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Course Title

Environmental Degradation of Materials

Lecture – 34
Broad Subject: Biologically influenced corrosion, Liquid metal attack

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So today we will talk about biologically influenced corrosion, and that can happen due to microorganisms or macro organisms, and sometimes we see that the corrosion of a metal which is supposed to be low in that particular condition, but due to the presence of this biologically active organisms the corrosion rate increases that is due to, that is basically nothing but the biologically influenced corrosion. So today's talk would be on biologically, and this is due to bioactive organisms, and this can be either micro level or macro level, so you can term it as microorganisms, you can call it as microbiological corrosion, microbiological or this macro one you can term it as macrofouling, so they can lead to increase corrosion rate, and they can happen in different environments, mainly you can experience this kind of cell corrosion in soil, ground water, then you can also have it in oil emulsion, cutting fluid, so even you can have domestic or industrial water, domestic or industrial water there we can have this kind of corrosion attack. And the characteristics of this kind of corrosion attack as I have told that and some cases we can experience a very low corrosion rate but because of this particular effect the corrosion rate increases and that happened due to either they will directly act, directly influence the anodic or cathodic reactions or maybe they can produce some products in that particular environment and that product can affect the overall corrosion behavior, so there could be one is direct influence, direct influence that means anodic or cathodic reactions, they can involve a lot of anodic and cathodic reactions and lead to more corrosion, or it could be indirect influence where the product, that products that are formed because of those microbiological or macrofouling organisms, this bioactive organisms you can have some products and that product can lead to affect the surface film, what is being formed, what is formed on the surface of the metal in that particular environment. And sometimes this microorganisms or macrofouling they can form on the surface of the metal and they can lead to the localized corrosion and even crevice can happen, so these are the common effects of microbiological or macrofouling related corrosion phenomena.

Now let us see if we come to microbiological corrosion that can happen due to the presence of two kinds of bacteria, one is called aerobic, another one is called anaerobic, and of course the name, as the name suggests these are basically the bacterias, anaerobic bacteria or aerobic bacteria as the name suggests that this can be active in the presence of air, and this can be active in absence of air, this is presence and this is absence of air, so that means if we have presence of air then this kind of bacteria can be active and that can lead to corrosion or vice versa, absence of air, this kind of bacteria will be active and lead to corrosion phenomena, it lead to affect the corrosion of the particular metallic object. Let us first talk about, let us see some examples of aerobic and anaerobic bacterias but before that they can, this kind of bacterias where they can form, as we have mentioned in case of, the cases where we can have sort of microbiologically, biologically influence corrosion we see that soil groundwater, oil emulsion, cutting fluid, domestic and industrial water system there we can have this kind of corrosion and this affected areas, these are the affected areas where you can have an excessive deposit, excessive deposits are biologically slimes, so there are this kind of bacterias can grow and lead to more corrosion of the metallic object. For example, in case of grey iron, in case of grey iron if we see let's say that grey iron is exposed to a mildly corrosive medium you can experience graphitization, graphitization or sometime it is also called graphitic corrosion, graphitic corrosion where we have seen that iron leaches out and then you have on the surface network of graphite flex that holds the debris and it becomes very porous in nature, and in that pores you can develop, you can have bacteria growth and that can increase the iron leaching phenomena.

