and let's consider that this acid is very pure in nature, that means and also we consider that this acid does not contain any dissolved oxygen. If it does not contain any dissolved oxygen, if we come to see the product that is coming out due to the reaction with zinc and hydrogen and HCL, we would see that the reaction would be, this reaction would happen. Now in this reaction, but before understanding this reaction the first thing, the first observation would be there would be bubble formation on the surface of zinc rod, and if we analyze this bubble we will see that this bubble is nothing but hydrogen gas. Now if we see this reaction, now if we break this reaction into two halves, we will see that zinc goes to Zn++, and H+ goes to H. Now let say 2H+, and how we come from, how we would be able to go from zinc to Zn++, so it has 2 electrons should be taken out from zinc, so that it goes to Zn++ and for this process if we add two electron here then it would go to this product which is 2H. Now this 2H will combine and then form H2 gas.

Now in this process if we see carefully that this process it actually an oxidation process or we can also see that this process we can also define it as anodic reaction, so this is anodic reaction, why? Because two electrons are taken out from zinc, zinc atom and it goes to Zn++ iron. Now whenever we have Zn++ iron that means from the zinc rod Zn++ iron is coming out that is the only source of Zn++, so Zn++ iron are coming out from zinc, and that means there is a loss of mass, there is loss of mass from zinc rod, a loss of mass of zinc rod that is happening because of electrons taken out from zinc, so that means it is an electrochemical reaction.

And same thing we need to satisfy, the mass conservation of charges since two electrons are taken out these two electrons will be consumed by 2H + iron, and this H+ iron is coming from the HCL acid, because HCL is acid so you have the pH of HCL acid would be less than 7, so we have lot of H+ concentration, lot of H+ irons that are present in the solution, so this 2H+ will consume this two electron and it will go to H2 and this is actually reduction process, and this is also we can say that it's a cathodic reaction. Now this is also electrochemical reaction.

Now if we consider these two reactions then we see that if we combine these two we'll get to this. So the final reaction actually it involves two electrochemical reaction, one is anodic reaction, one is cathodic reaction. And this is also termed as one half cell reaction and this is also termed as one half-cell reaction. And these two half-cell are combining each other and then forming our complete reaction is happening and this complete reaction leads to zinc chloride formation, and this lead to corrosion or degradation or the mass loss of zinc rod.

Now if we blow it up we'll see that if this side zinc iron comes out so here we have a small mass loss and this electron, two electron, this two electron would go, this conductor will conduct this two electron extra electron these two electron it will involve two half-cell cathodic reaction, so that means it is an electrochemical reaction and it involves two half-cell reaction and also it is in total its electrochemical degradation. So this means the electrochemical degradation of metal, so whenever we consider electrochemical degradation we must consider these two half-cell reactions and there could be many half-cell reactions we would come to know in consecutive lectures. So we see that there are two half-cell reactions and also it involves those reactions those half-cell reactions are happening on the electrode on the metal surface and this joint we have oxidation reaction or anodic reaction that is where this is called anode, and where we have cathodic reaction that part is called cathode.

So we see that there are four basic components for any electrochemical reaction, complete electrochemical reactions. One is anode, second one is cathode, then we see that there could be, there is iron movement in the electrolyte, so if we don’t have this iron movement so one hydrogen iron is taking one electron and going to hydrogen atom, so the next hydrogen iron would come here so that there would be always migration of irons in the electrolyte so we need one electrolyte. And finally we see thus these two electrons which are forming due to oxidation reaction those two electrons should go to the zone of cathodic reaction and there would be conduction of these two electrons, so we need a conductor. So these are the four components of any electrochemical reactions and always we will see any electrochemical reaction in the future lecture we would see that every time we have four different, four components in that particular electrochemical, complete electrochemical reactions.

And finally you would see that whenever we talk about this corrosion it involves four factors one is metallurgical, so if we see the corrosion so this is let us say the corrosion part so then it would have mechanical factor. Mechanical factor, it would have a metallurgical factor and then it would have thermodynamics, and then finally one side it would have electrochemical. So this involves rate, and this involve stress, this involves materials, so overall this is the basic understanding of corrosion or that we would say that what is the basic understanding of scientific definition of corrosion which says electrochemical degradation of metal as a result of reaction with environment with the metal.