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Course Title

Environmental Degradation of Materials

Lecture – 36 Broad Subject: Corrosion protection, Change of materials, Inhibitors, Coatings

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Today we'll discuss corrosion protection related to change of environment and corrosion protection by coating. So first let us see change of environment, for example this means that for example we can get rid of oxygen, we can get rid of moisture, so there are many ways and mainly the removal of corrosives that is basically incorporated in the change of environment or decreasing the activity of corrosive elements by adding some chemicals from outside, so let us see what are the ways we can do, one is we can remove moisture, moisture removal and for that we can add, we can do dehumidification and for that many a times we add, we keep silica gel, solid silica gel, silica gel we can put it which can absorb moisture and prevent corrosion, then we can also decrease the humidity, humidity we can decrease by increasing the temperature by around 6 to 7 degree Celsius though with the increase in temperature there generally the corrosion rate increases, but the increase in corrosion rate will be superseded by the decrease in corrosion rate due to the lowering of humidity, due to this increase in temperature, so this is another way.

Then we can have oxygen removal, oxygen removal because in case of neutral or basic medium we see that this is the major cathodic reaction or even in the acidic media we have dissolve oxygen then this reaction can form, can occur which is also cathodic reaction, if we can get rid of this oxygen we cannot have this two cathodic reactions, so we can reduce the corrosion rate of the metal object to a great extent, and for that how would we be able to do it? Either we can purge with nitrogen gas or argon gas which are inert gas through the solution, if we part that nitrogen or inert gas we can get rid of oxygen to a great extent or we can introduce evacuation if needed, evacuation or we can introduce scavenger, scavenger what it does it actually reacts with oxygen, dissolve oxygen and then get rid of oxygen in the solution, so one such example of scavenger is, for example on such example is NA2, this example NA2 SO3 if we add that in the solution then it will react with dissolve oxygen and form NA2SO4 and this is one scavenger

which is active, this is added at low temperature, this is a low temperature, this scavenger would be very good in removing the oxygen or we can at high temperature, we can add some hydrogen, which is N2 H4 which will also react with the dissolved oxygen and form nitrogen gas and water molecule. Now this dissolve oxygen, this oxygen is basically the dissolve oxygen which will be scavenged out by, which will be taken out from the system by these two molecules and in this case this is basically when the temperature is little high that time you can use one can use hydrazine which will take care of dissolve oxygen, and this nitrogen also would have the purging effect, so this is the effect of scavenger.

Now then we can also have, we can also remove acid from the solution acid removal, acid removal can be one option, if we remove acid then the corrosion rate can reduce, we can also take care of, we can also get rid of chlorine ion, since chlorine ion is a very active element, active ion which leads to pitting or crevice in a particular system or it will also act negatively to the passivity, so if we have chlorine ion then passive layer formation will be delayed, so if we remove this we can also increase the corrosion resistance. Then six, we can also get rid of solid particle removal, so solid particle if we removal it's basically a sort of trap filter to the inlet section of the solution, so if we remove solid particle we can increase, we can avoid the crevice related attack since we have seen in the solid particle can lead to crevice corrosion on the bottom of water tank or it can also lead to erosion corrosion if we have a relative movement of the solution with respect to the metal surface, then we can also get rid of salt, salt removal generally most of the salts they increase the conductivity, if we remove salt the conductivity will decrease or the resistance of the solid solution would increase and hence the corrosion resistance would also increase. And finally we can also add chemicals which are added in a very small amount maybe of the range of PPM level and which can increase the corrosion resistance of a particular metal by either taking care of the corrosive elements or corrosive species or which can also form some passive layer on the surface and also enhance the corrosion resistance those chemicals are either organic or inorganic, those are called, or vapor phase or it can be in the form of vapor, those are called inhibitors. So if we change environment in this manner we can increase the corrosion resistance.