Now let us first get into the anaerobic bacteria, what they can do? And this anaerobic, they can grow in deaerated water, they can grow in deaerated soil with the presence of more amount of clay so it can happen waterlogged, waterlogged clay rich deaerated water, there you can have this kind of bacterias and since you see that, this is deaerated water, no presence of air, almost less presence of air, and that’s what you have anaerobic bacterias presence and they can also be present in stagnant cutting fluid solution oily emulsion solution, and also it can, for example if we have aerobic bacteria and the aerobic bacteria they can form some deposit, inside the deposit you have this condition deaerated condition and there also you can have anaerobic bacterias and one particular important anaerobic bacteria is sulfur sulfate reducing, sulfate reducing bacteria which is called desulfur, desulfuricans, this is one particular bacteria and what it does, it reduces the sulfate that is present in the solution, so they, and these are inorganic sulfates, so inorganic sulfates if you have sulfate radicals inorganic sulfate that would be reduced in the presence of hydrogen and that can go to S - 2 sulfide ion can form and then 4H2O and this is in this presence of this particular sulfate reducing bacteria this reaction happens. Now these hydrogen, this hydrogen can be supplied either by cathodic reaction which is H+ +E hydrogen or it can be supplied by organic matter that is present in the soil or general environment.

Now once you have this hydrogen, now if this cathodic reaction happens, let’s say two hydrogen ions are getting reduced so that time, now that time you have this two electrons have to be supplied, so these electrons can come from, so iron oxidation can happen and due to this, this two electron can come here and then this would lead to hydrogen reduction, so every one gram, one equivalent of hydrogen is basically equivalent to one equivalent of iron that is going into the solution. So now that means you have increase iron corrosion, now same thing if this iron ion, this Fe+2 that can react with sulfate and it can form FeS, five ferrous sulfide and that's what whenever this kind of corrosion attack happens you always see the presence of iron sulfide and that also gives a proof that you have this desulfuricans bacteria presence, and this is basically the sulfate reducing bacteria.

Now you can also have, this is the effect of one sort of anaerobic bacteria you can also see the effect of aerobic bacteria, let us see the example of aerobic bacteria, so aerobic bacteria when we one particular example is it oxidizes, there it's basically the sulfate is getting reduced and here sulfur would get oxidized, sulphur gets oxidized in the presence of aerobic bacteria, so actually aerobic bacteria oxidizes sulfur and here anaerobic bacteria the sulfur reducing bacteria is reducing the sulfate radical, so actually now here the reaction would be $2S + 3O_2 + 2H_2O$ it goes to $2H_2SO_4$, so this one particular example of sulfur oxidizing bacteria is thio bacillus, thio bacillus, thio oxidant actually what happens, because of this sulfur oxidation you have the production of H_2SO_4, so pH level goes down the solution becomes acidic and as it goes to acidic solution the corrosion rate increases, corrosion rate increases. Now sometimes the slime which is basically there will be a production of slime which is polymer extracts of aerobic bacteria and this slime, let's say you have on the metal surface you have a slime generation and then it can also lead to localized corrosion attack, and it can also lead to in this slime you have this part you have less oxygen or less air and due to that in this part you can have anaerobic bacteria growth, and then this aerobic bacteria is leading to corrosion because of the sulfur oxidation, but at the same time you have this slime generation which is basically a polymer extracts of this kind of bacteria and there you have the less air content, you have less air content and that's what you can have a growth of anaerobic bacteria which would also lead to extra corrosion of the particular section.

Now this is one example, another example is there could be iron oxidizing bacteria also you can have the presence of iron oxidizing bacteria which is theo bacillus, ferro oxidant, ferro oxidants and what they do? This is basically, this is one bacteria, and this is another bacteria, so what this theo bacillus ferro oxidants they do, they oxidizes Fe^{+2} or Fe^{+3} and enhances the corrosion rate, so you can have the corrosion due to aerobic as well as anaerobic corrosion, anaerobic bacteria presence. Now generally in the case of aerobic bacteria if the dry condition prevails, you can have the corrosion which is due to aerobic bacteria, this is dry condition and if it is wet condition then you can have wet condition, then you can have anaerobic bacteria related corrosion phenomena, and this is of course in the rainy season, and this one is a hot summer season, or dry season, so these are basically some of the examples of corrosion which is related to anaerobic and aerobic bacteria.

