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Course Title

Environmental Degradation of Materials

Lecture – 41
Broad Subject: Degradation of Composites, Polymers and Ceramics, Corrosion And Society,

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We have discussed a lot about corrosion and oxidation of metals and alloys, now we will also briefly discuss about the degradation that happened, that happens in case of other materials, other than metals and alloys, now if we consider materials, the materials can be divided into four categories and accept metals and alloys the other three categories are polymer, composite and ceramic. So today we will talk about corrosion behavior and degradation behavior of polymer, ceramic and composite materials.

Now today we will talk about composite, polymer and ceramic. As I have mentioned that materials it can be divided into two broad categories, one is metals, alloys, and then this side we can broadly say that these are nonmetallic, and in the nonmetallic we have two sections, one is ceramic, another one is polymer. Now we have one more variety that is composite, and composite is a mixture of, so we have composite which is another variety and that can be formed by metal-metal, or it can be metal ceramic, or it can be metal polymer, or it can be polymer, ceramic, so the composite material would have combination of metals, alloys, ceramic and polymer, so this also constitutes one more variety in materials.

Now if we talk about corrosion behavior of composite, so if we come to composite corrosion then composite material then, we will first talk about corrosion behavior of ceramic material, no corrosion behavior of reinforced concrete. Now reinforced concrete is basically the combination of concrete and reinforced rod, or reinforced metallic mesh, so the reinforced metallic mesh that take care of the tensile component which is put on the reinforced concrete part, and the concrete it gives you the compressive nature.

Now before coming to this we would like to define what is composite? Composite is actually combination of, so combination of one or two or more materials, and in that composite this two or more materials they will also have their individual physical nature, so if we have a composite like this, so let's say this is my composite so where we have, this is my second material, this is material one, this is material two, so this forms a composite where we can easily physically see this, this part is there as well as this part is there in the composite, but in combination they will enhance the property of the material, so the composite will always have improved properties. Let's say for example in case of, if we consider the strength property, the strength if we have laminar composite like this the strength in this direction would increase that means we can, if we have this material if it is having some elastic modulus E1 and this one has some elastic modulus E2, then the overall composite will have better E3, so that way the composite has advantage.

Now while considering composite corrosion let us first discuss the composite corrosion of reinforced composites, reinforced concrete, so the reinforced concrete structure if we see the reinforced concrete structure then we have reinforced bars this is basically the iron bar and this is the concrete material, concrete material it consists of cement + stone + other chemicals, now when we talk about these chemicals, these chemicals we can think of a calcium hydroxide, sodium hydroxide, or potassium hydroxide, so these chemicals are added. Now when this composite structure is formed these chemicals, because of the presence of this alkalis they take the pH over the iron bar to the level of a 9.5 to 13 this pH level goes high.

Now in case of iron if we think about, if we see the Pourbaix diagram so if we see the Pourbaix diagram that means this is pH, this is potential versus pH diagram, that diagram looks like this in case of iron, so this is the pH diagram of iron where this part is Fe, this part is Fe++ and then here Fe+3, now here this section and this section are all oxides, oxides or hydroxides. Now in this section if we talk about in terms of immunity, corrosion and passivation zone, then this part is corrosion, this part we have immunity or immune zone and this part is passive zone. Now if we see the pH level so this is almost close to 1V – 1V and the pH at this section is around 7, and this section and around this part is around 14, so the 13 is this, and around 9 is like this, so 13, so if we see that, if we take a width section like this in this zone we see that we are basically avoiding the corrosion zone and another corrosion zone is existing that is this part corrosion zone, so if we mark this part this is corrosion zone, this is also corrosion zone. Now if we maintain this pH the iron bar is going to passivate and the passive layer will form on the iron surface so the iron surface we have passive layer formation, now because of this passive layer formation it gives very good corrosion resistance. Now if somehow, if we have some crack in the material so if there is a crack in the concrete section so in the concrete section if we have crack then we are forming one particular deleterious component that is deleterious effect that is we are forming crevice, and through this crack we can have the access of H2O as well as O2. Now then once we have these two component, these two constituents in the water, in the electrolyte and we have the crevice part so there is a possibility of crevice corrosion, there is a possibility of crevice corrosion so crevice corrosion would go along this and as well as go along this, so the crevice corrosion is starting and it is progressing inside the material, so the crevice corrosion is happening in the iron surface, okay, and the iron that means iron bar we have crevice corrosion, and who will supply the iron to this crevice part? The corrosion would happen from surrounding region, so the iron would come Fe++ would come here and then further this crevice would grow through this direction as well as through this direction, so we have crevice corrosion, that means and, but still if we see the pH level here the pH level would not maintain at 9.5 to 13 pH level, so if we see that there is a reduction of the pH level to 7 to 8 then we are not having any condition. For example if this is the section, this is the potential zone where we have this part we are maintaining at in between 9 to 13 pH level, but if we come to 7 to 8 we see that this zone we have corrosion, that means if somehow the pH level goes down or if we have a crack in the grown pit there would be access of this O2 or H20 to this or there could be another possibility if we have chlorine ion in addition to this that could lead to localized pitting, and that localized pitting can result local breakdown of passive film due to this chlorine ion, so that would also corrode the iron bar. Now if we have the corrosion in the iron bar the overall structure would lose its strength and if it loses its strength then there could be breakdown in the concrete structure.

