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

Lecture - 26
Crevice corrosion: Mechanism and Various stages

Let us start lecture 26 and the course is Corrosion Failures and Analysis. We have been discussing Crevice corrosion and today, we will finish Mechanism of crevice corrosion, as well as would like to see some of the protection routes. In fact, we will also see some of the case studies.

In fact, we have seen some of the case studies. For example, the crevice corrosion on the door crevice corrosion in case of a keyhole of a lock crevice corrosion at the root of ribbed rebar and in addition we will see some of the industrial problems of course, I will take up from some of the sources and of course, acknowledge those sources.

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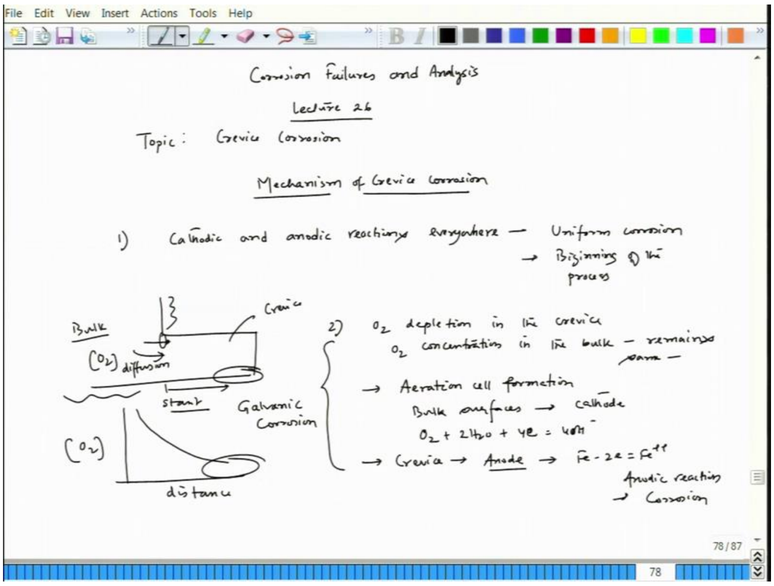

Corrosion Failures and Analysis

Lecture 26

Topic: Crevice Corrosion

Mechanism of Crevice Corrosion

1) Cathodic and anodic reactions everywhere – Uniform corrosion
→ Beginning of the process

2) O_2 depletion in the crevice
O_2 concentration in the bulk – remains same –
→ Aeration cell formation
Bulk surfaces → cathode
$O_2 + 2H_2O + 4e = 4OH^-$
→ Crevice → Anode → $Fe - 2e = Fe^{++}$
Anodic reaction
→ Corrosion

Now, the lecture is on corrosion failure analysis and lecture 26 topic of course, crevice corrosion. In fact, in the last lecture at the end of the lecture we started talking about mechanism so, but now we will try to complete that mechanism part. Now, we have seen that 1st we have reaction cathodic and reactions everywhere.

So, that means, if we start with the crevice like this so, this is the part where crevice. Now, everywhere you have these two reactions you just go back to the last lecture and then check that particular lecture and because of the cathodic and anodic reactions everywhere we have uniform corrosion in the beginning. So, it leads to uniform corrosion and that to remember beginning of the process, ok.

So, remember this does not complete continue for long because you have formed a crevice and that crevice part is large enough to access to allow solution to get into the crevice. And it will be small enough which disallow which will disallow the convection current into the system so that the crevice would not receive oxygen through convection.

There could be possibility of diffusion of oxygen because oxygen in the bulk let us say this is bulk. In the bulk would always be larger than the oxygen in the crevice because of the bulk part is exposed to the environment and that is what oxygen can migrate and diffuse in soluble oxygen. Now, here oxygen can access by diffusion, but that particular process would be very low because it is a room temperature process.

So, after some time, 2nd stage would take over where oxygen depletion happen in the crevice and oxygen concentration in the bulk remain almost same. So, what it does? Now, we have aeration cell formation. Since oxygen concentration away from the crevice, let us say this areas these areas are having much higher concentration of oxygen. So, the bulk surfaces would act as cathode since this reaction will continue.

Now, what happens to crevice? Crevice now since we have oxygen content would be very low in the crevice and that oxygen content if you start from the crevice entry, so, let us say this is the crevice entry part and if you try to plot oxygen content if oxygen percentage as a distance from let us say this point onwards the extreme part would be having the lowest oxygen content.