Now coming to these inhibitors let us discuss little more on these inhibitors, so if we see inhibitor, let us discuss this part so as I have told that inhibitors are chemicals which are added, very small amount is added in the solution and it may be of the range of PPM level, and when it is added that time it enhances the corrosion resistance and there could be inorganic or organic substance, so the main characteristics of inhibitors, the characteristics of inhibitors, let us see what are the characteristics, characteristics one is most of the situations if we think of having inhibitor in the system, the choice of the inhibitor is done through trial and error method, trial and error method to choose for the choice of inhibitors. Now in a particular situation and then we can also and they can be organic or inorganic, but most of the cases they are generally organic in nature and inhibitors many of the cases innovators are inhibitors composition exact compositions are not known because many a times those are copy written chemicals. Now inhibitors definitely are costly, costly as well as toxic and the amount of, and they are specific, specific it means that for a particular system, for a particular metal one inhibitor can work nicely, but that cannot work in other case, so it is specific in nature so, and then five, let's say we have a particular metal M, we need to protect that metal from corrosion then we think of some inhibitors, let's say two inhibitors are added so that two inhibitors will acts in justically

that mean, both will work in tandem, so synergistic in nature, so in case of two or more inhibitors, so these are and of course if we increase the temperature, if we increase the temperature or if we increase let's say the chlorine content is increased or let's say pH is decreased, so this cases inhibitor contain, amount of inhibitor would also increase, so these are a common characteristics of inhibitors.

And let us see there are how many types of inhibitors are there? Types of inhibitor they are mainly four types, one is passivator or anodic inhibitor and there could be cathodic inhibitor. And now in that cathodic inhibitor, and there could be another variety which is, which can be either cathodic or anodic that is called barrier type inhibitor, which forms actually a barrier on the surface of the metal and that barrier will not allow that corrosive species to react with the metal, so there could be a barrier type inhibitor, so then another and but mainly the barrier type inhibitor either cathodic or anodic, then organic inhibitor and for this actually it's a vapor phase inhibitor.

Now if we come to the passivator or anodic inhibitor, so actually what they do, this if we consider passivator let's say in terms of, in case of, if we consider in case of passive, they actually form a passive layer or helps in forming the passive layer so they effect the cathodic reaction what they do, the cathodic reaction they increase the electrode potential of the cathodic reaction or move it to the noble side so that it goes to the critical, it goes to the critical position so that the passivation is possible. For example in case of passive metal if we know that this is the passive metal potential versus log I curve, this is basically the passive metal curve, now in that case if a cathodic reaction is happening like this, this is my cathodic reaction, so this is initially the corrosion rate if we add those inhibitors it keeps on moving this cathodic reaction upward, so finally you can have like this, then this is the critical amount which actually crosses across this critical I critical which is the current density, critical current density. And then once you have the situation like this, so this is the corrosion rate has moved to this place, so actually inhibitor moves this electrode equilibrium potential towards the positive side or noble side, and that means this is actually above critical and these are, this is critical and these are all, these three are below critical, so that means that the amount of passivator, passivator type inhibitor that should be above critical value in order to maintain this passive current density so always the amount of the critical, amount of this passivating inhibitor should be above critical value.

Now this is one, this is the major thing, this is the major activity of this passivator type inhibitor and other things what it can do actually it can stabilize, stabilize passive layer, then also it can re-passivate, for example if the passive layer is damaged somehow if we have those inhibitors it can re-passivate immediately then they can also access to repair the film, so film repairing ability by forming insoluble chemical, insoluble products by chemical reaction, so repairing ability and of course as I have told you that the critical amount, the amount should be above the critical amount that is needed to maintain the passive current density all the time, and the critical amount would depend on the, depend on whether the temperature is increasing, if the temperature increases critical amount would also increase and also if you have the lowering in pH, critical amount would also increase so those are the cases. And then of course let's say you have this particular metal surface, okay, so this is the metal surface and for example, this is a tank where you would like to use this passivator and these are basically the dead zone where the liquid is stagnant, so care should be taken that the inhibitor presence is there in the dead zone,