Now you can also have the corrosion due to macrofouling, corrosion due to macrofouling, so the macrofouling for example in the water you can always have smell, you can also have mollusk or barnacles, so they can form they can attach to the surface of the metal and they can form a deposit and those are nothing but the macrofoulings and this macrofoulings are important, sometimes they are more important because of a different reason than corrosion. For example, this problem macro fouling problem is experienced in case of sea fell, when it is in the sea water and the sea fell for example if you have a sea fell like this and if you have macrofouling deposition here and that might be affecting the corrosion but more important is they will increase the drag force when it is moving like this and that time they increases the drag force. And increase in drag force means so drag force increases and that means increase in power requirement, increase in power requirement rather than corrosion so then time to time the removal of this macrofouling is important in case of sea fell, so where we can experience this off this kind of macrofouling sort of macrofouling related corrosion you can experience in case of metallic structures, vessels and pipelines which are exposed to seawater as well as freshwater system.

Now so, some of the characteristics of macrofoulings for example the stagnant condition, for example if you have stagnant condition or if there is low rate of fluid flow then the macrofouling growth would be more compared to the running condition or let's say the velocity, the relative velocity of the fluid across the metal surface is very high, so the macrofouling deposition would be less and sometimes this macrofouling can lead to crevice attack, crevice attack for example on the surface you have a macrofouling like this, this is macrofouling MF and then this portion you have crevice generation, also you have low oxygen content, so there you can have crevice attack then also the metabolic, metabolic byproducts of this kind of macrofoulings are acidic, so acidic byproducts, metabolic byproducts, since they are acidic they can also increases the corrosion rate, there is a possibility of increase in corrosion rate and since you have a very less oxygen content there of course you can have crevice setter at the same time, there could be a suitable condition for the growth of anaerobic bacteria, anaerobic bacteria they can grow in that condition because you have a less oxygen there, so these are the common characteristics of macrofouling related corrosion.

Now let us check what could be the preventive mechanism in order to avoid macrofouling related corrosion or microbiological organisms those can also lead to corrosion, so what are the preventive mechanism or preventive measures? Preventive measures in order to avoid macrofouling related corrosion or microbiological corrosion, so the one method is you can let's say the corrosion phenomena is due to anaerobic bacteria related corrosion, then of course aeration would improve, aeration would prevent corrosion because due to this aeration anaerobic bacteria would die and that would lead to decrease in corrosion rate or you can also have chlorination + biocides, in combination of those two they can also kill those bacterias. Then you can have coating, for example tar or enamel, or plastic, what they do? They generally have an impervious layer on the metal surface which should not allow the bacteria to interact with the metal surface. So then you can also have cathodic protection, cathodic protection is one way to prevent biologically influenced corrosion, then you can substitute material, substitution of material for example in a particular soil if you have a very high corrosion rate due to this biologically influenced effect you can go for plastic pipe, or you can also have asbestos pipe, so they will be inert to those bacterias, then you can also have for example in case of macrofouling time to time cleaning is very important, so then you can also have for example than 5 time to time cleaning that can avoid macrofouling related effect. Then you can also increase, then you can also have biocides so those can also interact with bacterias and they can kill the bacterias, so these are the common preventive measures which can control the biological influence corrosion and you can reduce the corrosion rate to a great extent, so this is about biologically influenced corrosion which have two major sections, one is microbiological corrosion and then macrofouling.