And, the oxygen schematic plot could be like this oxygen concentration from the start to the end. So, let us say this is the start point of the crevice part. So, oxygen condition so this part will act as or in this case this part will act as anode, fine. Will have reaction or this is anodic reaction which is nothing, but corrosion. So, now, differential aerated cell so that means, the second level so, this is the part which is nothing, but now we ended up to this.

Now, after that we said that the crevice mode of corrosion the distinction happens after this.

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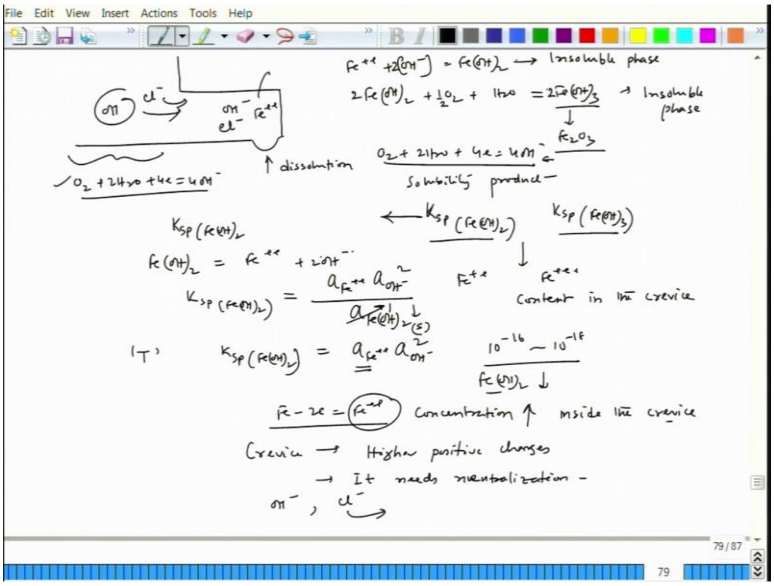

$Fe^{++} + 2(OH^-) = Fe(OH)_2 \longrightarrow$ Insoluble phase

$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O = 2Fe(OH)_3 \rightarrow$ Insoluble phase

$\downarrow$ Fe_2O_3

$O_2 + 2H_2O + 4e = 4OH^-$

$O_2 + 2H_2O + 4e = 4OH^-$

Solubility product –

$\longleftarrow K_{sp}(Fe(OH)_2)$ $K_{sp}(Fe(OH)_3)$

$K_{sp}(Fe(OH)_2$

$Fe(OH)_2 = Fe^{++} + 2OH^-$

$K_{sp(Fe(OH)_2)} = \frac{a_{Fe^{++}} a_{OH^-}^2}{a_{Fe(OH)_{2(s)}}}$

Fe^{++} Fe^{+++} content in the crevice

'T' $K_{sp}(Fe(OH)_2) = a_{Fe^{++}} a_{OH^-}^2$

$10^{-16} - 10^{-18}$

$Fe(OH)_2 \downarrow$

$Fe - 2e = \boxed{Fe^{++}}$ Concentration ↑ inside the crevice

Crevice → Higher positive charges

→ It needs neutralization –

OH^-, Cl^-

Now, what happens if we try to see again this crevice part? You have a dissolution here, right. Now, interestingly in this portion we have OH ion as well as Fe plus plus ion as well as chlorine ion. Now, Fe plus plus ion would react with OH minus to it will form Fe OH whole 2 and even if it has a little bit of oxygen presence, so, then it can also turn into whole 3 which is nothing, but hydrated you can write it as Fe_2O_3 H_2O you can write that way, ok.

So, now so, this is a kind of you can say that let us not write this because it is actually a ferric hydroxide which is nothing, but the red rust. So, it actually converts to Fe_2O_3 which is nothing, but the ferric oxide. Now, so, this form so, let me just balance this. So, you can write I think hydrogen is now 6 2 2 ok fine. So, this is the balance. Now, this also can happen.

