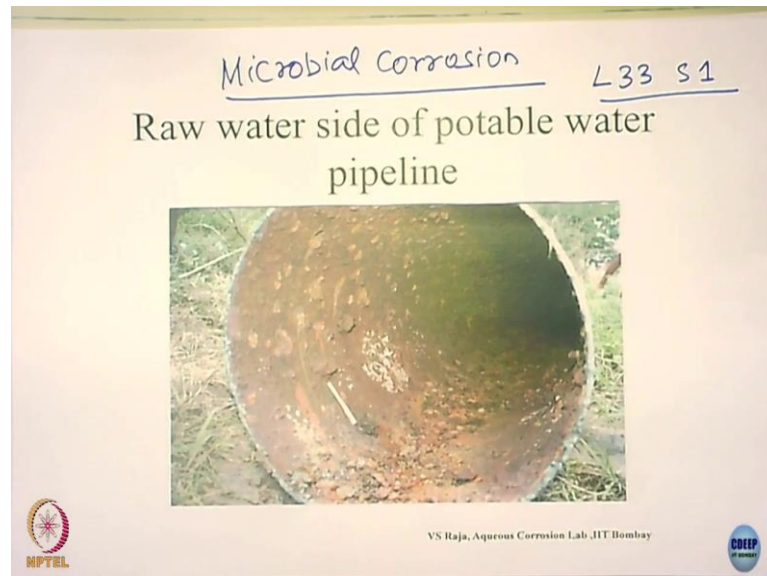


Aqueous Corrosion and its Control
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Lecture – 33
Forms of corrosion: Microbial corrosion

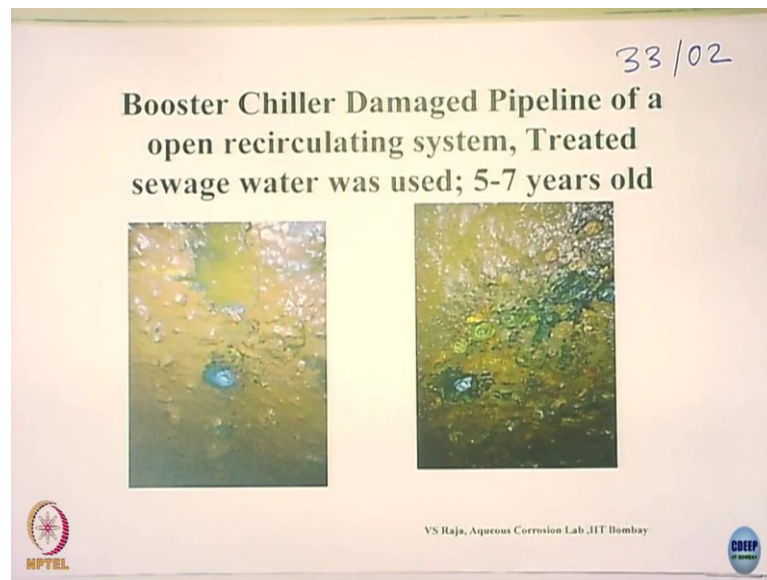
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Welcome to the next chapter on the Forms of corrosion. And today we shall be discussing on what is called as Microbial corrosion. What I have shown here it is a pipeline got corroded due to microbial corrosion. To be more specific; the presence of sulfate reducing bacteria and the iron bacteria were implicated in the corrosion of this particular pipeline.

The pipeline lasted only for about 6-7 years. This pipeline was transporting water from the river and this water went to a water treatment plant treated and then distributed. The corrosion occurred between what I would say the water treatment plant and where the water was taken out from the river; we call them as a raw water side. So, this is the kind of problems you normally encounter.