also one care should be taken that inhibitor this passivating inhibitor should be throughout the surface, otherwise if for example some case, some portion if the inhibitor percentage is less and if that is damaged then the severe corrosion attack can happen in that damaged portion, because the inhibitor is less at the same time there would be favorable area factor, unfavorable area issue that would come into picture, so that exposed part would act as anode and the surrounding unexposed part which is a huge area that would act as cathode. So this is and, they can be of two types, one is direct passivator, they can be this passivator, one can be direct or it can be indirect, so direct actually they are oxidizer, they are mainly oxidizer, oxidizes what they do they contains anions which oxidizes and then form insoluble, which will be incorporated in the passive film. For example, we can have chromate or we can have nitrites, so these are basically the oxidizer and they can form, they can combine with passive film and make the passive film very much adherent as well as impervious, so these doesn't need oxygen to form the product, but to form, to passivate the surface, but there are other oxidizer, for example molybdenite or molybdates, for example this is molybdates or tungstate, these are basically, they need a little bit of oxygen, they need a little bit of oxygen to passivate, and the use are basically the reinforced cement. In reinforced cement calcium nitrite is use or it can be also used in automobile antifreeze where sodium molybdate protects the iron, as well as copper brass others, so but these are the use. And indirect they actually what they do, they help to improve the adsorption, they help for passivating metal so they actually help to improve the adsorption of oxygen on the metal surface or also they can also help in a adsorption of those direct passivator oxidizer, oxidizing inhibitors. So for example one indirect passivator is NAOH, what it can do, it can take care of this OH- ion can take care of hydrogen ion, so if hydrogen ion is taken care of so the cathodic reaction is out, so the corrosion resistance would improve.

Now we can also think of some, so the barrier type inhibitors actually, barrier type which can be cathodic or anodic, so one particular, one example is let's say if we add Zn+ ion which in order to neutral environment, neutral solution which can protect iron corrosion, iron corrosion would reduce due to the presence of Zn++ ion, so the corrosion product which is OH- it can react with Zn++, so this forms a film on the iron surface or the cathodic zone regions and that can prevent corrosion, so this is one example. And there could be different types of barrier type, barrier forming inhibitors, one is organic adsorption inhibitors so they form organic, there could be a possibility of organic adsorption inhibitors, and this case the examples are for example sulfides or organic sulfides, or mercaptans so those are some organic sulfides, what they do? They form an oily layer on the surface and once we have the oily layer this can prevent adsorption of hydrogen on the metal surface or it can prevent the salvation of metal ion, so if we prevent any of the steps which are needed for corrosion, we can prevent the corrosion so they actually form oily layer on the metal surface, and sometimes they can also form stable surface complexes which can also prevent surface adherence of this adsorption of hydrogen ion or even it can prevent the salvation of metal ion. So this is organic type inhibitors or it can be inorganic type inhibitors, inorganic passivity, inorganic inhibitors which are basically barrier, barrier type and here we have the example of bicarbonate, bicarbonates or we can also have phosphate biphosphate, so inorganic inhibitors which are barrier forming those inhibitors are added which can react and form some insoluble product on the metal surface. For example, if we have bicarbonate iron bicarbonate can form and which can protect the metal surface in case of alkaline medium or we can have phosphate which can also react with iron which can form iron

phosphate, and that iron phosphate can form or insoluble protective layer and then prevent corrosion.

So then we can also have a poison, the poison is a special type of cathodic inhibitor, for example what they do? They actually poison the hydrogen reaction, cathodic reaction, poison the cathodic reaction, for example in case of acid medium we have this reaction which is then this hydrogen would get adsorbed and then two adsorbed hydrogen will react and it will form hydrogen gas, but somehow this poison are added which are nothing but phosphorus, arsenic, antimony, those are the poisons which are added, which actually prevents this combination reaction, if we prevent if the combination reaction is prevented the reaction is incomplete, so the cathodic reaction is not happening, so then if the cathodic reaction is not happening so the corrosion rate of course would be very low, hours of corrosion resistance would also increase, these are actually a poison which is basically taking care of this hydrogen combination reaction, there could be poisons for to prevent oxygen reduction, for example this reaction oxygen + H2O + 4e it goes to 4OH - so this reaction for example we add arsenic or antimony in brass which prevents in the amount around 0.1% is added, which actually prevents dezincification in the brass, the mechanism is the corrosion well initially the copper as well as zinc goes out both the ions go out and then copper redeposit back. And now what happens, there would be this one, this one would react with arsenic, and react with arsenic it can form arsenic (OH)4, so this phase would deposit on active cathodic sites, and active cathodic sites because the copper is redepositing back, so now the copper surface these phase would deposit and that further copper deposition will not be allowed, so that way it prevents the dezincification, this is the nature of the poison which actually poisons that particular reaction.

