Corrosion Failures and Analysis
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Lecture - 28
Pitting corrosion: Introduction and Case studies

Let us start lecture 28. And we will start a new topic which is Pitting corrosion. And of course, this is under the course Corrosion Failures and Analysis.

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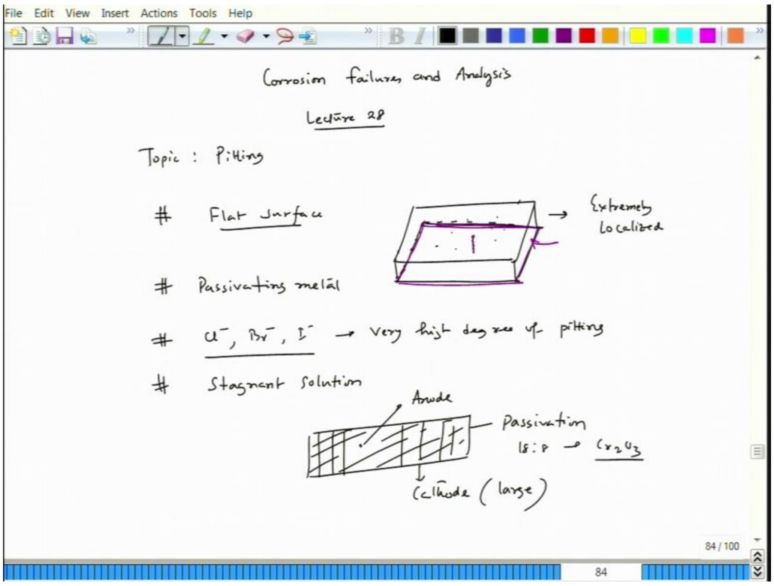

So, the course is and lecture pitting. At times you must have notice that on a utensils iron utensils, let us well let us say iron spatula, I have shown one example. I will show that picture again as well as if you see basin wash basin, if you do not use it for a long period. If it is used, no problem, but if it is not used for a long period, you might see that there are small, small black dots ok.

So, those dots are nothing but pits. So, the pits are basically formed on a metal surface, and it happens on a metal surface. That pit happens and it is extremely localized situation. And at times you would see another experience you would notice that those pits in case of stainless steel at least those pits are forming at a very localized point, and rest of the part is absolutely shining ok.

Now, in case of crevice at least you must have notice that as it starts within the crevice and then gradually it is spreads outs, actually you could sense that where that crevice is there, where is that crevice. But in case of pitting, the pitting point could be so narrow within with the naked eye one cannot observe it. And that narrowness leads to a problem in identification, and it can happen on a flat surface. And at the same time, it can grow in the depth direction at a rate which can be extremely fast, and then it might perforate that particular metallic object.

Now, couple of situations what I have said that it is extremely, it is an extremely localized form of corrosion, it is actually corrosion pitting corrosion. And that pit forms at a very narrow sections; and interestingly it forms on a flat surface. For example, in case of crevice, at least we could sense that where is the crevice as per the design aspects. But in case of pitting, even we will not be able to see that even without having any corners or edges we can have pits on the flat surface.

And in case of highly resistant alloys or metals like stainless steel, the pit can be more localized. And it will be very difficult to identify where is the pit. By the time, we identify the pit the material can fail drastically ok, so that is what the pitting corrosion is one of the extremely localized mode of corrosions, localized mode of corrosion. And it also leads to catastrophic failure of the material fine.

So, now what are the kind of things we have talked about? One is some of the basic traits of pitting corrosion. It happens on a flat surface. Till now whatever we have noticed that crevice corrosion, galvanic corrosion ok, uniform corrosion, uniform corrosion happens on a flat surface, but at least you can make out that it forms all over the surface. For example, dealloying, dezincification that happens on a flat surface, but it happens over the entire surface.

And at the same time, you would you could make out that in case of dealloying let us say dezincification you can make out from the color itself because the surface where dealloying is taking place in case of brass that surface becomes a red color. Gradually the color change from oranges to the red because the copper is getting copper is deposited over there, and it happens over the entire surface it except in case of plug type, but plug type also the dimension is much bigger ok.

In case of plug type, we happen, it happens on a small segments it does not happen over the entire surface which is actually a trait of uniform dealloying. Now, in case of uniform corrosion, of course, it happens over the entire surface. You can see, you can notice rust forming over the entire for example a bolt lying on a, lying on a in air ok. You see the corrosion is happening over the entire surface. For example pipe; pipe is also you see that rust is falling over the entire surface.