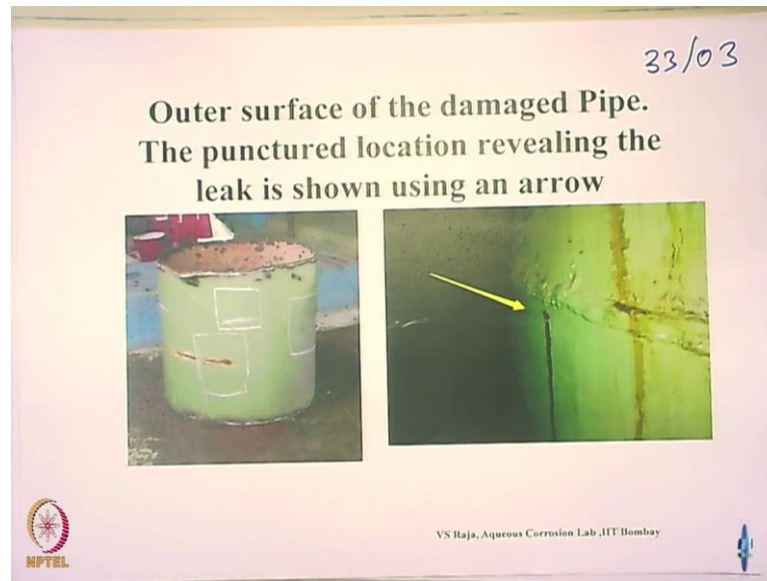
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There is other problem which we analyzed you know some time back; as corrosion of a pipeline you know carrying cooling water and it was lasting about 5 to 7 years old. The cooling water here was treated sewage water.

And you see here you know you can see very clearly the kind of appearance you see here this kind of silverish colored you have to see there. You see the silverish color here the silverish colored that you see here; are all due to the microbial corrosion more specifically it was due to surface reducing bacteria and such bacteria can lead to premature failure.

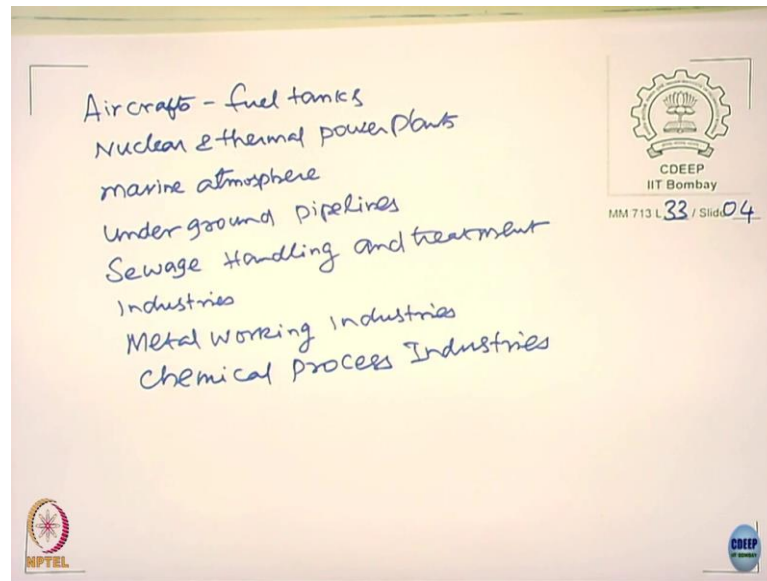
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You see it is a pipeline and in fact, this pipeline carries water from the chiller and goes to the heat exchanger and you know. In fact, it is it was used for one of the five star hotel where the air conditioned system. You know you know the air conditioned systems how it works. And you see this is this pipeline is carrying the cooling water.

Now, I do not know how much you can able to see visualize this here; there is a small leak you see here ok. There are lot of punctured holes coming from the pipeline and so there was this was the problem. Now the microbial corrosion as we see; it is a problem to several industries it is just not only some industries having problems. It happens in so many industries these problems really noticed.

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It could happen even in the aircrafts especially in the fuel tanks, it can happen in the nuclear and the thermal power plants, it happens in the marine atmosphere and it can happen in underground pipelines, sewage handling and treatment industries, metalworking industries.

See I have just listed a few examples actually you know it is just not only confined to this thing; chemical process industries you know. See chemical process industries is a generic name and it could be a fertilizer, it could be petrochemical, it could be various types of chemicals being produced. In all these industries you notice that microbial corrosion is one of the should I call a mechanism of corrosion that causes a premature damage to the structures.

Now, what I am going to do is; I am going to give you a very brief discussion you know deliberation I would say on microbial corrosion because this involves quite a bit expertise related to biology ok. So, I think you know we are not so comfortable in dealing with the biologic situations.

But nevertheless as a corrosion specialist you should understand broadly what kind of mechanism that operate in microbial corrosion. And what are the types of microbes they cause corrosion, how do you control them, and how do you monitor them. So, that is what I am going to discuss you know in this particular class.

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Microbes are involved.
Microbes process can affect various forms of Corrosion.