So now how we would experience this breakdown in concrete structure, what could be the overall mechanism for this break down in the concrete structure and that could be related to two main causes, one cause would be, two main causes, one is localized breakdown, localized breakdown of passive film and which is due to chlorine ion and that would lead to pitting, so that could lead to a breakdown as lowering of the strength of the iron bar an overall concrete structure. And second case would be the neutralization effect, a neutralization effect how it could happen, what does it mean this, what does neutralization mean here? Since we see that in the concrete structure we have calcium hydroxide, sodium hydroxide as well as potassium hydroxide those hydroxides are alkaline and then if we have some sort of chemicals which neutralizes that alkaline, who will neutralize this? In the environment we have CO2, now this concrete is permeable, whatever way we make concrete would always be there to permeate things through that so CO2 can permeate through the concrete layer and it can reach to the iron surface, that bar surface and then this CO2 can react with CA(OH)2 and then can form CA CO3 +H2O. Now in this case if we see carefully that the alkaline is getting neutralized by the, because of the presence of CO2 and then we are forming a neutral carbonate, and because of this neutralization what happens initially the pH level is 9.5 to 13, now that level goes down and it reaches to 7 to 8 pH or maybe 9 pH level. So now in this range we lose a overall passive layer, so that means there could be further corrosion effect on the iron bar, on the overall surface, so the neutralization effect is because of the CO2 presence.

And now what could be the localized breakdown? Localized breakdown once we have this carbonate formation and then if we have chlorine ion, that chlorine ion can get in and chlorine ion can locally decrease the pH level, so locally pH level would go down and the local, at the pit region, at the pit portion, this pit portion we can have huge decrease in pH and this P section the solution can become acidic, but overall other surfaces where the pH would be maintained, so that means we have the local reduction in pH which can become pH acidic and that part we have already discussed in case of pitting, how chlorine ion leads to increase in acidity in the pit region.

Now this neutralization can also happen in another way, for example we have this concrete structure and here we have the bar, here we have the bar, now we have water, presence of water if we have then this water is on the surface, on the surface section we gradually it can leach out those calcium hydroxide, potassium hydroxide, or sodium hydroxide, if there is a leaching,

leaching means it takes this calcium hydroxide or potassium hydroxide into the solution so the overall alkalinity of this section decreases, and if the overall alkalinity decreases the maintenance of passive layer would be difficult so that would also lead to corrosion of reinforce part. So now once this happens, once this thing happened then we have one more particular phenomena that is called a concrete cancer, concrete cancer can also happen what is this concrete cancer, now you have a concrete bar, so now we have this concrete structure, so this is my concrete region and this is the reinforce bar.

Now if we have locally, if we have some corrosion then we have iron oxide formation, that iron oxide is, the volume of the iron oxide is higher than the volume of the metal which is getting oxidized, so if it is high the volume is high it will push this concrete section, so if it pushes the concrete section upward but concrete at the same time concrete is very brittle in nature, if it is very brittle in nature there could be crack formation, so there could be crack formation and once we have crack then there would be further ingress of H_2O or CO_2 so or Cl^- those thing will again get into this section and then it will further damages the structure, so these kind of situation when it happens that time it is actually terms, it is termed as concrete cancer. Now there could be few more situations where concrete corrosion can happen, one more situation is let's say we have a concrete section, now this is my reinforced bar and this is the concrete zone, now there would be always some stress on this bar there could be sinkage effect due to differential heating now due to this sinkage or due to this expansion, this is the hot season or cold season that sinkage and as well as expansion effect those will lead to our debonding effect in this zone, in this interface zone, these two interfaces there would be debonding, that debonding can lead to further possibility of corrosion of this reinforced part.

