# Corrosion Failures and Analysis
## Prof. Kallol Mondal
## Department of Materials Science and Engineering
## Indian Institute of Technology, Kanpur

## Lecture - 30
## Various conditions favouring pitting corrosion (Part 2)

Let us start lecture 30 and the course is Corrosion Failures and Analysis. We have been discussing pitting corrosion and we started talking on conditions which favor pitting corrosion ok. So, we talked two conditions.

One was passivating metals generally they are susceptible to pitting and another was presence of halogen ions. Let us say chloride ion that leads to serious pitting in case of passivating metals. It can also lead to pitting in case of a normal non passivating metals, but in case of passivating metal it could be highly localized and it stops when the entire thickness becomes perforated.

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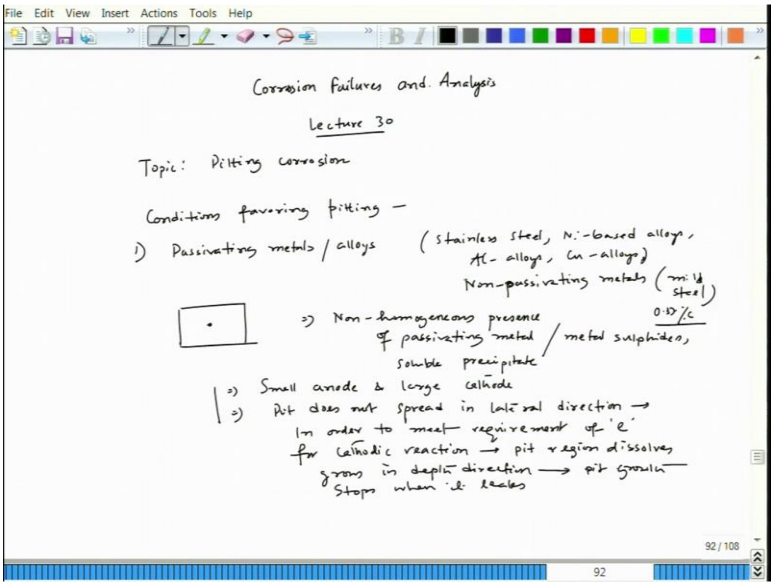

Corrosion Failures and Analysis

Lecture 30

Topic: Pitting corrosion

Conditions favoring pitting –

1) Passivating metals / alloys (stainless steel, Ni-based alloys, Al- alloys, Cu-alloys)
Non-passivating metals (mild steel) 0.15%C

⇒ Non-homogeneous presence of passivating metal / metal sulphides, soluble precipitate

⇒ Small anode & large cathode

⇒ Pit does not spread in lateral direction → In order to meet requirement of 'e' for cathodic reaction → pit region dissolves grows in depth direction → pit growth
Stops when it leaks

So, the course is corrosion failures and analysis and lecture 30 and topic we will discuss pitting corrosion. And as we said that two conditions we have already discussed and we will talk about some other conditions. Now, if we just revise what we have done, the conditions favoring pitting. If we try to look at those one is definitely passivating metal or alloys and let us say stainless steel then nickel based, alloys aluminium alloys let us say copper alloys.

So for example, this is non passivating metal, so let us say mild steel. So, it does not get passivated in 3.5 percent NaCl solution, but still we can experience pitting there. So, I have some pictures on that non passivating metals in case of mild steel 0.17 percent carbon steel. I have some pictures I will show you that how passive how pitting happens there.

Now the logic what we have put there is basically we have a surface. Let us say the entire surface is passivated and because of some reason that could be due to in homogeneous presence of passivating metal. Let us say chromium in case of stainless steel or due to some sort of local strain effect or due to presence of some soluble precipitates.

So, those cases we can achieve passivity and let us we can achieve breaking of passive layer ok. So, what are the conditions? Presence of non homogeneous, presence of passivating metal or could be some metal sulphide so, or could be due to soluble precipitate fine. So, for example, in case of stainless steel chromium could be in homogeneously presence in the weld zone and we can get serious pitting. Even there could be formation of a kind of complex inclusion containing sulfur a manganese sulfur and with addition of chromium those sulfides are soluble sulfides.

And so, those can get dissolved into the electrolyte and can have pitting local pitting, but the rest of the surface could be highly passivated. So that means, if some pit forms here a small tiny pit forms and rest of the places are passivated. So; that means, that small pit will act as anode and it does not get spreaded ok it does not spread out. So, since it does not spread out since it also provides sufficient area for cathodic reaction, since the entire passivated area will act as cathode.