Mechanism

- Produce organic and inorganic acids as a metabolic by product

C, N, P \rightarrow nutrients

organic acids: acetic acid, Citric acid, Succinic acid, lactic acid etc

Inorganic acid: 10% H_2SO_4 (Sulfur Oxidizing bacteria)

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The first and foremost that you would like to know is that the microbes are involved, but the microbial corrosion in a way is not a mechanism by itself ok. The microbes process can affect various forms of corrosion; what do you mean by that? Say pitting corrosion, stress corrosion cracking, the uniform corrosion, you know the inter granular corrosion. So, many of these forms of corrosion can be accelerated by the presence of microbes.

Now, how are these microbes really work on it ok. What is the mechanism through which these microbes really affect the metals. Now the microbes first of all you know they produce organic and inorganic acids. they produce these acid. How to produce? As a metabolic by product. What do they metabolize? They metabolize related to carbon containing compounds, nitrogen and phosphorus these are all the nutrients.

They take these nutrients they metabolize and the byproduct of that could be an organic acid or an inorganic acid. What are these acids? The organic acids are acetic acid, could be citric acid, could be a succinic acid, lactic acid etcetera. These are the prominent acids they form.

Now these organic acids are not as strong as inorganic acids right. But nevertheless they can bring down the pH of the environment significantly. And especially so in the localized areas of the metal surface; we will see how these acids are confined to the surface. They are not getting affected by the external environment bulk water is not

getting affected. So, these acids are secreted at the surface of the metal substrate and so they cause corrosion of the metals.

Inorganic acid; as much as 10 percent of sulfuric acid it can produce ok. And they produce how they produce it is a I just tell this is called as sulfur oxidizing bacteria. We will talk about in details about the nature of bacteria subsequently. So, they can produce these acids and these acids can lower the pH of the environment on the surface and so they in turn cause corrosion.

Now, you see that the bacteria per se are not going to eat the metals. They create in a environment and that environment in turn is very corrosive in nature; this is one type mechanism.

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• Produce sulfides under anaerobic conditions (sulfate reducing bacteria)
FeS, conducting (electrically) compounds
galvanic Corrosion.

• Introduce new redox reactions

• Produce concentration cells
(a) Chemicals and/or (b) O₂.

• Depolarize the cathodic reactions.

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \text{ (anodic)}$$
$$\text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{H} \text{ (cathodic)}$$
$$\text{SO}_4^{2-} + 8\text{H} \xrightarrow{\text{SRB}} \text{S}^{2-} + 4\text{H}_2\text{O} \text{ (Depolarization)}$$
$$\text{Fe}^{2+} + \text{S}^{2-} \rightarrow \text{FeS} \text{ Corrosion product.}$$

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The other one is they can produce sulfides under an aerobic conditions; this is done by sulfate reducing bacteria. Now, how does this sulfide affect corrosion? Let say it forms iron sulfide the iron sulfide are conducting; I mean conducting means what? Electrically conducting compounds, they can lead to galvanic corrosion. So, assume that you know I have metal surface and there is a one patch where you have iron sulfide formed.

The neighboring metal becomes anode the iron sulfide becomes a cathode there is a corrosion. Or you have a iron sulfide which is porous allows the water to enter into it, then there is going to be a galvanic corrosion between the iron sulfide and the base metal.

Assume that the iron sulfide is quite continuous impervious and nothing happens. In fact, the corrosion rate will drop, but that does not happen in practice.

So, you normally see that the presence of sulfides cause the corrosion of the metals; more so steels it can happen. We also introduced new redox systems; redox reactions I would say oxidation reduction reaction. Generally, what is a redox system you normally you see for corrosion of metals; either there is a oxygen reduction reaction, oxygen with the hydroxide equilibrium or H plus hydrogen equilibrium right these redox systems.

It can introduce one more and again cause the corrosion process that is a another cathodic reaction that will also assist the corrosion of the metals. You have seen in the mixed potential theory right. A more redox processes more corrosion can really can happen.

They can produce concentration cells. Cells either of chemicals and or b; the oxygen there. I can have oxygen partial pressure variation between two locations; one place is rich in oxygen content, other place is poor in oxygen content. There is a cell and so there is going to be anode and cathode can lead to the corrosion process. You know what it does do what does it do? In some cases they can depolarize the cathodic reaction.

I think you guys are very familiar with electrochemical concepts of kinetics right. If it is depolarizing what happens to the corrosion rate.

Student: Increases.

It increases right the over voltage decreases and so the corrosion rate increases. An example here is let us take this; suppose you have iron it gets oxidized it is an anodic reaction right. And you have water can get split into that it can form hydroxide it can form hydrogen it could be a cathodic reaction right. Water splitting water reduction could be a cathodic reaction.