So now let me shift to another topic which is, this is basically the two kinds of special corrosion form, one is biological related corrosion and then let me also get into liquid metal related attack or liquid metal related embrittlement effect. So the next topic could be the liquid metal related failure, so the topic is liquid metal attack. Liquid metal attack if you see it can have four different manifestations, now one is if you see the manifestation it can have instantaneous failure, instantaneous failure off the solid metal in contact with liquid metal and when the solid metal is under applied load or residual stress instantaneous failure of solid metal, solid metal in contact with liquid metal and that time this solid metal is under tensile stress and that tensile stress could be applied or residual, so this is one manifestation there could be sudden failure or sudden break in the system, solid metal system. Then you can also have delayed failure and that can delayed failure of the solid metal which is in contact with liquid metal and that time the failure can happen below the tensile strength of the metal, so it can happen below the tensile strength of metal, so the delayed failure that can also happen when it is under, when it is in contact with liquid metal. Then you can have, for example a solid metal you have, where you have intimate contact, this is solid metal SM, and this is liquid metal LM and then the solid metal has grain boundaries and there could be a possibility of liquid metal which can penetrate, which can penetrate through the grain boundary regions and this can happen this penetration can happen without the presence of stress, so this is one sort of manifestation of liquid metal attack. And then lastly you can also have fourth, you can also have high temperature corrosion due to liquid metal. So these are four manifestations, but we would concentrate our discussion on this fracture condition and little bit of this corrosion effect which is basically a delayed effect which can be either through the grain boundary, liquid metal can penetrate or high temperature corrosion in the absence of stress, but if you see this two condition they are more or less almost similar to stress corrosion cracking where you have a solution and then it can, due to the solution effect on the solid metal that leads to a stress affected, a stress and that leads to a failure when the stress as well as corrosion both are occurring simultaneously, but here the solution is nothing but the liquid metal, it's not aqueous medium.

Now if we see the liquid metal corrosion, actually it's basically catastrophic or delayed failure of solid metal when it is in contact with liquid metal and there could be, what could be the effect or result of this attack? One could be, there could be loss of ductility, then you can have loss of, you can have reduction in fracture stress, you can have reduction in fracture stress or strain, or strain, or it can be both, it can be both, then of course you can have there is basically a ductile to brittle fracture, and generally this brittle fracture could be intergranular or it can be transgranular, transgranular cleavage kind of fracture, then you can also experience, there could be, as I have mentioned already that it could be instantaneous or it can be delayed failure and fracture morphology. And now coming to fracture morphology as we have mentioned that ductile to brittle fracture, now it could be intergranular or transgranular cleavage, for example one example of intergranular fracture is experienced in case of brass when it is exposed to in mercury you experience generally the intergranular corrosion is experienced, intergranular fracture surface is experienced. Now this liquid metal attack or liquid metal attack mainly the failure or the fracture part that is specific to some environment, specific to environment it means that let's say you can have embrittlement effect that is or the fair fracture effect rapid fracture or instantaneous fracture effect of zinc in liquid AG which is nothing but the mercury, liquid mercury but you cannot experience that instantaneous failure and which is nothing but the embrittlement effect due to the presence of liquid metal it is also called liquid metal embrittlement, and all in short it is called LME, so LME can be experienced in case of zinc when it is in contact with liquid mercury but it cannot happen in case of cadmium the same thing you cannot experience any LME.

Now another example is liquid gallium embrittles aluminum, but it cannot embrittle magnesium so there is some specific nature of this LME effect or the liquid metal embrittlement effect, specific nature of environment that can guide or that can tell which in that can affect whether in a particular solid metal you can have liquid metal embrittlement or not, so this is and then we can also experience and we can also experience the severity of corrosion attack or liquid metal embrittlement of a particular environment severity of embrittlement, so this is another part which is basically sometimes you can experience a very high rate of liquid metal embrittlement or high degree of a liquid metal embrittlement, but if you add some element in the liquid then the embrittlement effect would go down so we see that the severity of embrittlement is another important issue, and here one particular example is let's say a polycrystalline aluminum if the embrittlement effect of mercury, liquid mercury is studied in case of polycrystalline aluminum and let's say the polycrystalline this is stress strength, engineering stress strain data where you have, if it is normal solid metal without the presence of liquid metal you have this sort of stress and behavior.