So, now everybody these are actually insoluble phase, this is also insoluble, ok. Now, so, this phases would have their own solubility product. So, now, it is basically Ksp of Fe OH whole 2 and Ksp of FeOH whole 3, ok. Now, that solubility product would decide iron plus plus or Fe plus plus plus, plus 3 content in the crevice ok. Now, once the solubility product concentration, so, that means, if I try to look at this part is basically Fe OH whole 2 equal to Fe plus plus plus OH minus 2 2.

$$Fe^{++} + 2OH^- = Fe(OH)_2$$

$$2Fe(OH)_2 + (1/2)O_2 + H_2O = 2Fe(OH)_3$$

$$Fe(OH)_2 = Fe^{++} + 2OH^-$$

$$K_{sp(Fe(OH)_2)} = \frac{a_{Fe^{++}}.a^2_{OH^-}}{a_{Fe(OH)_2}}$$

$$K_{sp(Fe(OH)_2)} = a_{Fe^{++}}.a^2_{OH^-}$$

$$Fe^{++} + 2Cl^- = FeCl_2$$

$$FeCl_2 + H_2O = HCl + Fe(OH)_2$$

So, now we can write this way. So, now, Ksp FeOH whole 2 would be equal to activity of Fe plus plus activity of OH minus square divided by activity of a FeOH whole 2 ok. So, this is the formula we can say. So, now, let us say this one settles down. So, we can take it as a 1 and if it is a pure so, then it we can take it as 1 since it is a solid. So, this is also solid remember.

So, now activity so, then K s p we can write it as ok. So, this will be the Ksp part which is a product of activity of iron ion concentration and activity of OH minus concentration OH my active OH minus ion. Now, if this Ksp exceeds so, now, if this is Ksp; Ksp value could be order of around close to around 16 to 10 to the power eighteen. So, this is the level of Ksp value. So, that means, the concentration of iron ion in the solution would be very very low.

Now, once this particular value exceeds because the K then only iron ion will once it because the temperature is constant so, this equilibrium will have a situation will reach. Now, once this concentration is reached so, this FeOH will settle down will form again because it has to maintain it is equilibrium. So, once this activity of Fe plus plus or concentration of Fe plus plus exceeds the value required for equilibrium to maintain that Ksp value. So, then the rest of the iron ion will again dissolve will again combine with OH minus ion ok and then settles down.

But, now let us say we have do not have this reaction do not have this reaction. So, this reaction is very minimal there, fine. So, that means, Fe plus plus ion that is forming so, that excess amount once this Ksp value exceeds will try to combine with OH minus ion and settles down, but now it does not have much of OH minus presence there ok because this reaction is not taking place in this crevice portion.

Outer side? Outer side of course, this reaction is taking place this reaction taken is taking place. So, that means, we have a situation that Fe plus plus ion concentration increases inside the crevice inside the crevice. Why? Because as this Fe plus plus ion is increasing it will try to react with OH minus ion and try to form K FeOH whole 2 which will settle down.

But, now if we do not have OH minus ion so, then the amount of Fe plus plus which is forming big just to supply electron for this reaction which is happening outside the crevice which have which is cathode. So, that ion concentration will keep on increasing inside the crevice.

So, now at one place this place is basically having higher and higher a negative positive charges. So, this crevice now higher positive charges. So, now, this positive charge needs to be neutralized. So, that means, it needs neutralization. So, now for that we have OH minus ion at the same time chlorine minus ion.

Now, one possibility is OH minus ion, here OH minus ion is forming which can go here, chlorine minus ion which can also go here. Now, if chlorine ion goes there ok so, now that we will try to since chlorine ion has a higher negativity and it is a small smaller ion. So, that will have a higher speed so, that can go into the into that particular crevice part.

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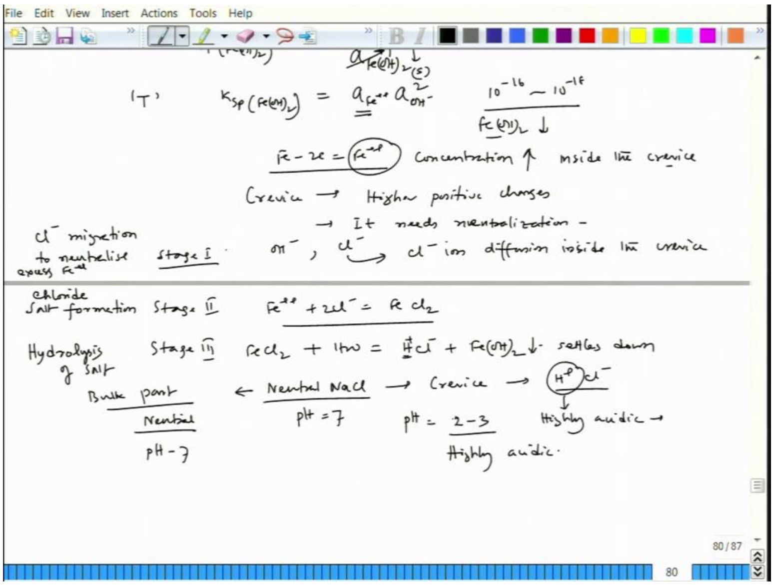