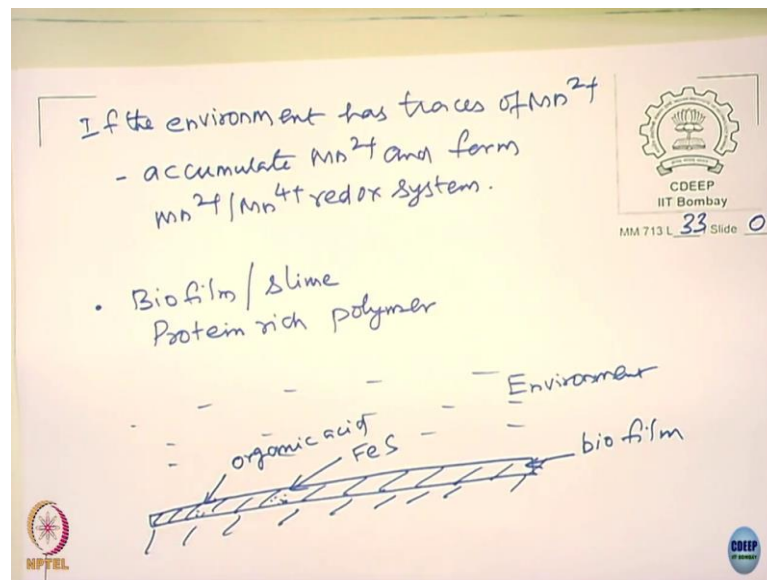
If I can accelerate this reaction if I can accelerate the cathodic reaction then what will happen to anodic reaction? It will increase provided the cathodic reaction is the rate determining step. If this is slow step if you can fasten this particular reaction then the corrosion reaction overall increases.

So, what is happening now? Suppose I have a sulfate and I can combine with this what happens? It can form with SRB sulfate reducing bacteria. Please notice that SRB takes away hydrogen to combine with the sulfate to form sulfides. So; that means, this is what is this called? This is called as a depolarization. Please look at it is not an electrochemical reaction right the hydrogen is already in the atomic form. So, this in fact, facilitates this one so this is called depolarization process.

Now what else can happen? This iron 2 plus can combine with sulfur sulfide it can form iron sulfide right; as a corrosion product. So, you notice here now sulfate reducing bacteria is not really doing anything to the metal directly; it just facilitates corrosion indirectly by depolarizing the cathodic reaction and producing iron sulfide which also get catalyzed through a galvanic action.

So, this is going to be a problem if you have sulfate reducing bacteria in the system. So, this is a another kind of mechanism that can cause the corrosion of metals. We talked about introducing a new redox systems you know.

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Suppose if the environment has traces of manganese ions. It can accumulate right; it can accumulate Mn^{2+} and form Mn^{2+} and Mn^{4+} redox system. This is another type of bacteria right. So, it can now introduce increase the rate of corrosion quite significantly.

The bacteria can also form biofilms; it is also called as slime it can form on the surface. Actually it is a byproduct of the metabolic product in a metabolic processes. And these are all called protein rich polymers; if you have a metal biofilm it is also called as the biofilm.

Now, can consist of an acid we talked about before. It can consists of iron sulfide so it can be corrosion products and it could be a metabolic products they sit on this biofilm right. Now assume then I have some acid at local places or I have iron sulfide at local places. So, here I have let us say organic acid, here I may have iron sulfide. Now what happens? Now the corrosion is now confined to that particular place; because the biofilm it separates the environment you know this is your environment.

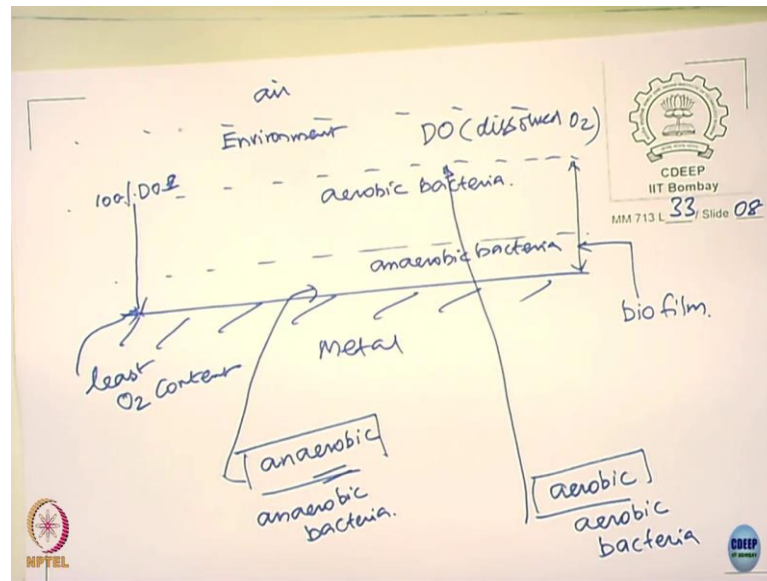
The biofilms are formed as a result of the metabolic activity of the of the microbes, but any case you see some kind of folding happening on the metal; on the metal surfaces if you have some organic products in water right.