So, in order to supply electron for those cathodic reactions serious dissolution along the depth direction happens in that local tiny microscopic pit zone ok. So, that is the initiated pit zone and that is what the pit grows very rapidly through the depth direction. So, that is the situation happens and there one galvanic corrosion theory prevails a small anode and large cathode. This is one and second condition; pit does not spread in lateral direction ok.

So, that is what in order to meet requirement of electron for cathodic reaction pit grows pit region dissolves rapidly and grows in depth direction and interestingly it stops when it gets perforated when it leaks. So, that is the situation these are the two situation, which actually lead to serious pit growth along the depth direction in case of passivating metal.

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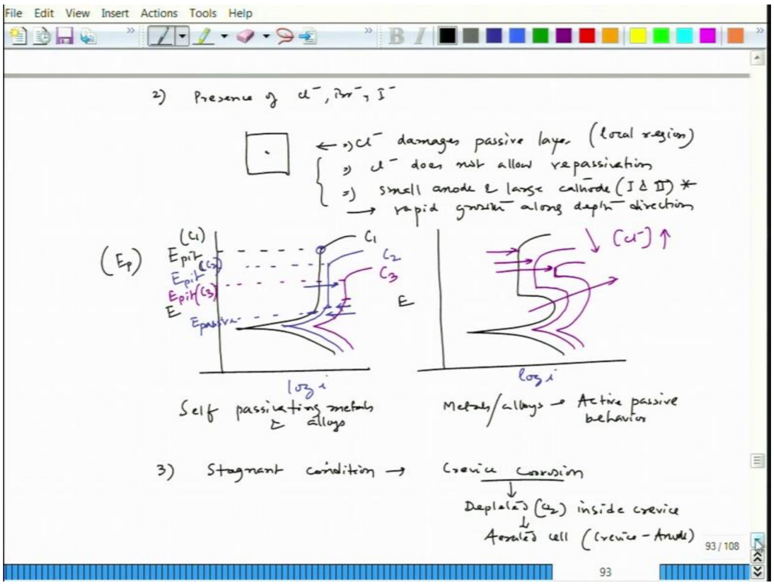

2) Presence of $Cl^-$, $Br^-$, $I^-$

⇒ $Cl^-$ damages passive layer (local region)

⇒ $Cl^-$ does not allow repassivation

⇒ small anode & large cathode (I & II) *

→ rapid growth along depth direction

Self passivating metals & alloys

Metals/alloys → Active passive behavior

3) Stagnant condition → Crevice Corrosion

↓

Depleted ($O_2$) inside crevice

↓

Aerated cell (crevice - Anode)

Now, that we have discuss and the second point we talked about is presence of chloride bromide iodide. So, these are the kind of halogens those will lead to breaking of or damage of passive layer. And for example, you have a small surface and it is passivating there could be possibility the local region the chloride concentration if it is in chloride based solution aqueous solution.

So, the local region chloride content can go up ok and that might be the initiation of pit at some location. And then once that pit forms then because of the chloride ion even if it tries to cover up that pit or it tries to repassivate ok, but it will not allow, it will not be allowed because of the chloride ion presence. And the next steps will be same as these many steps. So, the chloride damages passive layer ok. Second part, what it does? Chloride does not allow repassivation and this is in the local region fine.

And then third; and once that pit initiates then the small anode and large cathode would lead to rapid growth along depth direction. And in fact, these all those stages first and two first and two, so, in case of we can say the first and second whatever we have mentioned here ok, so this thing will prevail. Now, another interesting part we have started discussing about we talked about effect on polarization diagram. So, we had two systems, so this is log i, this is E, this is E, this is log i.

Now, in one case if it is a self passivating metals on alloy. So, the diagram look like this. So, this is my E pit, we write Ep fine and if we let say this is at some percentage of chloride ion concentration C1. Now, if we increase the concentration of C1, so, the graph would change like this it will move to the right it will move up this point where the passivation start that will move up and the entire curve will go to the right.

Because of the chloride ion concentration let us say it is C2, the entire polarization curve shifts towards right. And then this passivating where the passivation happens that particular potential if this is the potential E passive potential that potential will move up. So, it will go there, so, initially it was here it will go up because of the chloride ion concentration increase in chloride ion concentration.

