Corrosion Failures and Analysis

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Lecture - 25
Crevice Corrosion: Mechanism

Let us start lecture 25. The course is Corrosion Failures and Analysis.

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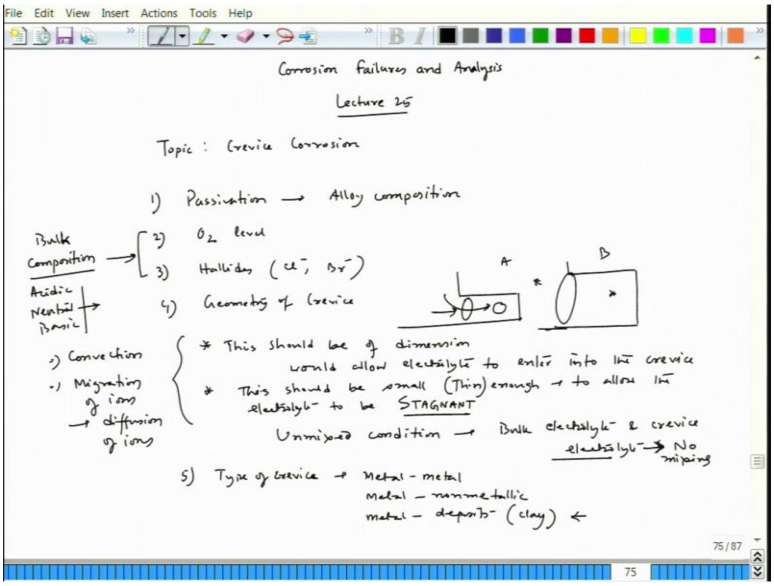

And we will continue our discussion on crevice corrosion. And if you recall our last lecture, we have in general discussed that where you do experience crevice corrosion. In fact, wherever you have a formation of slit, a thin slit, where you can the electrolyte can get access to it and which is not visible to naked eyes, so that particular part is basically the region where crevice corrosion starts.

And then of course, from there it grows now that slit can be metal-metal, metal-nonmetal, metal-deposits metal kind of dirt ok, or metal or and nonmetal objects falling on a metal surface anything which can create a slit or thin crevice we call it crevice. Now, at the same time we have given lot of examples of the photographs and looking at how the crevice corrosion initiates, and how it grows ok.

We have given the example of door, the side of the door where you have sheet metal is actually bent over there to make a thin, thick shape thick portion of there at the at the edge of the door, and their crevice corrosion starts. And even in fact, in fact we have seen an example of lock whether it is a excellent lock, highly corrosion resistant lock does not matter which company it is made of which company has made it.

If there is a crevice and if there is a possibility of water accumulation which acts as electrolyte, we can experience crevice corrosion. So that is what if you had noticed that key hole of the lock the stainless steel lock actually it did had crevice corrosion ok because around that keyhole portion, the corrosion was very prominent. Even we have seen that rho decide ribbed rebar reinforce bar, around that reap portion the foot of that reap portion actually does have a little bit of extra rust or red rust that is crevice.

And we started discussing about different factors ok, for example, we talked about passivation. The metal which is passivate which can passivate easily that metal crevice corrosion can be very aggressive if the passivation layer destroys ok. So, then the rest of the part would act as a huge cathode at the small section where the passivation part is destroyed, we get a very rapid rate of crevice corrosion growth.

Now, then there could be possibility of formation of deaerated cell. In fact, crevice corrosion starts with the deaeration ok, general the mechanism as we go ahead with the mechanism you would say that it is actually a galvanic mode of corrosion, but it is very localized. In case of galvanic corrosion, still it is a localized corrosion, but still for example, let us say anode area and cathode area they are of equal area still you will experience galvanic corrosion.

But that galvanic corrosion effect will not be that severe provided the condition is not like a small anode and large cathode. But in this crevice corrosion case, you would notice that actually it generates the situation, it creates the situation that the anode area would be extremely small and cathode area would be extremely large, and that lead to a favorable condition for extreme galvanic localized corrosion ok.