$a_{Fe(OH)_2(s)}$

'T' $K_{sp}(Fe(OH)_2) = a_{Fe^{++}} a^2_{OH^-}$ $10^{-16} - 10^{-15}$

$Fe(OH)_2 \downarrow$

$Fe - 2e = Fe^{++}$ Concentration ↑ inside the crevice

Crevice → Higher positive charges

→ It needs neutralization -

Cl^- migration to neutralise excess Fe^{++} Stage I OH^-, Cl^- → Cl^- ion diffusion inside the crevice

Chloride Salt formation Stage II $Fe^{++} + 2Cl^- = FeCl_2$

Hydrolysis of Salt Stage III $FeCl_2 + H_2O = HCl + Fe(OH)_2 \downarrow$ settles down

Bulk part ← Neutral NaCl → Crevice → H^+Cl^-

Neutral pH = 7 pH = 2-3 Highly acidic →

pH - 7 Highly acidic.

So, the chlorine ion will react with. So, this particular salt will form now this salt since there is water. So, this salt will hydrolyze. So, the chlorine ion diffusion inside the crevice just to neutralize the extra positive charge that is developing because of the excess Fe plus plus ion, once this Ksp value of FeOH whole 2 is exiting.

So, that means, we do not have much of OH minus ion presence there. So, that is what we have to have excess chlorine ion coming there and trying to neutralize that particular situation where excess positive charge is developing. So, now that chlorine ion would now react with H_2O and try to hydrolyze and that hydrolyze hydrolysis would lead to this particular situation, ok.

So, now, this is again this will again settle down and now you have H plus ion generation. Now, ok so, this is for this is stage I, stage II and this is stage III. So, now, stage III is nothing, but hydrolysis of salt, stage II is chloride salt formation and stage I is chlorine ion migration to neutralize Fe plus plus excess Fe plus plus.

So, now again there is now interesting stuff. So, this particular phase which is insoluble settles down in the crevice. At the same time, now in the crevice initially we started with a neutral NaCl solution neutral NaCl. Now, in the crevice part it generates H plus this acid which is a strong acid and the outer part bulk part it remains neutral, ok. So, that means, in the crevice part now H plus ion which is actually making this crevice part which is a small section a small fluid or liquid highly acidic.

Now, this is basically if we try to look at this particular part so, this is galvanization corrosion and then 2nd part galvanic corrosion and then 2nd part which is basically you can say that this is ok. So, let me go to the first.

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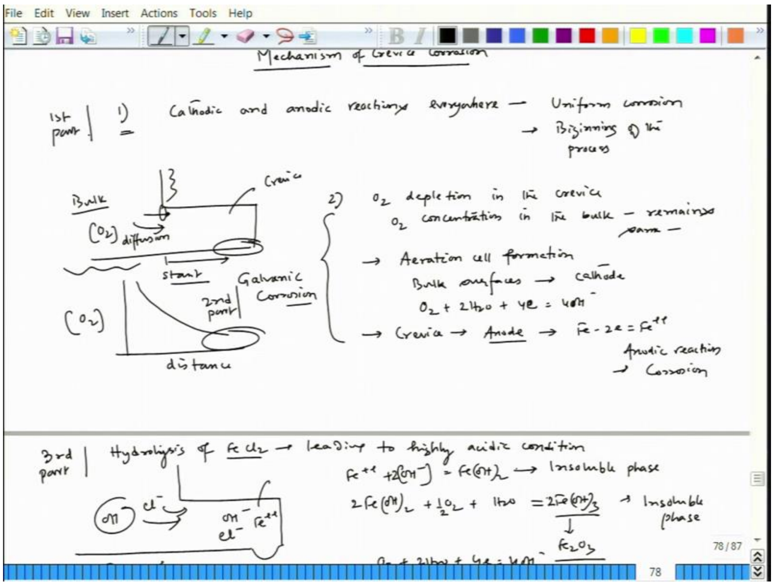