And then this passive zone will also shifts towards right and also this E passive E pit point will also go down and it will break early. So, this becomes my E pit. So, let us say this was corresponding to C1. This is corresponding to C2. Similarly, if we increase the concentration of chloride ion further. So, it will move like this it will move up the passivation point would be like this and then I can move like this. So, this is the point corresponding to C3.

So that means, this is E pit C3 like that the entire graph will in general will move like this so; that means, the passive zone will shorten means that it does not allow the passivity to achieve. Second thing is it passivates at a later stage of potential if we go from go to the anodic or noble site and at the same time the E pit appears at much lower potential.

So that means, the pitting tendency would go up. So, this is in case of active a self passivating metals and alloys. But if we try to look at active passive case metals or alloys giving active passive behavior so, that time graph will look like this ok. So, this is the graph. Now, in that case again the effect would be very clear. The graph will move like and then this point will go up this point will also go up and move towards right. The entire graph will try to go right, so like this. So, this one would be like this.

So, like that way the entire curve will shift towards right as the concentration of increases ok. So, this is the trend of polarization diagram you would notice in case of passivating metal when there is a there is chloride ion presence in the particular solution fine. So, now at the same time you could see every time that E pit is actually shifts towards lower potential and it also the total current also shifts towards right. So that means, the passivating passivation becomes difficult.

So, now, this is about the passivating metal. Now, there are conditions like stagnant condition. Stagnant condition is not good for metal where we do see passivation do see pitting ok. So for example, if we have noticed that plate what I had shown you that plate was kept in that particular ferric chloride and NaCl medium for one month for the test what we wanted to do to check the failure of concrete cover that the cover around the rivet because of the corrosion of rivet and we wanted to calculate the critical corrosion amount which leads to that particular failure.

So, that particular stainless steel cathode was kept for one month time, but the particular solution was not stirred or shaken. So, it was very stable and stagnant and that is what you could see that in one month time the entire stainless steel 18 8 stainless steel got perforated. There are lot of pits and that pit went through that particular thickness and the thickness was almost about close to 2 millimeter which was quite thick fine.

So, that is what happens if we have a stagnant solution, but that particular solution if we churn it the problem would not have been that severe ok pit would have formed, but it will not grow through the thickness. Now, in that regard stainless steel pump one has to be very careful. If a stainless steel pump is in operation where all the time the water is getting pumped, circulation happening pitting tendency pitting possibility would be less.

But, if sometimes those pumps are to be repaired and those are taken out from the boat and then it was taken to offshore for repair and there if it is kept for kept for long time without having any pumping operation the internal part of that particular pump will get severely pitted. So, that is what the only possible solution could be every week or after a regular interval short interval that pump needs to be use needs to be use operation should be done. So, that the pitting condition is not favoring the pitting condition does not favor the pit to grow ok.

So, that is what stagnant condition we have to avoid in case of metals which show pitting tendency. Now, this is somewhat also related to if we had noticed crevice corrosion. It is actually due to stagnancy ok because there because of the stagnancy we have depleted oxygen content inside crevice and that leads to differential different or simply aerated cell. Crevice becomes anode and outside large area becomes cathode since there we have lot of oxygen, but inside we have less oxygen and that leads to crevice corrosion localized attack.

Now, if somebody opens a crevice ok, so, you will see lot of pits. Those pits are not pits are actually coming due to crevice ok. In case of crevice one advantage is it actually shows the signature because when crevice starts it actually grows outward ok and then you can see the rust is appearing, but in case of pitting it could be microscopic. Sometime that pit is covered up by the rust layer which may not be able to we may not be able to guess by looking at it ok.

So, that cases that is what pit becomes difficult to recognize. At least in case of crevice you know that there is a crevice. So, there is a possibility, but in pit can happen on a flat surface. And many a times those are so microscopic that nobody can check whether there is a pit is growing or not or pit has a actually formed or not.

So, that would lead to a situation that when we come to know that pit has happened and the pit has grown. The pit might have grown considerably in through the depth direction and that would lead to a serious failure of that particular component.

So, that is a pitting becomes more serious. So, now here also in the crevice corrosion somehow if we maintain a flow ok, so, that flow would allow oxygen to reach crevice and that would allow avoidance of aerated cell fine. So, that would prevent crevice to a great extent or control crevice, minimize crevice formation to a great extent. Similar thing happens here. When you talk about the mechanism of pitting you would see here also the deaeration happens within the small crevice part a sorry pitting part pit part.