And then there are other factors, so that means, one factor is of course passivation. And once we talk about passivation, definitely it brings in alloy composition. For example, normal mild steel, it is not passivating type of metal, but once you add chromium around 12 percent, more than 12 percent, 18 percent generally in 304 it becomes highly passivating ok. So that is what alloy composition becomes important.

Then of course, we have oxygen level in the solution as we have seen that we have explained that if we heat the water or the electrolyte, oxygen level drops. And that would lead to a situation where crevice corrosion may not grow as fast as the situation where oxygen level in the solution in the beginning of the process is very high, so that is what oxygen level becomes very important.

Then third is halides; chlorine, bromine, this kind of halides, if they are present, you would see that the crevice corrosion becomes very aggressive. Now, fourth is geometry of crevice. This is very tricky, very critical, extremely critical part. For example, we have a crevice let us say this is a small crevice, let us say this is the crevice ok. Another crevice is this much let us say this is the crevice. And they are if we consider their magnification level they are of naked eye.

The naked eye, so that means, this area is much larger than this area. So, this is let us say B case, this is A case. And interestingly the A case would have higher crevice tendency rather than B case. The major important factor is the crevice should be as small as possible but at the same time, it should be as large as possible also. So, now, let us understand this. This should be of dimension which would allow electrolyte to enter or rather to enter into the crevice.

And this is one and second part, this should be of that dimension that means it should be large enough which will allow electrolyte to go into the crevice. And this should be small enough or thin enough to allow the electrolyte to be stagnant. In fact, let me just put this particular thing as capital, so this is extremely important. So, it should allow that crevice should allow sufficient electrolyte to sip in, at the same time it should be stagnant.

That means, if it is as large ok, see this opening is a large o large wide opening then of course, if there is a ripple in the electrolyte, then electrolytes are in this electrolyte and the outside electrolyte, so this electrolyte and this electrolyte they can get mixed up ok. But, in this case, since it is a small opening, electrolyte can enter. But at the same time, even if there is ripple in the system in the water, this particular water which has gone in or electrolyte that has gone in will not have any chance to go out and get mixed.

So, that means, unmixed condition, unmixed condition means bulk electrolyte and crevice electrolyte. So, they should not mix, no mixing, and that is only possible if it is stagnant ok. So, this of course, there could be migration ion migration, but that ion migration would be much sluggish compared to the situation where the crevice orifice is much larger. So, that time there could be a convection of liquid or fluid ok. So, that is avoided that should be avoided in order to have a crevice kind of attack.

Now, this is another factor. Now, of course, then 5, if you consider then bulk composition of the media, bulk composition of the media in the sense I think we should not have that particular same thing separately. This constitutes the bulk constituents composition, bulk composition fine. Now, that could be acidic, it could be acidic in the beginning, it could be neutral, or it could be basic. Interestingly, even thing will be neutral would come to see that within the crevice, it becomes highly acidic.

So, we will see that when we go into the mechanism part of it. Of course, the mass transport, in fact, geometry of crevice, it talks about mass transport in the form of convection. And the second part is migration, migration of ions or you can say diffusion of ion, diffusion of ions ok. So, that means, these are the factors which can lead to crevice mode of corrosion. Then lastly we can say that type of crevice, type of crevice means it can have metal-metal.

For example, washer metallic washer used for during tightening of a bolt, or it could be nonmetallic washer and metal during tightening of a bolt, or it could be metal or and deposits you can say clay deposit ok so that could also lead to a problem.

For example, in this case one can also think of a kind of plastic bowl falling at the bottom of a water tank made of mild steel so that could also lead to a crevice ok. And of course, there could be a situation like this is metal-metal when we are talking about two different metals.