Mechanism of Crevice Corrosion

1st part | 1) Cathodic and anodic reactions everywhere — Uniform corrosion → Beginning of the process

2) O_2 depletion in the crevice
O_2 concentration in the bulk — remains same —
→ Aeration cell formation
Bulk surfaces → cathode
$O_2 + 2H_2O + 4e = 4OH^-$
→ Crevice → Anode → $Fe - 2e = Fe^{++}$
Anodic reaction
→ Corrosion

3rd part | Hydrolysis of $FeCl_2$ → leading to highly acidic condition
$Fe^{++} + 2[OH^-] = Fe(OH)_2$ → Insoluble phase
$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O = 2Fe(OH)_3$ → Insoluble phase
$\downarrow$
Fe_2O_3

So, this is the 1st part which is a uniform corrosion then galvanic corrosion 3rd stage we can write it as hydro like hydrolysis of $FeCl_2$ leading to highly acidic condition. So, this is 3rd stage 3rd part. So, this is 2nd part, ok and this is of course, the 1st part ok.

So, now once we have this situation that H plus acidic condition is generating and this crevice part can go to even the pH, initially it was pH 7. This is maintaining pH 7 the bulk part, but the crevice part it might become highly acidic even pH can go up to 2 to 3. So, that means, it becomes highly acidic, ok. So, let us see what happens to that.

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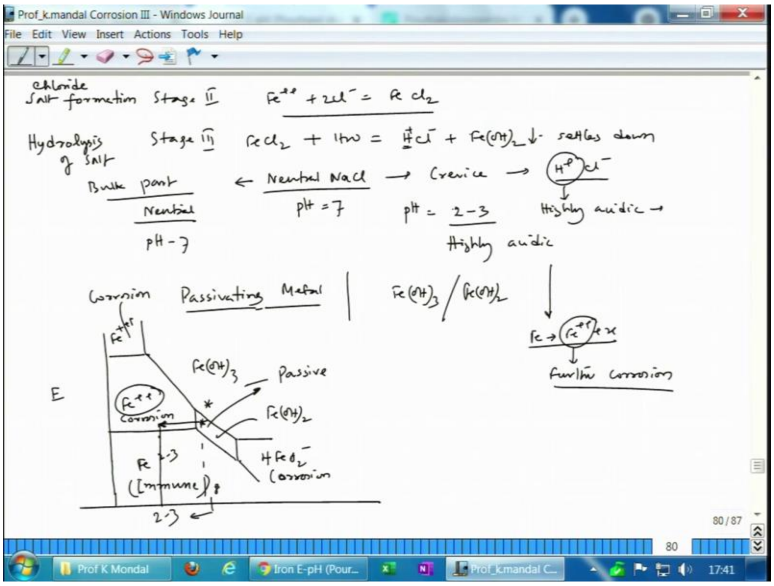

chloride Salt formation Stage II $Fe^{++} + 2Cl^- = FeCl_2$

Hydrolysis of Salt Stage III $FeCl_2 + H_2O = H^+Cl^- + Fe(OH)_2\downarrow$ settles down

Bulk part ← Neutral NaCl → Crevice → H^+Cl^-
Neutral pH = 7 pH = 2-3 Highly acidic →
pH - 7 Highly acidic
Corrosion Passivating Metal | $Fe(OH)_3$ / $Fe(OH)_2$
$Fe \rightarrow Fe^{++} + 2e$
Further corrosion

Now, let us say this particular metal is passivating; passivating metal. In the beginning we have a passive layer. Let us say the passive layer is basically made of FeOH whole 3 or FeOH whole 2. Now, if I try to see schematic of iron Pourbiax diagram E and pH. So, the iron Pourbiax diagram looks like this.

So, here we have Fe, here we have Fe plus 2, Fe plus 3, here FeOH whole 3, this is FeOH whole 2, this is H FeO 2 minus. So, that time this part is again corrosion. Since ion is forming this part is corrosion, this part is corrosion, now this part is immune, this part is passive, even this part is passive, ok. So, that means, we have this phases formation on which happens more than around close to 6 to 7 pH. So, let us look at Pourbiax diagram.