Maybe that you know some kind of fold leaves for example ok. And many of this the organic products can sit on the metal surface a few layers can form. And in fact, that only invites the microbes; you see the microbes will not go to the surface unless otherwise they finds and nutrients in the surfaces.

These nutrients are what they are consists of carbon, nitrogen, phosphorus, compounds they are nothing but organic you know organic substances actually. So, there is a relation between the cleanliness of the water or the environment and then relation to the microbial activity. If the water is quite clean and everything and the microbial activity comes down.

So, that apart when you have a organic fouling then you have microbes colonizing this. And the microbes colonize it they secrete the extracellular substances as a biproduct they are all form at the surface; and these are all called biofilms. And this biofilm plays a critical role in corrosion of the metal. First of all it localizes the environment here; it can also.

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Air is environment now, I am going to magnify this biofilm and I make it quite bigger right. This is the; please look at this it is a membrane type you know the biofilm allows the water to diffuse through it; is not going to be a barrier like you know for water.

The water will be there anyway; that means, the water will be in fact, the metal being wet completely it is not that metal be totally dry at all metal be totally wet. The biofilm in fact, the major fraction of the mass is due to water only. So, water is going to be there.

Then what else; your water your air there is a dissolved oxygen present here DO; is a dissolved oxygen content right. Now please look at there is a biofilm what will happen to the concentration of oxygen as move from here to this what happens? The oxygen is let us say here it is 100 percent dissolved oxygen here right and as you move down here least oxygen content in the water. So, it can form a concentration cell with respect to the oxygen content.

So, what will happens now here. That means, this place is totally an aerobic this place is anaerobic right. And this place is what? Aerobic; that means, you have reasonable amount of oxygen present here, here the oxygen content is reduced. So, this leads to a different situations for the microbes to persist to live. And the microbes live here that are called as aerobic bacteria and these bacteria called as anaerobic bacteria.

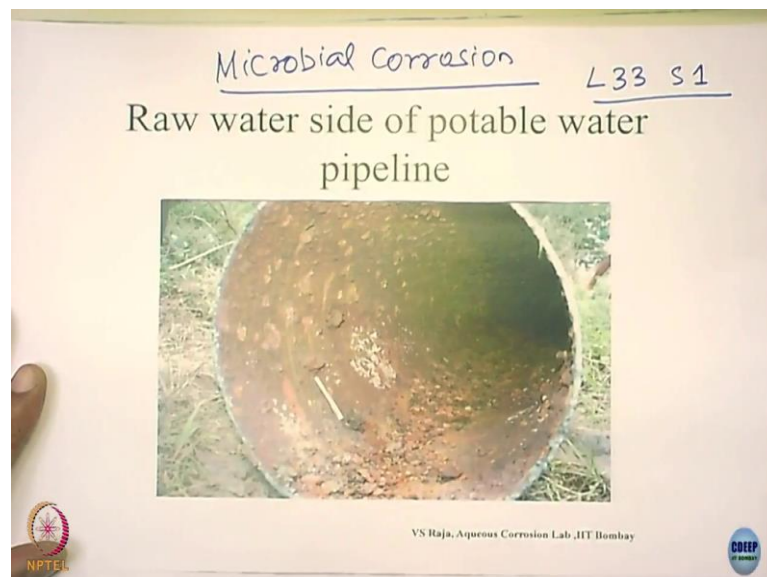
So, it is possible that you have somewhere here anaerobic bacteria, you have aerobic bacteria sitting on the metal surface. This is very dangerous you know combination for the corrosion of metals; we see that shortly.

So, the idea of showing this right now is that how these biofilms can localize the processes. The corrosion products, the metabolic products on the surface can cause localized corrosion thing and so that leads to severe amount of corrosion; like a pitting and leaking can happen at these places.