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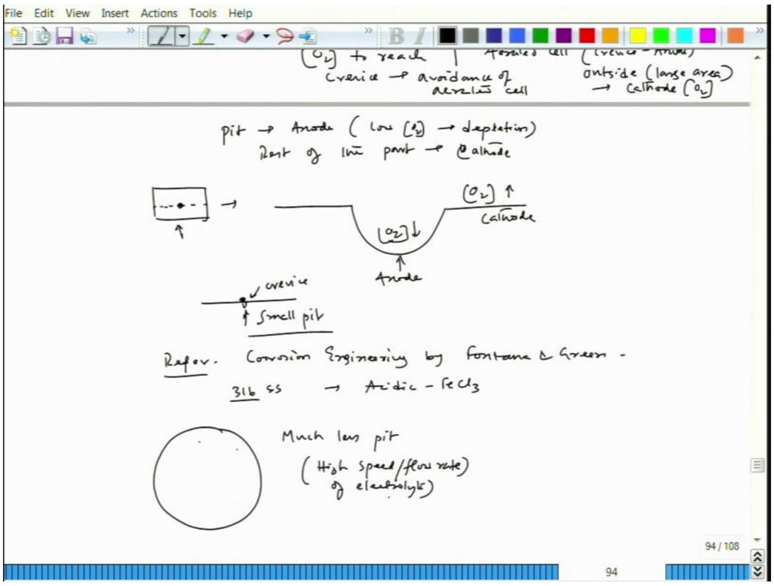

$[O_2]$ to reach | Aerated cell (crevice – Anode)
Crevice → avoidance of aeration cell
outside (large area) → Cathode $[O_2]$

pit → Anode (low $[O_2]$ → depletion)
Rest of the part → Cathode

Refer. Corrosion Engineering by Fontana & Green -
316 SS → Acidic - $FeCl_3$

Much less pit
(High speed/flow rate of electrolyte)

So, because of the pit, so, the pit becomes anode due to low oxygen. So that means, here also depletion, depletion leads to anode and the rest of the part becomes cathode. So, like if I try to let us say there is a surface and there is a small pit. If we try to look at cross section wise let say along that this is a pit and along that we cut it and then see under from this direction to the cross section direction.

So, the pit would look like this. This is a zoomed version of that particular pit. In fact, here oxygen content would go down, but here oxygen content would remain same or if we try to find out the relative this is high ok, this is low, this is high. So, this becomes anode, this becomes cathode fine. So, now of course, that would lead to a serious galvanic effect as we have discussed large area cathode small area anode.

Now, in apart from that now let us say we have some deposit ok. So, a small deposit has happened. So, that deposit would create a small crevice here fine. So, that crevice can lead to a small pit here, this is a small pit ok. So, now, crevice and pitting both are actually associated when we consider about presence of debris leading to pit. Now, if we have flow there then debris would not stay at one location all the time ok.

So, that when debris will move by here and there ok, so that would allow every position of that flat section to have equal amount of oxygen. So, differential aeration cell formation would be difficult. So, pitting can be stopped. So, that is what the movement can avoid pitting. Similarly, another way for example, chloride ion concentration is presence is present.

Let us say because of some possibility that locally chloride ion concentration has gone up fine. If it is stagnant, so then that local position can create a pit. Now, if we have a flow in that particular medium then definitely chloride ion concentration cannot build up at one location, it will get spreaded out ok. So, that possibility is also there. So, that is what stagnant condition is very bad about on a system where it shows pitting. So, it allows it hastens a pitting ok. So that is the one example.

For example, in a in a book written by Corrosion Engineering written by Fontana and Greene ok, so, that book if you see there is an example ok. So, that example is a acidic ferric chloride solution. There they have exposed stainless steel which is 316 stainless steel. So, refer Corrosion Engineering by Fontana and Greene. So, I am just writing there the last part of the author Fontana and Greene ok. So, in that book you can see that particular example where 316 they have taken SS.

And then it was basically acidic $FeCl_3$ that is the medium they used ok. So, that medium if the flow is very high around they have mentioned around 40 feet per second. So, that plate does not has a bit of pitting small pit, but much less, pit high speed or high flow rate of the electrolyte ok very less pit.