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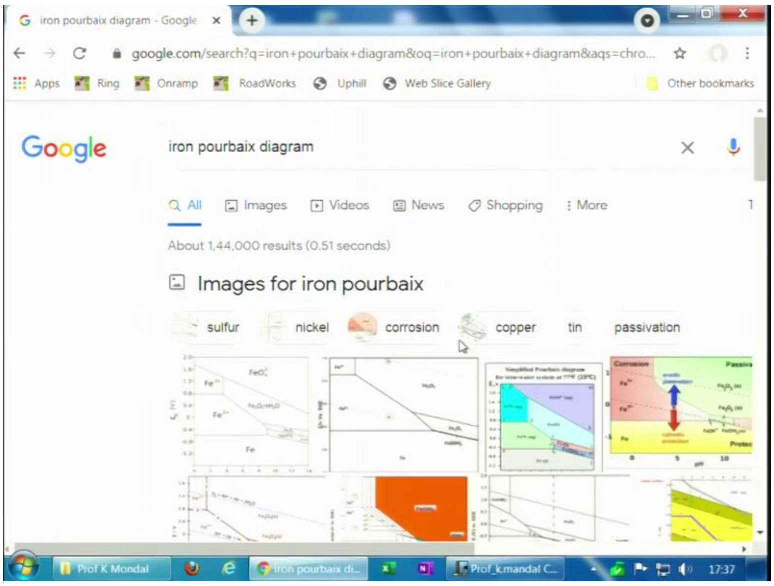

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iron pourbaix diagram

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Images for iron pourbaix

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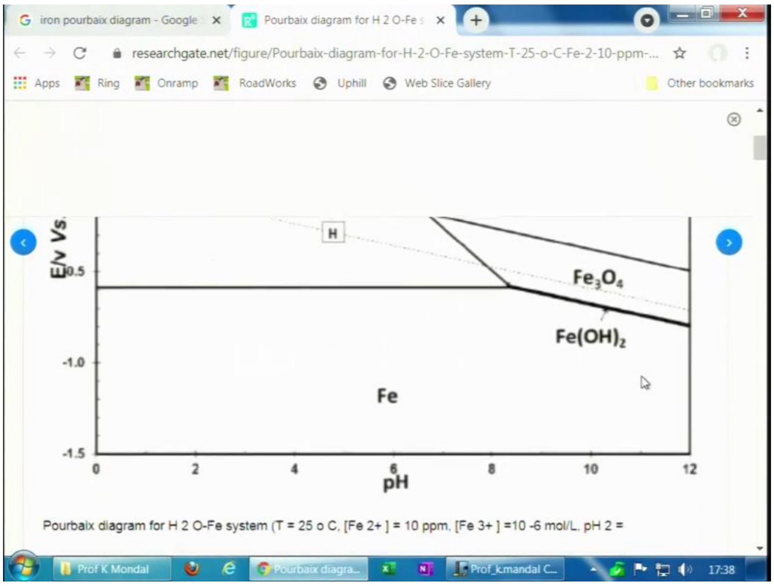

Pourbaix diagram for H 2 O-Fe system (T = 25 o C, [Fe 2+] = 10 ppm, [Fe 3+] =10 -6 mol/L, pH 2 =

So, let us look at this particular diagram. So, now, this is Fe_2O_3. So, just a minute. Yes, we can look at this part.

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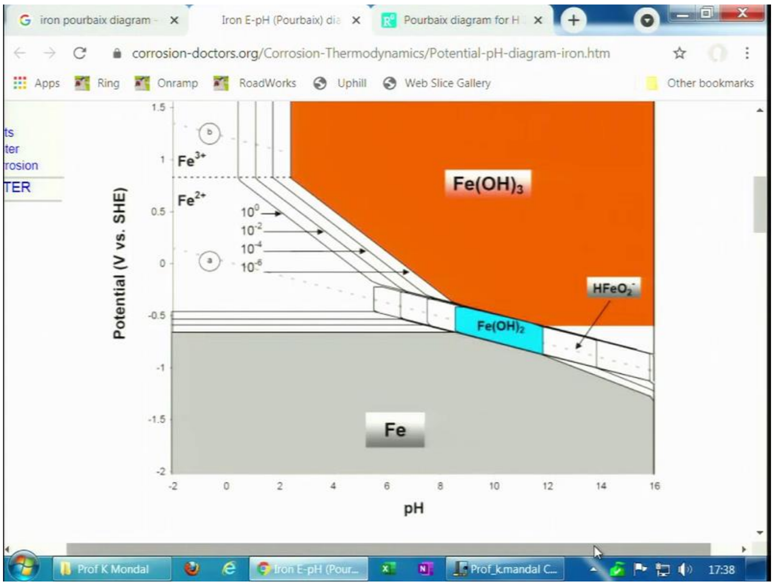