Now if we see the embrittlement effect of liquid mercury in case of polycrystalline aluminum let's say if we add if it is only mercury, there will be break which is happening right to its normal fracture stress, now if it is alloyed with the mercury, liquid metal if the liquid metal if we have mercury + 1.3% tin then your embrittlement effect becomes more severe, and then if we have mercury + 3% zinc severity effect is maximum, severity is maximum that means here where the mercury as well as zinc those are present in the liquid metal then your embattlement effect in case of aluminum would be maximum, this is the severity of embrittlement and that decides, that is decided by one is chemical nature of the liquid metal as well as of course the solid metal, then you can have the embrittling species, then you can also have the effect of alloying elements then grain size then of course presence of crack, crack in the material and the nature of the crack that would decide the severity of embrittlement in case of liquid metal embrittlement effect, then you can also have the effect of stress-strain curve there could be effect on stress-strain curve, so for example one such example is in case of copper if we want to see what would be embrittlement effect in the presence of bismuth, then this is stress, this is strain and if it is uncoated that means without the presence of any liquid metal you have the characteristics like this and if it is 100% lead then you can have the character like this, this is in case of a 100% lead and if you consider 100% bismuth and the nature would be like this, so you see the in case of when it is 100% lead and this is uncoated, so you don't have much change but only thing is there is a little decrease in the total fracture strength but your yield point as well as ultimate tensile strength that those two things remain unchanged, but once we have 100% bismuth you have a very aggravated embrittlement effect and if you alloy this 100% bismuth with lead, let’s say 20%, let's say if 40% lead then you can have little improvement in the, little improvement and there will be delayed embrittlement so this is let's say 60% bismuth + 40% lead, so this is basically the effect on stress-strain curve there could be reduction in fracture stress, total fracture strain and this is one particular example, this is in case of polycrystalline copper, polycrystalline copper and then you can also have this is basically the common characteristics of liquid metal attack or liquid metal embrittlement effect.

Now there if you would like to see what could be the requirements for liquid metal embrittlement, so requirements for liquid metal embrittlement first thing is there should be intimate contact or proper weighting of the solid metal by the liquid metal, so that is one particular one first requirement, then the solid metal, solid metal must be stressed and sufficiently stressed to produce that means there should be stressed which can produced, which can produce plastic deformation in the solid metal.

And third thing is, this is the requirement of for LME and third thing is there should be adequate supply of liquid metal. So these are three conditions or the requirements for liquid metal embrittlement and if we don't have intimate contact the liquid metal embrittlement effect would not be experienced and if the solid metal is not properly stressed, if there is no plastic deformation liquid metal corrosion can happen but the embrittlement effect cannot be observed, may not be observed and there should be adequate supply of liquid metal.

And lastly there are several factors we have already talked about those factors which can influence liquid metal embrittlement, now this is the factors which influences, which influence, influencing liquid metal embrittlement, one is of course if we have grain size effect, grain side effect generally we see that if it is course grain structure that means there we have more embrittlement that means the course grain structure, course grained material experience embrittlement more than the fine grain material, then you can have a temperature effect and generally that the main temperature should be more than the melting point of the liquid metal then you have the strain rate effect, higher the strain rate more would be the embrittlement, so higher, more would be the embrittlement effect and then of course effect of alloying that is also important factor in case of liquid metal embrittlement.

Now if we come to see what are the mechanism by which liquid metal embrittlement can happen in a particular solid metal, there are three different routes or mechanism through which liquid metal embrittlement can happen in a particular material, so the mechanism so this is mechanism generally one would be the reduction in surface energy so the presence of liquid metal can it lead to reduce the surface energy at the crack-tip, at this crack tip zone if we reduce the surface energy then you can have a lower fracture stress at which liquid metal embrittlement can happen. Then second case is stress assisted dissolution model, stress assisted dissolution where you have the crack-tip, this is the crack-tip and here this is under stress and because of that there could be localized dissolution and that lead to increase crack growth or the crack growth would be possible due to the localized resolution and the stress is always there to keep the crack open, this is stress assisted resolution, then also you can have another mechanism which is adsorption induced reduction in tensile strength, tensile cohesion or shear, shear strength this is in tensile cohesion or shear strength, what it says, for example in this case the last case let's say you have a crack like this and here you have the material, this is my crack, this is the solid metal optim, and here you have the bonding and you have the embrittle mean embrittle in atom which is B due to the surface, this is the adsorption of this B which can go and sit here and let us say here you have the shear stress tau, shear stress which is active on active plane of shear plane and this is my tensile stress axis, so now once P gets in there this is B so it weakens this atomic bond strength and because of the weakening effect and the shear strength or tensile cohesion strength both the things would go down and the crack can propagate through this, so this is the third mechanism which is adsorption induced reduction in tensile cohesion or shear strength. Now these are the three mechanisms.