But crevice that is also a localized form, but the crevice happens at the edge where crevice is there, the dimension of crevice is meeting the criteria for crevice corrosion, so that particular portion also you can notice by naked eye when of course it happens you can notice at a later stage, but at least the spread of corrosion rust happens starting from the crevice to the outside if you have noticed that door corrosion ok or the ac corrosion ac the wherever crevice is happening that particular spreads out.

But in case of pitting, even if it is a flat surface, the pit forms small, small dots, those pit forms. And those pits are highly localized. And those pit dimension could be such those could be microscopic. So, you cannot see with a naked eye. In case of crevice, at least you could observe that there is a crevice. So, there is a problem. Of course, initial stage of crevice, you will not also see because it is hidden within the crevice, but at least you could make out that there is a crevice, there is a possibility of crevice corrosion.

But, in this case, even you cannot make out that where the pit has formed until unless it becomes macroscopically large, and then it becomes visible fine. By that time it becomes visible, it can create hole ok.

Now, coming to the second part, it actually is more prevalent in case of passivating metal, passivating metal fine. So, and third part is actually wherever you have those kind of halogens or halides, so there we have very high degree of the pitting corrosion, high degree of pitting. Now, flat surface, at the same time, dimension that creates a situation which is extremely localized right.

And at the same time, before it becomes visible to naked eye, it might have grown if this is the thickness, it might have grown to the other edges other surface. So, this is the top surface, and this is let us say, let us say this is the this is the bottom surface, bottom surface, this crevice can this sorry not crevice this pit can grow through this, and it can go last part of that particular other surface and it forms a hole into it.

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So, let us see an example ok. So, this is the plate I have collected. So, this is a stainless steel plate 18 8 stainless steel plate. Of course, this is 0.08 percent carbon. And this plate was used for an experimentation in our lab ok. We wanted to see the chloride entry into the concrete, and that leading to corrosion of rebar within placed within this concrete.

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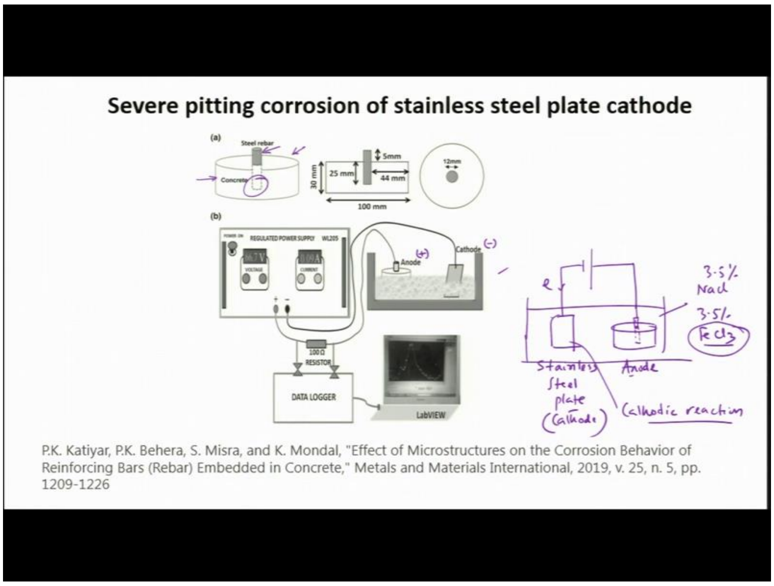

So, now, let us see that experimental setup first. If you go to this particular paper, this is a work done at IIT, Kanpur. In fact, Mr. Katiyar and Mr. Behera, they are all now PhD holders. So, they are my PhD students. So, they did this experiment. What the experiment was that this is a rebar coupon, this is a rebar coupon. And this is basically a concrete coupon.

And at the center part which is a basically cylindrical in shape and center part we have a steel rebar ok. And we wanted to see that how chloride enters into it through the concrete, and it gives you the corrosion of rebar. And because of the corrosion because the corrosion products have got a lower density compared to iron, and that is actually entrapped with a, with concrete ok which is not expandable ok.

It is a situation where some flocculated product is forming which has a higher volume, and higher specific volume, and that would lead to a kind of stress exerted on that concrete. And since concrete does not have any malleability or tensile properties or elongations – a tensor elongations, so it will start cracking ok. So, now, that crack we observe because of the once that particular corrosion becomes a critical amount the crack happens, that means, corrosion amount becomes critical. What does it mean? That the stress becomes critical. And beyond that stress, it fails.