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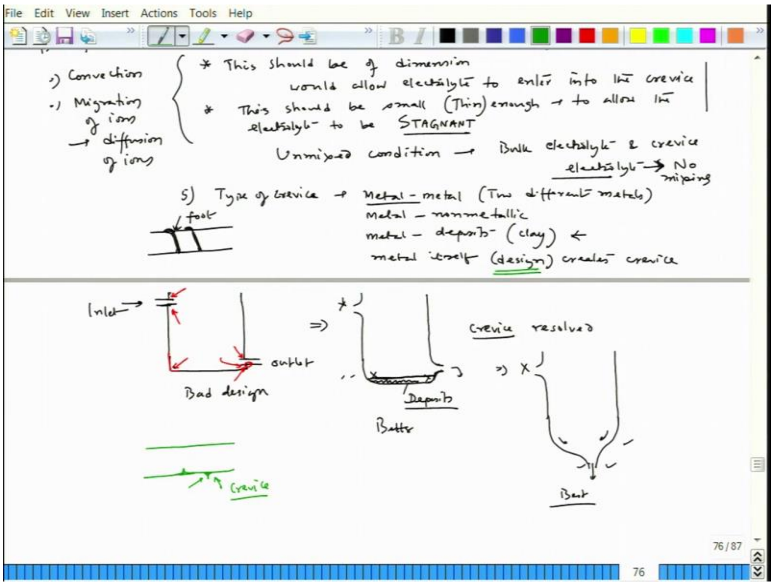

Two different metals, for example, washer and bolt, they could have different compositions, but there could be possibility of metal itself due to design create crevice. One classic example what I showed you last class was basically a ripple rebar. So, ripple rebar is basically like this fine. So, this is the ripple rebar right. So, now, this is the foot of the foot of that particular ripple or rid this called ribbed ok. So, this particular part is creating a tiny crevice.

So, here you have do not have any different metals, it is a same design factor is actually creating such kind of crevice. For example, design part creating crevice. Another for example, let me show you one design. Let us say you have a water tank. So, this is a water tank let us say this is inlet, this is outlet ok. Now, there could be possibility that this pipe has gone inside ok. So, there is a small pipe which is entering into it. Here also there could be possibility that this pipe has entered into the tank.

And let us say those pipe compositions and the tank composition metal composition both are same, so no galvanic corrosion. But here you it is interesting, there are lot of crevice portion. For example, let me just pinpoint those crevice part ok. So, this is a crevice. This is a crevice wherever that particular sharp edge is forming between that pipe entering into the tank, and the tank wall. Here is a crevice, here is a crevice in fact, this corner is a crevice.

This is a crevice, so in fact, it should not look at outside, so this is a crevice. In fact, if you see this, this is another crevice, here another crevice is forming ok. So, those are the crevice parts. And these parts are forming because you have not made any different metal contacts or different metal making a crevice rather the same metal is creating. For example, this particular bottom of the tank. This is a crevice ok, so this crevice is formed just by because of the design. So, the only by changing design, one can change this crevice part.

So, let us make this particular design modification, we can avoid crevice. So, only concern is how to avoid crevice. So, in order to make that, you make a design like this. Instead of giving sharp corners, we are giving a curvature or radius root radius, and that would allow not to have crevice. So, now, the crevice is out. Crevice is out because we are creating a situation similar to this.

Now, in this case, we are creating, in this case it was thin enough to allow water to go in at the same time it is large enough to allow the water to go in, and it is thin enough at that local portion to allow that water to become stagnant. But now once we have this, all the time there will be flow, and that flow would not allow the crevice corrosion to take place.

We will talk about how crevice happens the mechanism part, but at least if you somehow without knowing crevice part at least if you can avoid crevice the sharp corner, the problem is resolved to a great extent. Now here there is one more problem. So, now the crevice is out, crevice resolved with this design, but there is a problem.

If for example, if let us say there is a need for a regular cleaning of that particular tank generally at the tank bottom we have deposits. So, that deposit need to be taken out time to time, scrapped off. In order to do that, you have to take the water out. If it is a small tank, no problem; if it is a large tank, it is not easy to tilt this tank.