Now one more effect that could be possible that is stray current, so stray current effect, see if we see the stray current effect, let's say we are running by locomotive, so if we run a locomotive this is the wire, so this is my locomotive, so this locomotive is running on a track, now here we have DC source, so now there and, this is my reinforce bar, so this is my reinforce bar, now the current is flowing like this and it is coming here and then going out like this, okay, so we have corrosion in this zone, we have seen in the stray current effect while we discussed a current effect we know that wherever current leaves the metal structure that portion is vulnerable for corrosion attack, so here we can have a corrosion attack because the rail line is stationed on a concrete structure and if we have this reinforced part that reinforced part the current is coming through this because this is in a very high electric, very high potential so there would be a current flowing into it and then leaving this current through this and this circuit is maintained, so here we have corrosion, so the stray current effect also would be active there.

Now the in brief these are the corrosion phenomena in concrete and concrete mainly the reinforce bar the corrosion can happen like this, now how we could protect? We can protect reinforce corrosion, reinforce concrete corrosion, so the protection roots are, so how we could prevent, we can prevent corrosion of concrete corrosion that is, one is this is prevention, one is somehow if we can make the things dry, so the dry environment that would not allow any electrolyte to be present.

Now second thing is dry at atmosphere, then we can have epoxy coating on reinforced bar, we can think of improved material, improve steel, maybe which is having a stainless property, in stainless property then we can think of adding fly ash into the concrete mixture, so if we add fly ash in the concrete mixture what it does? It reduces the pores in the material or it makes the concrete very compact, so if it reduces the permeability, so permeability if it reduces then this carbon dioxide or water that cannot seep in and it cannot reach to this concrete surface, this reinforced bar surface so the corrosion can be prevented to a great extent. So these are in common, there are other techniques so these are the common techniques, how we can prevent corrosion or we can control the corrosion of reinforced concrete, so we can also have corrosion in case of metal-metal composite or metal-metal matrix composite, so the metal-metal matrix composite we can think of one example, so in case of metal-metal matrix composite so in that case let's say we have a metal M1 and in that you have other metals which is basically gives you a laminar metal strips which are there embedded in M1 which is basically M2. Now if we have these two material they can form galvanic couple, so galvanic couple formation and the material which is anode there that could corrode at a higher rate, so this is one, one example is tantalum wire in copper matrix, so in case of highly acidic condition the matrix dissolves, so this is one example of corrosion of composite material in case of metal-metal matrix type of composite, so we can, and in order to prevent this what we have to do? We have to somehow choose this two components in such a way they are very close in the galvanic series, if they are very close in the galvanic series then the potential develop between this two metals would be less so the corrosion would also be less, so this is about corrosion of composite material.

Now let us talk about corrosion of polymer material, corrosion of polymer material, now what is polymer? So polymer is it polymer constitutes small, small units which are called monomer, so it's in hydrocarbon, it's basically a hydrocarbon and that hydrocarbon consisting of repeating monomers. Now let's say if we consider polyethylene, polyethylene its structure is or if we extend it, if we extend it, it would be like this, let's say four and this is my smallest unit and if we have this four mars that are connected so let's say we assume that the four mars actually there could be in number of mars so H, H and the smallest unit which is the mode is actually C2H4 so this is ethylene, and now polyethylene actually polyethylene, poly means many, so the many ethylene structure combination of many ethylene structure is actually the polyethylene, so this is one polymer. Now in case of polymer how the corrosion can happen, not corrosion actually in case of polymer we would say degradation, degradation means the deterioration of polymer property. So now how we would experience polymer degradation? One is, now detoriation polymer, so different ways by which polymer degradation can happen, one is swelling and distortion, and then we have bond rupture, and this bond rupture can happen due to radiation, then it can happen due to chemical reaction or it can happen due to thermal effect, now there could be also another way polymer degradation can happen, that is weathering.