In fact, if there are stresses it can lead to stress corrosion cracking as well. So, there are cases where the stainless steels are suffered stress corrosion cracking because of microbial presence. Because it gives an acid, gives a chlorides and there are stresses and in fact, that is going to pitting and so that leads to stress corrosion cracking of metals.

What is this is as I told you before microbial corrosion is not a corrosion any different from the normal tracks of corrosion. It only microbes assists the various forms of corrosion that we saw so far. Now in practice what in fact, it happens I think if you can recollect my the photo I shown before; this is very interesting actually right.

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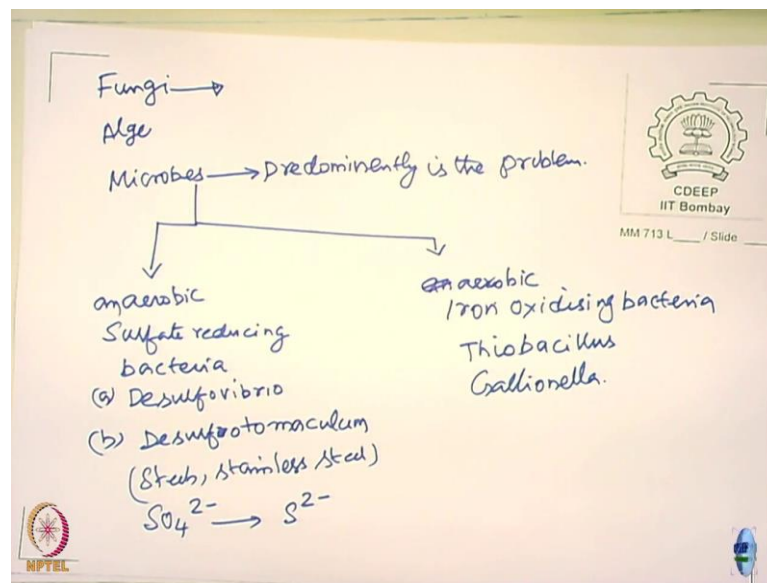


If you see; I do not know how visible it is it visible to you near this one these are all this they are all called as tubercles it is called tubercles right in lumps you can see lumps of them.

You break it break open it you see the black here and this black is nothing, but this anaerobic thing; because over there the oxygen content is very less the sulfate reducing bacteria remain there and create hydrogen sulfide. And then what and then they create what is called as iron sulfide lead to corrosion process. So, is this what happens when you have you know microbes present in the water.

Let me touch upon a few things about the microbes; what they are present here ok. Again as I told you it is a huge classification I will be make it a little bit more simpler here.

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Probably you can classify them as fungi, algae and you can also as a microbes. In fact, the fungi is known to induce corrosion in aluminum alloys happens but these are all predominantly the problem. And these microbes can be classified as; aerobic and anaerobic.

And sulfur reduced bacteria is among this; there are of course, several sub classifications I just given only two examples and what are their biological name. So, one is called as Desulfovibrio one and you also have desulfo it is called desulfoto maculum ok.

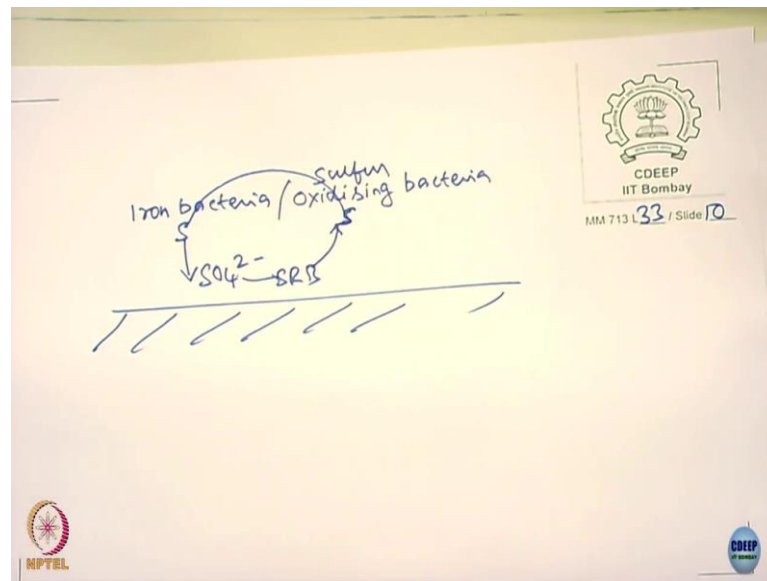
So, these are all; these are all affect this affect the these all affect the steels, stainless steels etc they effect actually; all of them reduce sulfate to sulfides right. All these what they do is they convert this into sulfides they do that. This anaerobic. I think I made a

mistake you know I am sorry for that. These are all this is actually is a anaerobic bacteria ok. Please make this change it is anerobic bacteria and this is say aerobic bacteria.