So, small tank, tilt it fine, absolutely fine; all the water can be taken out. But if it is a large tank, it is impossible to tilt it. So, that time you just open the tap over here water, and this one you closed ok, this one you closed. And so then once you close this water inlet outlet, you just open all the water would go out, but still you will see that the small amount of water up to the edge will be there. And that water at the same time cleaning also becomes difficult in the sense that somebody has to go in, and then clean everything.

You cannot use any mechanical stuff, even if you want to use mechanical stuff still there will be a possibility of water logging. Otherwise you have to wait for a long duration to let the water evaporate. And since for a large tank, this water could be a huge amount even that residue water. So, the best design in this case could be just to avoid that water logging off during maintenance part or cleaning part, one can have a design like this.

Instead of having water outlet from the outside, we can have water live outlet from the bottom ok. So, now, we make such design. If you want to clean it off, what you do? You just close this part, open this part, and you also create a little bit of churning entire deposits whatever they will go out. But in fact here the deposit formation would be much less in this design, deposit formation would be much less compared to this. Because deposit whatever comes down there could be a kind of motion that motion would take the deposit along with the water.

Of course, you have to take care of the clogging of this particular thing time to time, but otherwise the tank deposit problem can be resolved to a great extent. So, this could be a better design than this ok. So, this is the bad design, this is better within this framework it is the best fine. So, like that way without knowing the nitty gritties of crevice, but just by avoiding crevice one can resolve the crevice corrosion fine.

So, this is the type of crevice at the same time, I would say different out of different types there is one more factor which is very important the design related crevice formation that is very important. For example, sometimes the pipe if it is a cast pipe the problem becomes very prevalent. For example, in case of cast pipe sometimes, so there could be a sort of extra metal object which is going or outside there could be a extra metal which is coming out.

So, it is not the wall is not smooth here also a crevice formation crevice. So, this is also a kind of casting defect kind of crevice. So, one has to smoothen you off smoothen it off ok. So, then only the crevice part can be avoided ok. So, those are the different factors associated with the crevice. Here the factors if you see some are of course, from the point of mechanism, some are mostly they are of the from the point of the appearance of crevice ok. So, let us get to the mechanism part of it ok.

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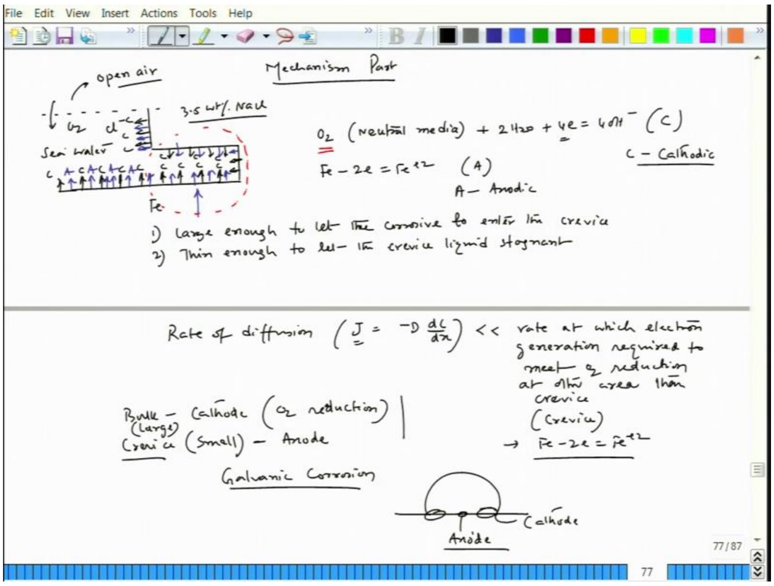

So, if we want to see a mechanism part, in the mechanism part, one can look at this way for example, let us make a crevice. So, let us say this is a crevice. Now, let us say this is the level of water let us say it is exposed to the open air, and that open air a allows oxygen to come in ok. Now, initially everywhere we had the similar oxygen level. Now, let us say this is iron.

Now, and there are chlorine ion also lets say this is sea water; or if we do lab scale experiment, 3.5 per weight percent NaCl ok. So, now there are sufficient chloride ion ok. Now, there would be possibility since it is a everywhere cathodic and anodic reactions can take place. And here cathodic reaction is because we have lot of oxygen, and this is open air, and this is neutral media fine. The neutral media you react with $2H_2O$ plus 4e, it forms 4OH minus.