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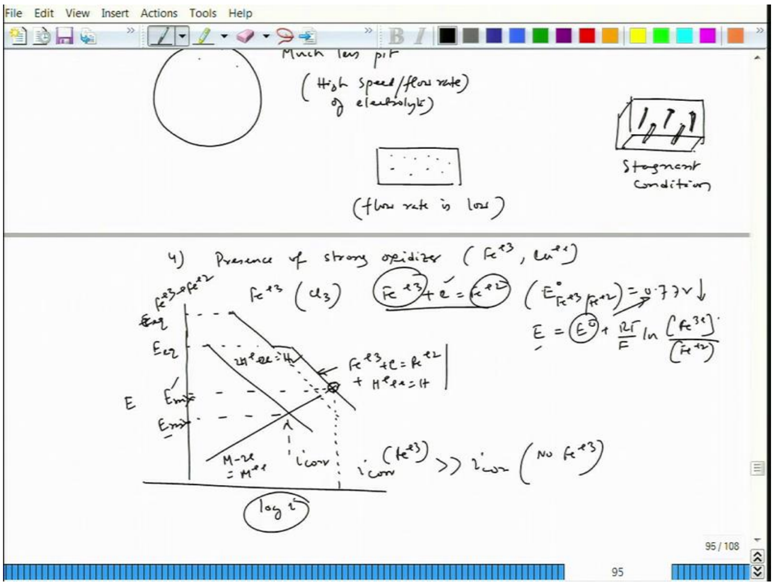

Much less pit
(High speed/flow rate of electrolyte)

(flow rate is low)

Stagnant condition

4) Presence of strong oxidizer ($Fe^{+3}$, $Cu^{+2}$)

$Fe^{+3}$ ($Cl_3$) $Fe^{+3} + e^- = Fe^{+2}$ ($E^\circ_{Fe^{+3}/Fe^{+2}}$) = 0.77 V ↓

$$E = E^0 + \frac{RT}{F}\ln\frac{[Fe^{3+}]}{[Fe^{+2}]}$$

$i_{corr}(Fe^{+3}) >> i_{corr}(\text{No } Fe^{+3})$

Now, there is one more extreme where it is stagnant ok. In case of stagnant case, so, that time. So, the picture they have shown is this rectangular one. So, pit happens small number of pits, but two pits are wide, wide pit. And at the same time if I look at from the depth wise, so, that pit might have most of the pits have gone very deep inside the metal.

So, small number of pits, but quite a deep penetration of those pits, but this is in case of stagnant situation, but there is one more situation which is intermediate speed. So, there we have small pits large number of pits, but their depth is very shallow ok. So, this is few pits of we can say flow rate is low not stagnant, but low.

So, that case we have quite a large number of pits, but those pits could not grow through the depth direction, but when it is stagnant it has gone through in the stainless steel 316, this is an example given in Fontana and Greene.

So, that is what stagnant medium is very bad. Now, coming to other conditions, now coming to conditions like we have talked about passivating metal, chloride ion presence, stagnant condition, 4th is we can talk about presence of strong oxidizer ok. Like Fe plus 3, copper plus plus, those are the strong oxidizers compared to iron. Now, now Fe plus 3 that can presence with the presence of $Cl_3$; $FeCl_3$, so, it is basically $FeCl_3$. And interestingly $FeCl_3$ is used in the lab scale just to make the corrosion process faster.

For example, if somebody wants to see the comparative corrosion behavior of two metals and alloys then people use $FeCl_3$ inside that in the in the particular sodium chloride medium. If we use mainly it is observed in case of stress corrosion cracking test. For example, if one has to compare the stress corrosion ability between a metal and b metal. If we both expose it to the sea water the process should be so slow the corrosion process could be so slow that one has to wait for months and maybe six months seven months.

So, nobody wants to wait that long time in order to have a comparative behavior ok. So, that is what in order to increase the degree of corrosion people add $FeCl_3$ around 0.1 normal or 3.5 percent in its $FeCl_3$ people add ok in the lab scale. So, that that actually increases the degree of corrosion. And why $FeCl_3$ increases the degree of corrosion that is explained with respect to mixed potential theory.

For example, if we recall that mixed potential theory it says that this is log i current density and this is polar voltage. Now, let us say some metal is corroding and let us say it is corroding in acidic medium. So, this is hydrogen evolution reaction is basically your cathodic reaction. So, now, this is my corrosion rate icorr and this is the metal dissolving metal dissolving. Now, if we have $FeCl_3$, so, $FeCl_3$ in case of $FeCl_3$, $FeCl_3$ actually has a very high let us say depending on the concentration of $FeCl_3$ Fe plus 3.