In fact, if you recall that failure of concrete pillar of iron pipe is inserted into that pillar, and that the concrete pillar got fractured. And that example I showed you while explaining the galvanic corrosion ok, and that was related to differential aeration cell again fine. So, now, after that what we did if we try to use this particular object and left it to the air and it could take almost about more than a year to have a crack. Because that time the increase of electrolyte through that particular concrete would be very, very slow.

And interestingly the iron part is exposed to the outside. That exposed part is actually painted. We want we did not want to have corrosion happening through the top rather we wanted we made sure that the corrosion would happen only the bottom part. The top part actually remain absolutely fine because of the painting good painting, so that it was having a kind of corrosive resistant paint ok. So, basically it does not allow electrolyte to sweep into, and then touch the rod iron rod. So, corrosion was actually there with the part which is inside the concrete.

Now, since we cannot wait for that long, so we thought that let us use the accelerated corrosion test. And this is the basically a usual accelerated corrosion test which is used performed in the lab. And we use that particular concrete as anode. So, this is anode which is basically positive terminal, and this is cathode which is negative terminal, since this is we are supplying current from outside. So, we are actually using external circuit. So, this is the circuit. So, this is a stainless steel plate used as cathode, fine. And this is the, so this is the part which is connected to that metal part. So, this becomes anode.

So, now because and then inside that this is a container. And in that container, we use NaCl 3.5 percent, and 3.5 percent, $FeCl_3$. And $FeCl_3$ is a very strong oxidizer. I wanted to use this strong oxidizer just to increase the rate of corrosion ok, because we wanted to check when the what is the stress level because of the rust formation on top of the metal creating that critical stress to achieve creating that situation where critical stress is achieved, and then finally, the cracking of concrete happens fine, so that is what we use this strong oxidizer.

Now, this is a cathode in an electrolytic cell, cathode does not corrode because cathode only supplies. So, you know electron is coming here, so that means, cathodic reaction happens over here.

Then it should not get corroded fine. At the same time, since it is a very strong corrosive, so that is what instead of using any other metal, we use stainless steel, so that is what we thought that it will remain safe. Now, after operating this system for 1 month ok, we operated this system for 1 month just to have those failure of that concrete we wanted to fail that concrete just to have that idea that what is the amount of rust that creates that failure ok.

So, after 1 month, we took out that particular plate let me show you that plate. So, this is that plate. This is a stainless steel plate. And this stainless steel plate and it if you could see that it is a quite shiny. And this is almost about if I recall correctly 4 years back he got doctorate and then even after leaving this particular stainless steel in open atmosphere, it is basically lying in my lab ok, still there is no corrosion other than those places where you could see that is there are small black dots ok.

And those dots, let me show you one interesting feature of this black dots. Can you please put off the light?

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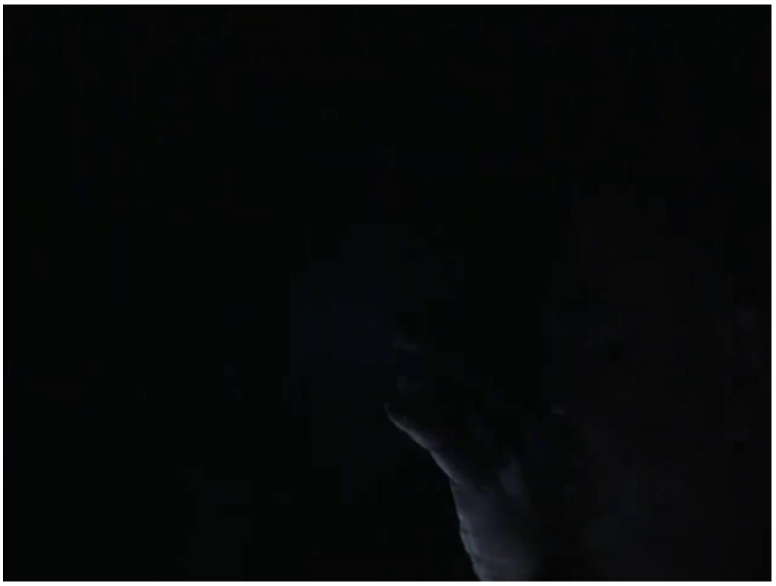

So, now, this is the black this is the portion. So, you can see little bit of this part this is my hand.

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And you are not able to see this. Now, let me show you this. This is the plate. This is the plate ok.