Now we can also have a vapor phase inhibitor those are used in case of electronic products for, this is for used for storage purpose or for shipment purpose, those are basically for example one is dicyclohexylamine in vapor phase inhibitors, so here what happens? It actually forms one example is DCHN which is nothing but the dicyclohexylamine, so these vapor they have a very low vapor pressure, for example for this the vapor pressure is 3×10 to the power of -7 atmosphere at 25 degree Celsius, so they vaporize and form a thin layer on the metal surface and prevent corrosion.

Now let us see what are basically the mechanism by which the inhibitor works from mixed potential concept, backing mixed potential theory on the inhibition effect, for example if we have this log I versus E, for example these are my two reactions, this is my anodic reaction, anodic polarization, this is cathodic polarization, and this is the corrosion rate. Now if we add anodic passivator, anodic inhibitor they can react in two ways, one is they can either shift this which is basically exchange current density of this cathodic reaction, sorry for an anodic inhibitor they can change this, exchange current density of the anodic process and decreases its value without changing the polarization or over voltage, so if this point is shifted to this which is basically getting lowered due to the presence of anodic inhibitor, if we have again if we see, if this again mixed potential theory is seen so actually this has moved to this way and the corrosion rate has also gone down, this is my initial corrosion rate, let's say CI and this is C anodic, CA means corrosion rate with the action of anodic inhibitor. And now there could be one another possibility so it changes the exchange current density or decreases the exchange current density, at the same time it increases the degree of over voltage or if we increase the

degree of over voltage so that means in over voltage is also increase, the polarization is increased as well as the exchange current density is decreased, so this combination of these two process the corrosion rate is further decreased. So this is the effect of anodic passivator, anodic inhibitor.

Now if we see the cathodic inhibitor same way it can work, the exchange current density for the cathodic process can go down so it can go like this, my corrosion rate would be here, or both the things can happen, this corrosion rate, exchange current density would go down at the same time the polarization will also increase so like this, so this is my process, this is my new corrosion rate, so corrosion rate is decreasing like this. Now if we combine both the process that means anodic and cathodic inhibitors both are present, so then new corrosion rate would be this one, so due to this anodic inhibitor this has moved to this, and into the cathodic inhibitor this has moved to this, so this is my new corrosion rate which is basically the synergistic action of both anodic and cathodic inhibitors.

Let's discuss protective coating, so protective coating the purpose of coating is mainly to improve the corrosion resistance of the metal surface or the wear resistance, and there are other effects for example if we have coating, then we can improve the fatigue property of a metal, so but in the current situation let us talk mainly on the, with respect to corrosion, improvement in corrosion resistance so the basic importance of coating with respect to corrosion improvement corrosion resistance the basic importance, one it should improve the corrosion resistance and what it can do it basically acts as a barrier, acts as a barrier for those cathodic or anodic reactions or they themselves interact or function in the cathodic or anodic reactions and that way they can prevent corrosion, so actually this barrier type of coating, for example paints, simple paint they generally do not interact with the species, actually they prevent those corrosive species to come in close contact with the metal surface so that reaction anodic or cathodic reaction would not happen on the metal surface, so the barrier type, third is it can be cathodic protection one famous, one very important example is anodic sacrificial anode which is galvanized iron, zinc coating actually they dissolves and on the way they protect the metal surface iron so the cathodic protection it can do cathodic type coating or we call it sacrificial coating, then we can also have inhibiting type of coating, so they will have action just like inhibitor, then many cases they simply provide electrical resistance, resistance which is mainly the electrical resistance increases, if the electrical resistance increases then for those anodic and cathodic reaction that reaction process would go very slow, so these are the main importance of protective coating. And then mainly, and then key characteristics of the coating, key characteristics of coating they should provide good corrosion resistance or excellent corrosion resistance. Then second is, they should adopt to the surface perfectly, so adherence to the surface, then we can have on the metal surface if the coating is done it should be continuous, and in case if this discontinuous for example in case of paint, if we paint the surface let's say this surface is painted and this is the paint zone, this is the paint zone, now by chance if the paint zone, on the paint zone there is one small discontinuity and that discontinuity is called holiday, which is basically also called holiday defect in case of painted surface and this part the corrosion would be huge and then the metal object can fail if it is under stringent, so the coating should be continuous and completely covering the surface.