Now let us get into the preventive measures, what could be the preventive measures? Preventive measures one is you can have impurity atoms in the solid so introduction of, in the solid so that intuitive atom can share its electron with the liquid atom and thus the metal, solid metal would be protected from embrittlement effect then also you can introduce solute in the, in the liquid metal the solute addition, solute addition in the liquid metal one particular example is addition of blood in liquid bismuth generally reduces the embrittlement effect in aluminum, so in case of aluminum embrittlement, sorry this is in case of copper, solid copper if we introduce lead in liquid bismuth we can have less severe embrittlement effect. Then also we can have let's say if a solid, this is my solid, this is my solid metal and this is my liquid metal, if we can produce if we can put some sort of barrier around this metal surface which can be either ceramic or metallic that would give you protection against liquid metal embrittlement.

Then fourth is cladding, generally zircaloy that is cladded with pure zinc, pure zirconium, that is pure zirconium cladding that reduces the zircaloy embrittlement effect in the presence of liquid cadmium, liquid cadmium this is experienced in case of atomic reactors where zircaloy is used and the liquid cadmium, cadmium related liquid embrittlement effect is experienced so if we have a pure zinc, pure zirconium cladding then we can protect the material from liquid metal embrittlement, and of course if you can reduce applied or residual stress, so these are some preventive measures. Now these are basically all together, this is basically the whatever discussions we have done that is on the liquid metal embrittlement as well as overall the liquid metal attack. Now there are many examples of this liquid metal embrittlement effect one, few examples the case studies let me put forward, so few examples of liquid metal embrittlement effect one is, this is case one sometime in case of copper containing steel when that steel is hot rolled we sometime experience hot shortness, hot shortness in case of steel is related to low melting sulfide component formation along the grain boundary, so in this case if we have a high copper, high copper in the stilt, so you have this stilt and on the surface you can have oxide and just below the surface in this part you can have high copper compound formation, low melting compound formation, low melting phase. So now if we roll it like this, now you are rolling it so this thing also can happen this side also, during rolling this one would form a liquid because that is a low melting phase and that can lead to hot shortness, this is one example of liquid metal attack, and that liquid metal is nothing but the liquid, this high copper low melting phase which is getting melted and that phase can get into let’s say these are my grain boundaries that can go penetrate along the grain boundaries.

Now another case is sober, this is basically the practical example, this is also another practical example that happened in 1974, in one of the factories in flixborough, so there we experienced this sort of liquid metal attack which is due to liquid zinc, liquid zinc and the unsupported pipeline these unsupported pipeline in there Factory which is basically producing cyclohexane, cyclohexane producing factory unsupported the pipeline, on that pipeline the liquid zinc related embrittlement effect would be, was experienced and the entire pipeline broke into pieces and there was fatal experience, fatal accident and around 28 people died and there this liquid zinc is basically, the source of that liquid zinc was that factory they used to use galvanized staircases and due to the heat the galvanic staircase, the zinc droplet fail on that pipeline and that led to liquid metal embrittlement of that pipeline, so this is another example so that means the liquid metal embrittlement can be fatal in some time, in some cases, so this is about liquid metal related attack and more, more specifically the effect of embrittlement due to the presence of liquid metal.

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