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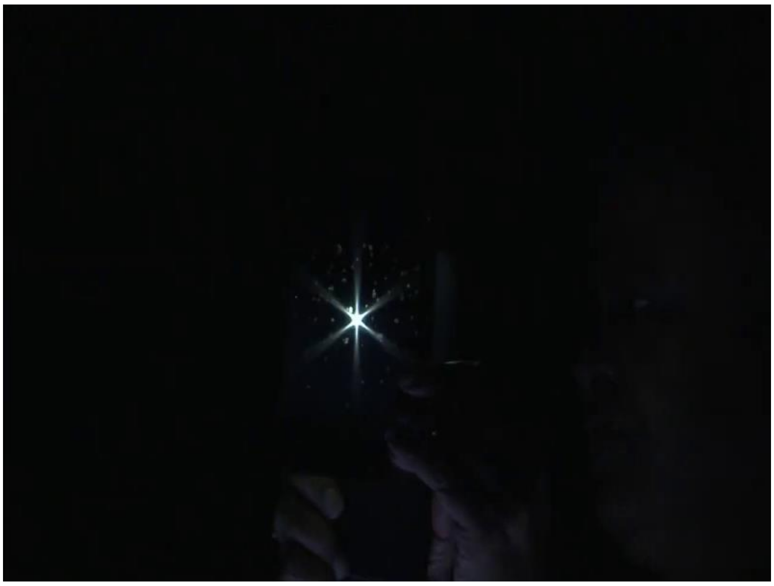

Now, let me just take the light on the opposite side of the plate. Could you see something? It looks like stars – glittering stars. You know, what happens, this plate is completely perforated you know. So, this you see at some portion the those holes are little bigger and that is what you could see those steady appearance, is not it? So, this full of small, small holes you know.

So, please put off, put on the light. So, this is the plate. It is all over shiny. But if you closely look at this, there are lot of small, small holes. And those holes I have just demonstrated by putting a light on the back of that particular plate.

So, this plate thickness is almost about close to 1 millimeter. it is a quite a thick plate more than 1 millimeter actually. This is a quite a thick plate and this is a stainless steel plate 18 8. And after doing this particular experiment for enhancing the of corrosion of that rebar within the concrete, we had the situation. This failure of this particular this hole formation in that particular stainless steel sheet which is almost more than one point at least it should be around 1.2 millimeter thick which is a quite a thick plate ok.

So, now question is what are these? These are basically pits. And these pits are extremely localized. And it actually perforated this particular steel in 1 month time ok. Now, you can imagine what is the severity of pit, severity of pitting corrosion. So, now, let us say if you want to do a kind of tensile say let us say this is a kind of load carrying part. Now, initially the entire cross section is actually holding that load. Now, since there are so many of pits and those pits are actually making the cross section lesser than what was there for the actual load carrying ability.

Now, you have designed some load on the basis of some cross section. And now your cross section has reduced many fold because of the small, small pit perforated pit, and that actually would feel the structure. And if you do it like this, it will feel like anything because it is not able to hold that load because it is cross section has reduced to a great extent drastically the cross section has reduced because those small, small holes are actually reduced in the cross section to carry the load. So, this is one example I just wanted to give you that how dangerous the crevice could be and how localized it is.

So, if you see that rest of the part is quite shiny, only those small small portion where the pit has initiated and it has grown aggressively. And another interesting part, if you see the edge part ok, can you show it through this? The edge part, if you see the edge part, edge part is actually let me go close to that ok. So, zoom.

The edge part if you see the edge part, the edge part is you know it basically a kind of serration has happened. There is a serration you know if I roll my hand like this, I might get a cut on my finger because the serration also happens because of the small small edge pits ok. So, those pits are actually making a serrated. And if you cut it, you can cut some object very nicely because this edge is very sharp now fine.

So, this is a condition of pitting which has happened in 1 month time, and that too happen in a stainless steel ok. And this particular experiment you can just if you want to do, if you want to repeat that experiment, you can do it after following this particular paper ok. So, this has been published.

Now, coming to some of the other examples of pits. So, this is in case of a stainless steel which is highly resistant to corrosion.

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For example, one such example of pit let me just show you in a spatula iron spatula. So, this is one iron spatula. If you see that, in case of iron this a mild steel lamp iron spatula this is not passivating, but still there are pits. But it is not that aggressive as compared to stainless steel ok because though it is localized, but more or less it is uniform apart from there are couple of small small pits which is localized. So, this is one pit. So, this is another pit. So, if I can make it little bigger, then things will be better. So, let me take it to a different page.