The potential would be very high compared to hydrogen and then it will also have its own reduction process. And the reduction process is Fe 3 plus plus electron equal to Fe plus 2, so this reduction process happen. If there the concentration is 1 mole per liter, so, that time the if the activity is maintained at 1, so, then the potential becomes in E naught which is the standard reduction potential plus 3 Fe plus 2. It becomes 0.77 volt fine.

So, now if the concentration of these two species will be less this voltage will also drop down ok because you have to use reduction this Nernst equation which is E0 plus RT 2 F and here it is 1 F because 1 electron is in involve ln concentration of ox which is Fe 3 plus and concentration of red which is reductant which is Fe plus 2. So, now, if these values are less automatically this value would also change this value would remain same right.

$$E = E^{O} + \frac{RT}{F} ln \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

So, like that way this potential would be much higher compared to hydrogen evolution reaction potential. So, this is E0 or E equilibrium you can say and this is the E equilibrium for Fe plus 3 going to Fe plus 2. So, now, that one will also come as per its own polarization curve activation polarization line as per the Tafel equation. And then at this point when it reaches to this particular potential it will add up all the cathodic reactions and then it will move there like this fine.

So, this particular portion is like this. So, this particular part is addition and plus H plus plus e equal to H. So, these two cathodic reactions are added because as per the mixed potential theory. The mixed potential is will be achieved at a point where both total rate of cathodic reaction would be equal to total rate of anodic reactions. So, now, this is the point now which is the point which is the mixed potential now, E mix prime and let us say previously when there was no FeCl Fe plus 3 this was E mix.

So, now, you could see that after addition of Fe plus 3 our corrosion potential has gone up or the E mix has gone up, but the corrosion rate has actually increases have actually increased to a great extent because it is a log scale. So, now, this is i cor when Fe plus 3 is present would be much higher than icorr when no Fe plus 3. So, now you could understand why $FeCl_3$ is added for making it a conducive atmosphere for having a very high degree of corrosion. So, those oxidizers if they are present that can actually prevent passivation as well as that can induce pitting.

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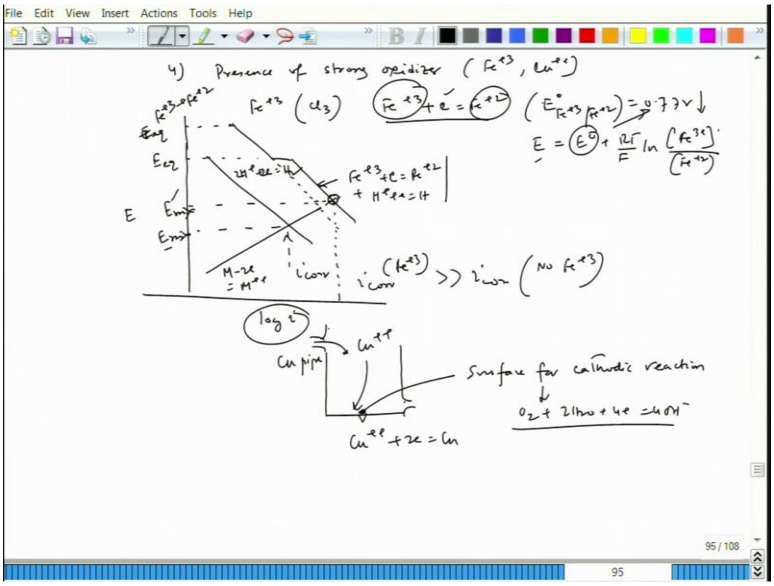

Similarly, copper also would act like that way. For example, if we have a tank if we have a tank and that tank you have a this is outlet and this is the inlet. Inlet pipe is copper made let us say copper pipe. So, that copper pipe can lead some of the copper ions to go in and that copper ions can have a cathodic reaction Cu plus plus plus 2 equal to Cu. So, that copper deposit would have, oops somewhere it has gone ok.

So, the copper deposit would happen and this copper a small bead would happen. So, that bead would now act as a source for or the surface for cathodic reaction cathodic reaction and that would hold that cathodic reaction 2 $H_2O$ plus 4 e equal to 4 OH minus. So, this is the cathodic reaction happening before, but now locally you have a strong cathode where this reaction would happen and there could be a pit formation here.

So, those are the kind of situations because of the presence of strong oxidizer we do have pitting on a particular metal surface. So, couple of more conditions are there we will discuss in our next lecture. So, till then let us stop here.

Thank you.