And then fourth is basically the life of coating should be excellent or the good, long life or long life of the coating it should not decompose with time quickly, then the another process is another thing is when we have a coating the surface finish, for example on a metal surface we are, this is the metal surface on that metal surface we are planning to have coating at that time the surface preparation of the metal surface on top of which the coating is to be done that is very important. For example, if the good coating is done on a badly prepared surface that can give you a very and deadly effect, corrosion rate would be very high, at the same time if the bad coating is done or for example a coating which is not that resistant to the environment if it is done on a very well prepared surface, then it can function well, so that means the surface finish or preparation is another important issue, so these are the key characteristics.

Now we can have different kinds of coatings, it can be either metallic, broadly it can be either metallic or nonmetallic so the varieties of coatings it can be broadly classified into two varieties one is metallic, another one is nonmetallic, so the metallic generally the characteristics of metallic coating they are durable, more durable, their aesthetics is good decorative, then they can give a very good shielding against corrosion, good shielding, so these are the basic characteristics or importance of metallic coating, and for the metallic coating to be done the metallic, the surface preparation this key factor or we can say that characteristics or factors, so key factors, one is surface finish of the metal surface on which the coating is to be done that surface finish is to be very good, for example it should not have any coat, it should not have any rust on the surface, it should not have oily or greasy surface so that, and so that those things will negatively interact with the metallic coatings, so the metallic coating can be, the strength of the metallic coating would be less, so that's what the surface should be very clean and that cleaning has to be done properly by either solvent emulsion or pickling or acid leaching so those who are the, yeah those are the acid treatment, those are the ways to prepare the surface.

And the metallic coating it can be divided into two section, one is cathodic, another in is anodic, so that means one particular example for anodic coating we have seen many a times the example, that is galvanizing, galvanizing that means zinc coating on iron surface, and cathodic one particular example we have seen while we discussed about the effect of, different effect of areas the unfavorable area on the corrosion of the base metal, so that time we have discussed about tin coating as well as tin coating that means SN coating and zinc coating on metal iron surface, so that time we have seen that the cathodic coating would be very good, this is basically one example of cathodic coating, cathodic coating would be very good if there is no crack or discontinuity in the coat, but if there is any crack or discontinuity that would be a very deadly effect because that the entire surface would act as cathodic area, and the small section of the iron which is exposed to the solution or the environment atmosphere that would act as anode, and so unfavorable area should come and the corrosion rate of that exposed part would be very, very high. So one another example of cathodic coating.

Now coming to the nonmetallic coating, so nonmetallic coating one variety is there are inorganic or organic coating organic coatings are generally paints, enamel or varnish. And inorganic coating, there are various ways we can have inorganic coating, one is vitreous enamel, so these are basically the hard glassy surface, glassy, vitreous means glassy, hard glassy layer, hard glossy layer on the metal surface and due to that protection is done, then we can have Portland cement coating, Portland cement generally they are very thick and in that Portland cement generally the pH is maintained, pH is in the range of a, pH is more than 7, that means it goes to alkaline, alkaline the surface becomes alkaline in nature, so actually the pH is raised Portland cement is one important inorganic coating on steel object, then we can also have chemical conversion coating, chemical conversion coating actually what it does, that the coating material intentionally or the metal surface the way it is done actually the metal is intentionally reacted with the environment and during that reaction of impervious layer is formed and that layer would be resistant to corrosion. For example, one example is anodizing, anodizing of aluminum, what it does? The aluminum is intentionally taken to nobler site, the potential of aluminum, so that means it's intentionally taken to the nobler side so when it is taken to the nobler potential the aluminum oxide forms and that aluminum oxide due to this anodizing effect which is happening a very high potential beyond that, beyond the potential where oxygen evolution occurs, so the anodizing aluminum is one important chemical conversion technique by which aluminum oxide layer is forming on the surface, and it would give very good corrosion resistance.

Then we can also have phosphate coating, phosphate coating here in case of iron if we dip it in dilute phosphoric acid, then the iron phosphate is forming, iron phosphate would form in the metal surface and that gives the protection, okay. So then we can also have chromate coating, chromate coating so again here what it does, what is done, actually the either the metal object is, which could be aluminum, could be zinc, could be cadmium, so there this metal object is dipped in chromate solution or the chromic acid solution and the chromate layer is forming, or there would be wood form on the metal surface and it would give protection, so the chromate coating. Then also we can have oxide coating, here aluminum for example in this case aluminum, aluminum is oxidized in the presence of chromate or dichromate to obtain a thick strong oxide surface on the metal surface. So these are a few techniques, another technique could be nitriding or carburizing, so these are basically the gaseous technique with the metal surface is heated in the metal, in the presence of gas, nitrogen gas, gas and then carbide or nitrides are forming on the middle surface and it would give very good corrosion resistance. Then there could be a rust converter, there could be a rust converter for example E and then F rust converter, so for that some chemicals for example tannin is added and that on the metal surface, for example steel this acid is forming and then if we have tannin, the tannin ships through the oxide layer and it forms a non-porous stable passive surface film, non porous stable rust so that way we can protect corrosion.