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You could see that there are pits. For example, you see those are the pits, these are pits. In fact, here you could also find some pits ok. Now, here interestingly, this one was interesting this part you know multiple pits have joined together ok so, but still it has not perforated. I need to operates for a long long period.

Now, interestingly this particular thing and the thing what we showed that particular plate stainless steel plate, the only difference is this spatula is used everyday ok. And then it is washed. This is the Indian style of using spatula. And in fact, this is South Asian block people use this spatula – iron spatula.

So, now there this is used all the time it is under motion. And at the same time, you wash it and then keep it for drying. During drying, it accumulates some sort of rust. And the next day again you wash and use it ok, so that is what that. And interestingly in this particular plate case, in this particular plate case, we did not provide any sort of a movement in that particular fluid. If you see this part, in this case, this was no stirring was done in the solution and because no stirring was done actually it created a stagnant situation.

But in case of iron spatula it was not stagnant, stagnant for a while. And then again you use it for cooking, and then again wash it. Now, interestingly it is a character of pitting corrosion that if it is stagnant, if the solution is stagnant, the pitting ability goes up ok. And if it is for example, if this particular solution was stirred, you would not might not have gotten this particular situation ok. So, that means, there is a small that is a typical character of pitting corrosion is that it happens when it relates to the stagnant solution ok.

So, if the solution is stagnant, pitting can grow like anything. And pitting can grow localized. Interestingly the localized growth can be explained in a while. For example, if we have seen this particular plate, is not it? So, this particular plate one small pit is formed because of some reason we will talk about those reasons. And those pit apart from that pit, rest of the places we have passivation. And if it is a stainless steel 18 8, then the chromium oxide passive layer is formed.

Now, this small part where the crevice has formed that there actually passivation has broken. And now because of the breaking of passivation that small part would act as anode. And the rest of the part which is large cathode, they will act as cathode, and it is large. And if you try to find out the ratio between area ratio between anode and cathode, it is much lower than in case of crevice.

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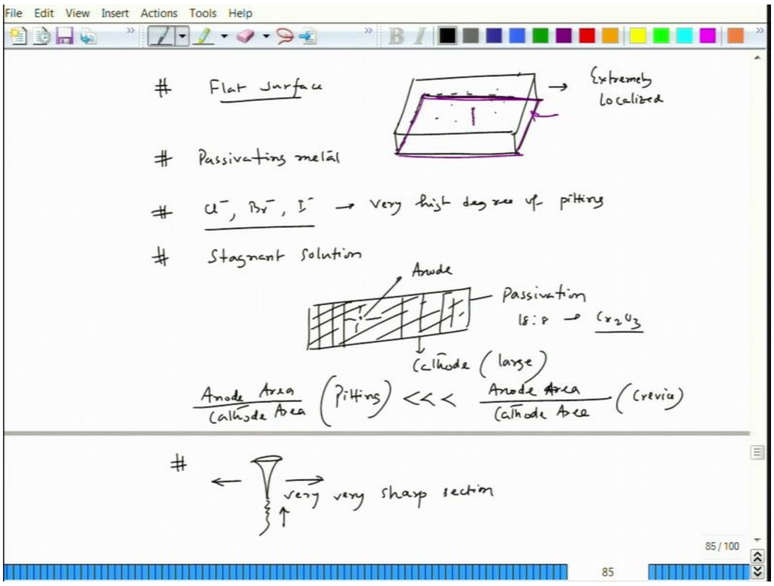

So, if we try to compare crevice area ratio that is anode divided by cathode area in case of pitting would be much much lower than in case of crevice. Now, that also leads to extremely high degree of localized corrosion in case of pitting ok and that is what it does not spreads, does not spread. In case of crevice we could see that it is spreads starting from the crevice.

But it actually does not spread rather it goes inside the body, and it creates perforation or hole in the body. And that hole could be here at least we could see a bigger hole all those holes are bigger ok, but sometimes those pit could be so narrow and still it can go inside. This is, there is one more problem.

Even if it does not let us say the pit has formed, let us say this is a pit. Even if that pit does not go across that particular thickness, but at the tip of the pit would be very very sharp section. And it leads to a typical situation which is called triaxiality of stress. And triaxiality of stress can lead to catastrophic failure. And if the stress is acting like this, the crack can grow catastrophically. And there could be failure there could be a kind of entire structure can crumble down starting with a small pit ok.

So, let me stop here at this moment. So, we will continue our discussion on pit. And we will show some of the typical examples of pitting ok, and where you would see that those pits can create industrial accidents ok, even household accidents. So, we will check about those kind of accidents. Let us stop here.

Thank you.