The aerobic bacteria some of them are called as you know iron oxidizing bacteria; in general terms ok. And these are called as Thiobacillus some of you might be aware of this Thiobacillus and all you know some of you would be knowing about biology some you might have studied in the mineral beneficiation process you know they are used these things.

So, Thiobacillus is one, Gallionella is one another one Gallionella. Anyway so these are all you know the one we thrive in the aerobic conditions. These guys thrive in the anaerobic conditions. The situation where I talked about in normal pipelines or you know in industries you can also have; on the top aerobic bacteria on the bottom they can have anaerobic bacteria right. And they can they get synergized the corrosion process.

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See for example, you have iron bacteria here iron bacteria or oxidising bacteria it is sulfur oxidising bacteria ok. What it can do? It can take sulfur converted to sulfate, SRB what it can do; convert this into sulfur and the cycle again continues in the process.

So, they can keep on you know the corrosion can continue even though you may not have large amount of sulfur; sulfates with the limited sulfates the corrosion can continue and abetted in the actual situations.

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The slide contains handwritten notes under the heading "Prevent". The notes are as follows:

- To keep the system free from microbes & clean.
- Hydrotesting
 - Sterilized water + biocides
- Cathodic protection of underground pipeline.
- Increase the pH above 9 to 10; aerobic bacteria will not live.
- Close system
 - Use biocides.
 - Open recirculating system (Cooling water)
 - Cl_2 , ClO_2 , activated Br, Ozone — Oxidising agents
 - Enzymatic poisons.
 - Surface active Agents (Quaternary ammonium Compounds)

The slide also features the CDEEP IIT Bombay logo in the top right corner, the NPTEL logo in the bottom left corner, and the text "MM 713 L 33 / Slide 11" in the bottom right corner.

Now let us go into how do we; how do you prevent micro aerobic corrosion. There are several ways that we can do. So, first and foremost is to keep the system free from microbes and also clean. What do I mean by keep the system free from microbes; it is not possible always, but where it is possible you should do that.

A good example is hydro testing; people do hydro testing ok. So, this is what pipelines heat exchangers any pressure vessels that we talk about is designed to take a certain pressure right. Before you put them into service you need to pressurize it the best way to pressurize is with water. They cannot do with the gas because it can be dangerous.

So, when you use water there are many cases the heat exchangers hydro tested and even before commissioning the tubes started leaking. Primarily because; the water that I used contain the microbes. So, what you can do in this case; use sterilized water I can also add along with this some biocides.

We should be talking about this Gallionella right this is what is very common in water and it can cause corrosion problem. In a pipelines people use cathodic protection; underground pipelines you do not have much control over the soil nature right. The soil you know we are going to 100s of kilometres of pipelines you are laying and you have no control over that. So, it is not possible to keep the soil free from microbes. So, you do cathodic protection.

In fact, the microbes can also degrade the coatings. The paint coating that you apply microbes can disintegrate lead to corrosion and happen.

Student: (Refer Time: 41:29) coatings are there.

We can do that.

Student: (Refer Time: 41:31).

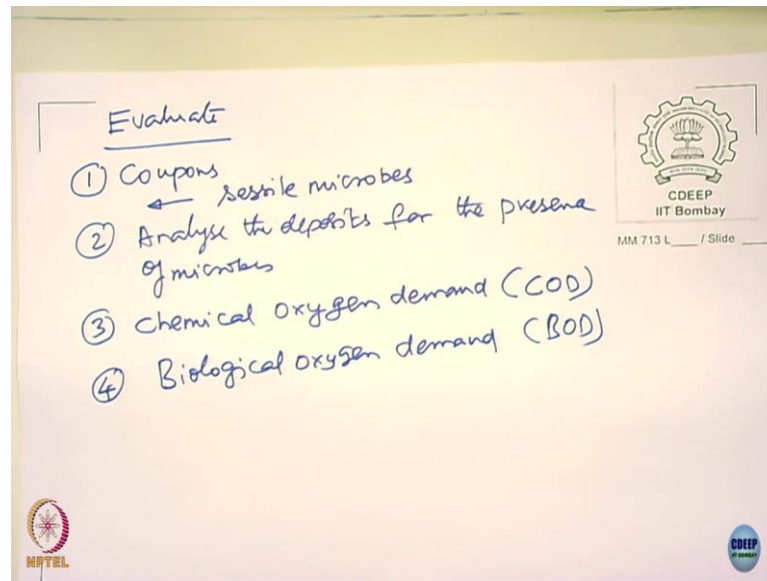
Of course where possible we can do that yes. It will also increase the pH in the range above 9 to 10. So, what does it do? The aerobic bacteria will not live. So, the cathodic protection when you do it has two purposes; one of first of all it does not allow metal to corrode. Secondly, in the cathodic protection it will create a hydroxide is not it there is going to be hydrogen evolution. So, both the way it is beneficial to that.