Now, everywhere you have the formation of reaction of this. So, let us say this is C, so I just put C; C means cathodic. See cathodic reaction is taking place; C is cathodic fine. Now, of course, initial to begin with the everywhere we have anodic reaction. So, anodic reaction would be, so this is anodic let us say A anodic. So, now, there would be anodic reactions ok, so now, these are the anodic reactions. So, like that way everywhere initially we have same, both the reactions taking place.

Now, since this crevice part, we have two conditions. One is large enough to let the electrolyte or corrosive here the corrosive I would say corrosive is nothing but the electrolyte to enter the crevice. Second condition, thin enough to let the crevice liquid stagnant ok, to let the crevice liquid stagnant ok, so these are the two conditions.

So, now in the beginning everywhere you have oxygen cathodic reaction, oxygen reduction and iron oxidation. But now after sometime, within this crevice we will have a situation like oxygen is depleted. In order to have that oxygen to maintain the balance with the bulk one, one has to have a very good convection movement of fluid, but since it is a stagnant convection is not allowed.

Of course, there could be possibility of diffusion of oxygen, but the diffusion the rate of diffusion is lower or slower than the rate at which the cathodic reaction should occur to maintain the electron requirement for cathodic reaction ok. What do I say? The oxygen diffusion is possible. This stagnant convection is not possible oxygen cannot go in by a convection route from the bulk to the crevice, but oxygen diffusion is possible, so that diffusion rate rather the rate of diffusion or flux J ok which is if I consider the steady state diffusion minus D dC by d x.

$$J = -D\frac{dc}{dx}$$

So, this J which is the flux and moles of moles of oxygen per unit area per unit time, so that is much lower than the rate at which electron generation required to meet oxygen reduction at other area than crevice. And interestingly, though there is no oxygen, oxygen has depleted in this crevice, but the rest of the part of that particular metallic component has same oxygen level. So, the oxygen reduction will go on rest of the part. And the small that means, everywhere cathodic reaction is taking place. So, the everywhere would become now cathode.

The only the part which can supply electron now is basically the crevice part crevice. And this crevice part, that means, in order to do that, we have to have this reaction taking place ok. So, that means, anodic reaction would now preferentially happen in the crevice part, and cathodic reaction would happen on the bulk of the metal part. So, that means, we have a situation like bulk cathode oxygen reduction, and crevice which is small.

And this is large part, large cathode and crevice is a small part becomes preferentially anode to meet this requirement for the oxidation oxygen reduction process. There we need electron ok. So, that is what this becomes anode. And now this is you see is a classic example of galvanic corrosion fine. So, this is the galvanic corrosion. And, here why galvanic? Because oxygen reduction happens outer side, and iron oxidation happen in the crevice.

This is exactly same as the example what we have cited that this is a water droplet around this area will be cathode, and the center part will be anode. And these happens when oxygen is depleted at the center part of that particular tiny water droplet. So, this is exactly same as galvanic corrosion. But now that it is not about anything like crevice. So, there is no extraordinary part of crevice here except that thickness of that particular thin slice, thin portion of that crevice where it allows water to seep in, but it does not allow to water to have a convection.

So, it is a stagnant liquid, so except that is everything about galvanic corrosion. So, the next class, we will get into the crevice the important aspects of crevice which is basically the metal chloride hydrolysis and leading to hydrogen generation, hydrogen ion generation. And that hydrogen ion generation would lead to acidity much more that particular crevice portion will become highly acidic. And because of the acidic nature even if it is a passivating metal, that passivation will be broken ok.

So, that hydrolysis part, metal chloride hydrolysis part and acidity, increase of acidity will actually get into the situation where crevice becomes auto catalytic in nature ok. So, there it actually comes out of basic galvanic mode to a crevice specialty mode ok. So, that part will talk in our next lecture.

Thank you.