And then there could be organic coatings in case of nonmetallic coating we can also have organic coating, nonmetallic section we can have. Then 4, organic coating generally they are plastics or enamels or it could be resin, or it could be a lacquer, so these are the organic coating which is actually, physically deposited on the metal surface. And then we can, actually those acts as a barrier which will not allow the corrosive species to come in contact with the metal surface that way they prevent plastics, they prevent corrosion or they increase the corrosion resistance. And as we have mentioned in case of organic coating there could be a possibility of holiday defect and that's what, it's always preferred to have a multi coat rather than a single coat, the single coat holiday defect would be more or the middle surface or the coated surface or the plastic or the organic coating would have many more defects, so that time that can be very bad from the corrosion resistance point of view, so this multi coat is essential and there could be and this one criteria is this coating should be resistance, high electrical resistance they should have, if they have a very high resistance electrical resistance then they can prevent the cathodic or anodic reactions, or the anodic or cathodic reaction rate would be low, so those are the common characteristics of organic coating.

And let me also come to the fact that what could be the common failures associated with organic coating, so you see that high resistance of those organic coating is one of the important issue then sometimes with this organic coating generally, sometimes inhibitors are added, let's say sometimes we add zinc in the paint, so that zinc would act as, this basically would be sacrificial, it would have sacrificial action, sacrificial action with respect to iron, so zinc is added, and many times sometimes red lead or zinc chromate is added, which will be acting as inhibitor.

Now let us see what are the common problems that are experienced with respect to the organic coating? So one problem could be the problems, blistering, so the organic coated surface due to the action of oxygen and water or gas, that there could be a blister formation on the metal surface, there could be early erosion, before the paint gets dried or there could be problem of delamination during exposure of that coated surface to the corrosive media or there could be filiform corrosion, filiform corrosion is also another type of crevice corrosion where you have let's say this is the metal surface and this is the paint, so the paint basically, this is the paint so actually the paint is peeled off like this and there could be, there could be a problem of, they will form a sort of filament on the middle surface, see if this is the middle surface so there could be filiform corrosion can happen on the metal surface, on the painted surface, so these are the common problem with organic coating.

Now let us finally discuss what are the methods by which we can apply coating metallic surface coating or different other coatings, so the methods of application, now it can be mechanical way, mechanical way it could be cladding, it could be mechanical painting, mechanical plating, due to the mechanical action there could be mechanical plating there could be painting, so then we have the physical method these are basically mechanical method where mechanical method where we add the mechanical action, mechanical force in order to have the player coating. Then we have physical method, physical method in this case it could be high temperature, high temperature method or it could be low temperature method, in the high temperature method we could be a hot dipping, hot dipping or for example zinc coating is done by hot dipping, then we can have welding, we can have spray fusing or it could be laser. Then in the low temperature process we can have cathode sputtering or it could be metal spraying, then finally we have one more method which is chemical methods, in case of chemical methods we have different varieties, so the chemical methods in that which could be either high temperature again, or it could be low temperature methods, some of the examples of high temperature methods are either chemical vapor deposition or we can call it as CVD, we can also have autocatalytic, autocatalytic electroless plating, electroless plating or it could be chrominizing or aluminizing, aluminizing, and low temperature case we can have it could be electroplating or it could be anodizing or it could be phosphating like that, even brass painting brass plating, or it could be brass plating or it could be a vacuum deposition, it could be vacuum deposition so these are many techniques which are available in order to have coating on the metal surface.

So now we finish the discussion on the methods by which we can have protection against corrosion or we can improve the corrosion resistance of a material, so we have majorly four techniques, one is by changing the design, another one is by changing the environment or changing the metal or material selection, and then fourth one is electrochemical ways of protection, and then finally we have the protection by coating.

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