In a closed system you can use biocides. Please look at when I say closed system and you know and what are these closed systems? It is a cooling water system right; open recirculating system it is the cooling water system. In fact, it is invariably they all use this and these biocides some of them are could be like chlorine gas.

Cl, ClO₂ chlorine dioxide, activated bromine, ozone and so these are all they are all oxidizing right. They simply these are all called as; these are all called as oxidizing agents. People also use what is called as enzymatic poisons. They simply attack the protein structure of the microbes and so these this will be died. You can also use surface active agents an example is a quaternary ammonium compounds they are used actually ok.

So, they can penetrate the lipids cells you know and then they simply damage the walls of microbes and so they also you know kill the bacteria.

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The next is how do you evaluate; actually it is rather difficult to exactly prove that; the microbials are the reason for corrosion of the structures many times it can be done indirectly. For example you take the material and you expose the same conditions in the sterilized water. And if the corrosion of the metal is better corrosion rate is you know lower then we can say that it is suffered microbial corrosion.

Alternatively you take the sterilized water and you dip the metal you add microbes. And find out that the corrosion is any way any way different at all. Or the visual examination you just look at it and see there are any microbes present at localized areas.

So, from the point of view of diagnosing whether the particular failure is due to corrosion or not; is many times is indirect of that. You can take the corrosion product you can analyze for the presence of the various microbes. So, it is a kind of indirect evidence that you normally collect. So, that the microbial corrosion is in action. If you really want to monitor whether the corrosion occurs or not; what people do is; people install the coupons. The coupons are installed in a system you take out periodically see whether there are microbes or not.

Very interestingly when we talk about microbes they are sessile microbes; they only cause corrosion. When I say sessile what I mean by that? The microbes which stick to the surface the one that flows in the water they may not really cause any corrosion. So,

suppose you take water and you found that there are microbes present in water it does not automatically indicate to you that the system is suffering microbial corrosion.

Alternatively you would take water you analyze for microbes there are no microbes are present you cannot say that microbial corrosion does not exist; because some microbes are sitting on the walls as a cell bacteria. So, it is always a difficult exercise to analyze, evaluate the microbial corrosion of any systems.

But nevertheless you can use coupons you can analyze the deposits; for what you deposits for what? For the presence of microbes. You can also do what is called as chemical oxygen demand they called it as C O D correct. And what is this chemical oxygen demand it is oxygen required for what for the?

Student: Degrading.

But degrading the various biological systems; it could be organic things also right. So, the oxygen is required to degrade them actually why are they important? Because these are the systems which are used as a nutrients by the microbes if I am having too much of C O D that means, the system is full of nutrients available for the microbes to survive. It talks about the quality of the water that can support the microbial activity. So, it is a indirect way of saying yes there can be microbial corrosion.

Next is called as B O D it talks directly about the living organisms microbes the microbes require the oxygen to survive. So, you can also look at determine the B O D content. I am not going to talk about how we are going to do that, but it is enough to say that these are some all of the ways to assess the probability of microbial corrosion happening in a given systems ok.

Again as I told you and the when you talk about the bacteria you know there is only sessile bacteria is important. The bacteria that move around which called as planktonic bacterias. That is they are not that important, but more often people only determine the planktonic bacteria in the systems.

Well, I think I have tried to give you a broad overview of that the microbial corrosion, but this is just the beginning. I think you guys can read further and you know I am sure

that it will be very useful. Because when you talk about a corrosion problem microbial corrosion is one of the causes of corrosion of metals ok.

So, with this we shall now complete almost all aspects of aqueous corrosion of course, in the introductory level of course.