Now there could be other reasons, so other reasons those are actually either mechano oxidation or it could be ultrasonic degradation, and here the mechanical effect that would lead to the degradation and polymer, so if we talk about the swelling, now swelling talks about when we have moisture or water that water can be absorbed, water can be absorbed inside the structure, inside the structure and when the water absorbed in the polymer structure that water molecule would try to force the molecule, force that two parts, and that leads to swelling, okay, so now there could be also another effect if the swelling effect can be, can also lead to softening and that time the secondary bonds which are existing in the molecule, those secondary bonds can be broken and that time it would lead to softening of the polymer, and that one example is so actually if we consider swelling, so if we consider swelling then one example is hydrocarbon, example of swelling, one is this hydrocarbon rubber, it swells readily after absorbing hydrocarbon liquid, after absorbing hydrocarbon liquid like gasoline, so that time there would be swelling effect. Now that time, but generally the polymer has a better protection against acid for one example is HF solution, now the HF we generally keep it in plastic bottle, so it has but HF can damage iron bottle to a great extent but a plastic bottle can store the HF gas, so HF acid. Now see this polymer corrosion resistance is much better than metals and alloys in case of strong acids but there could be degradation which is the loosening of strength due to this swelling or now let us also talk about bond rupture, if we talk about bond rapture as we have seen that there would be three effects, three causes for bond rupture, one is radiation, so in case of radiation, so radiation for example x-ray or gamma ray, x-rays, gamma rays or UV radiations, all can break the bond of the polymer, so if we have a long-chain polymer and if it breaks the polymer then it loses several properties it becomes brittle, there could be discoloration and there could be a crack all things can happen and that polymer can fail. There are several examples, one is let's say the plastic, thin plastic tent material that could crack due to the exposure of, due to the exposure of this radiation, UV radiation, and then there could be then dashboard for example crack in camp material, camp, camping plastic, there could be break in dashboard, dashboard these are the defects that can happen due to this radiation damage, due to this radiation damage.

Now we have a chemical reaction effect on the bond rupture, so the chemical reaction effect so if we have the presence of ozone or oxygen those things can break or rupture the chemical bond for a long-chain polymer, so one example is let's say in case of vulcanized rubber, in the presence of O3, so if we see the rubber, now if we have O3 so it can result, so it breaks the rubber, so this is one example. And this effect would be more prominent in the area where we have a smoggy atmosphere and where we have the presence of ozone to a great extent in environment.

Now third thing is thermal effect, the thermal effect if we consider the thermal effect, if we increase the temperature of polymer if we put it at a higher temperature there could be chemical reaction, there could be breakdown as well as gas formation, now one example is polyvinyl chloride, and if we heat this so that time a color changes and there would be, there could be evolution, there could be formation of HCL, so HCL formation would be possible, so this polymer chain is broken and the bond is broken, this is the effect of thermal, this is the thermal effect. Then we have weathering, so weathering it involves radiation, then it can involve a moisture O2, O3 or there could be sunlight, so those can degrade the polymer, there could be effect of bond scissor, born scissor actually the two bonds if you have, if we have a polymer, long-chain polymer there could be bond breakage due to these effects, and this for example if there is degradation due to sunlight that we call it photo degradation, so this way also the polymer can degrade. So this is about degradation of polymer.

Then we have degradation of ceramic, so if we consider degradation of ceramic, the ceramics are generally corrosion resistant, and the ceramic forms by metal, by the reaction with metal and nonmetal, and there are many ceramic materials one example is a glass, glass is more or less a resistant to moisture, and one example is alumina silicate, so this is a silicate glass, silicate glass variety, so alumina silicate this is resistant to water, but this is not much resistant to acid, so acid resistance is poor. Now we have one of the best silicate, window glass is also resistant to water, and now we have one best silicate glass which is borosilicate, that borosilicate glasses are very much resistant to acid as well as bare alkaline material.

Now we have acid brick another this is one variety, then we have acid brick, so the acid brick we use, the acid brick can be used for a storage tank, the lining of a storage tank, so the lining of a storage tank because it has very good resistance to acid the storage tank which handles acid, strong acids there we can have this acid brick lining. Then we have earthen wire so they are generally made of porcelain, porcelain material mixture of clay + silica as well as feldspar could be there, so the porcelain, porcelain is one example that also has relatively good resistance towards, against this acids. Now concrete is one example, another example is concrete, this is also a ceramic and this can corrode in acid medium, so acid medium this can corrode, we have previously discussed the reinforced concrete, corrosion of all the inputs concrete already, so generally the ceramic has very good resistance to resistance, very good corrosion resistance but they are brittle, they're generally brittle thermal shock resistance is poor, poor thermal shock resistance but they can their melting temperature is very high, melting temperature is very high, so the ceramic material can be used in handling many of the hot acids, strong acids, strong solution, strong corrosive solution, okay, so the ceramic material in general has very good corrosion resistance.

So now we have talked about in brief the corrosion behavior or rather degradation behavior of composite polymer and ceramic, in very short, in very brief manner, now we see that till now what we have discussed over last 40 lectures we see that it involves lot of scientific understanding called thermodynamic understanding, kinetic understanding and also we need to think about what are the reactions that are going on, so those altogether can lead us to understand the corrosion mechanism and then once we understand corrosion mechanism then we can think of the protection roots and judicially we can decides different protection roots and finally of course it would, because it has lot of implications on the economy of, lot of economic implications so before concluding this particular course we have already, before concluding this course we have already seen that this corrosion or the degradation it involves lot of material loss, it involves our materials loss, lot of property loss, lot of material can be, material needs to be replaced time to time and there could be expensive protection methodologies and finally it lead to lot of, it involves huge money. And now one example is we have cited many data, few data, one more data if we see that in case of direct cost, so direct cost in India 1984-85 data it involves around Rs.4076 crore, and there could be indirect cost or avoidable cost, avoidable cost means indirect cost because the direct cost for example the material has collapsed then we can replace that material and then because of that failure of the material due to corrosion that particular structure is held up or that particular operation is held up for some time and that time we have a lot of productivity loss, and that loss is actually coming under indirect loss and that can be avoided if we have, if we take care of the initial corrosion of the material, so that time this loss is coming out to be around Rs. 1804 crore, so if we consider this huge money and that time it was coming around 2% of Indian GNP so India's GNP so it's a huge loss of money, but if we consider only the loss of money the story doesn't end here, now it involves it impacts the society also.

Now how it impacts the society, now let us have some examples, how it would affect the society. Now first example if we see, one example is the failure of Thane bridge in 1984, so that bridge suddenly, this bridge was planned to have initially it was projected that this big bridge could operate for about 80 years, but I think 8, 9 years there was some crack noticed in few of those got girders , few of those girders and that girder corrosion actually led to stop the communication over this bridge and then that girder failure was due to corrosion and there was lot of waste materials that were basically leading to that corrosion of the girder material, okay, so this is one example where the communication was stopped, so the communication that means it leaves affect to the human life, human society.

Now another example is the famous example that is Bhopal gas tragedy, Bhopal gas tragedy it was in the year 1984 and this is in 1981 this Thane bridge failure, and Bhopal gas tragedy 1:00 in the morning time there was leakage from union carbide that leakage care, there was a leakage of toxic gas and that gas was called MIC which is Methyl Isocyanate and that MIC killed thousands of people, and till now the data says around 30,000 close to 30,000 people died because of this toxic effect of this gas and the greater part of this disaster stories many infants took birth with disabled organ and that basically this and this gas tragedy one of the causes was corrosion, corrosion of pipelines, so it's not only cost it's actually taking the lives of people as well as it, and the still there is a problem even after how much here they said 84, 84, 20, almost close to 30 years still the problem is existing, so this is another tragedy.

Third tragedy is, third example is, one example is this is physically it happened in Panaji, it happened in Panaji on Mandovi River there was a bridge and that bridge some part of the bridge failed or cracked and that cracking was due to the use of pre-stressed reinforced bar, okay, so that led to stopping of communication and then government had to spend a lot of money to take the people from one end to the other end of the river and every day government had to spend around lakh rupees for the communication of people from one end to another, so this also leads to damage to the society and then if we consider foreign incidents, the one incident is one example is in case of silver breach collapse, one example is, one another example which says the silver bridge glory collapse at Ohio so that killed around 40 people, so we see that it's not about cost it also talks about the lives of the people it's taking lives of the people and it also leads to hinder the human communication, okay, so we have to be aware that the corrosion study is important, so the corrosion study before that we need to understand what is the scientific understanding of, scientific feature of corrosion or degradation. And then finally we can think of control mechanism, and then we can also do auditing, the auditing is very important because we need to category there where past experiences, we have to categorically write it on a piece of paper, on a piece of register or in the in the register to know why the damage has happened, and what could be the possibility of preventing that damage, and if we have all sort of data bank then future we can think of some better design, some better material or so that we can prevent damage which can affect, which would involve cost as well as, it could damage the human society. So finally we would say that corrosion awareness is necessary. Thank you.

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