Now, if you see this diagram. So, this is the same as the schematic diagram what I have shown to you. Now, in this case if you see the pH level around close to 7 so, if you take it to around this level. So, this particular cursor if you see so, around this level if you see so, once you go there you will have passive layer ok. So, this is passivity, this is passivity.

Now, coming to our discussion, so, now, if the pH drops down so, if pH drops down. So, then let us say if the situation is at this place or at this place pH drops down; that means, the pH goes down. So, initially it is let us say close to 8, now once it goes to there so, there the pH become this particular pH becomes 2 to 3 and this has stepped into this has stepped into a corrosion zone which is Fe plus plus.

So, that means, because of this higher acidic nature or lower pH the situation goes into. So, this particular situation goes into so; that means, it is actually leading to further corrosion further corrosion. So, that means, in the 3rd stage itself it actually a breaks down the passivating surface.

And, once it breaks down then you have more and more Fe plus plus formation because it has broken from the passive layer to the corrosion zone because the pH and the if the potential remains same. So, that means, the pH if let us say this is pH 2 to 3. So, it has gone into corrosion zone and it actually leads to further Fe plus plus ion formation.

And, once Fe plus plus form formation happens then it has to neutralize again. So, then again chlorine ion will come back to the chlorine ion will reach to the crevice it will react with Fe plus plus and react form $FeCl_2$ and then after formation of $FeCl_2$, it will further hydrolyze and then form H plus and Cl minus.

So, like that way that cycle that iron ion formation more electro positivity, more chlorine ion coming into neutralize formation of iron chloride and then hydrolysis of iron chloride formation of HCl and FeOH whole 2. So, like that way system will keep on happening.

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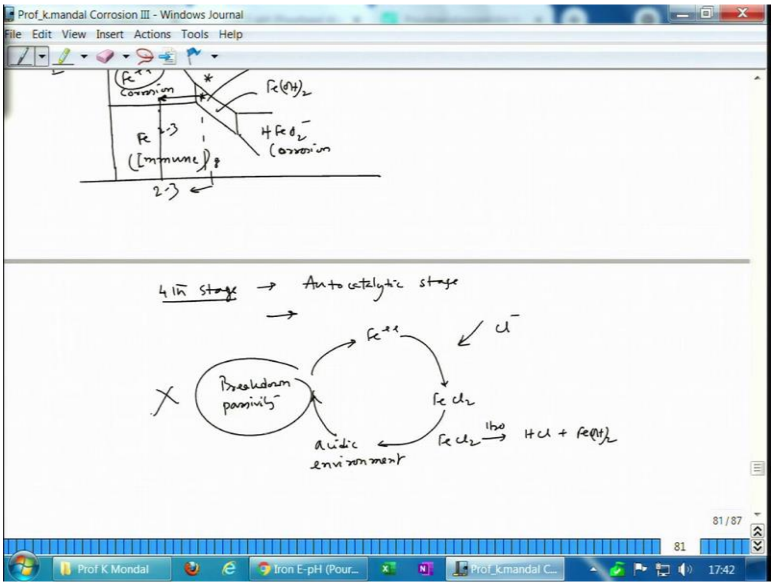

And, so, that time we have the 4th stage 4th stage which is basically auto catalytic auto catalyst catalytic stage which is nothing, but the cycle. So, this cycle Fe ion plus plus formation chlorine ion comes in the crevice $FeCl_2$ hydrolysis and then acidic environment breakdown of then you have breakdown of passivity. Now, and then again Fe plus plus formation.

Now, question is once this breakdown of passivity happens to that stage this stage goes out. So, you do not have this stage anymore. So, it becomes this stage formation.

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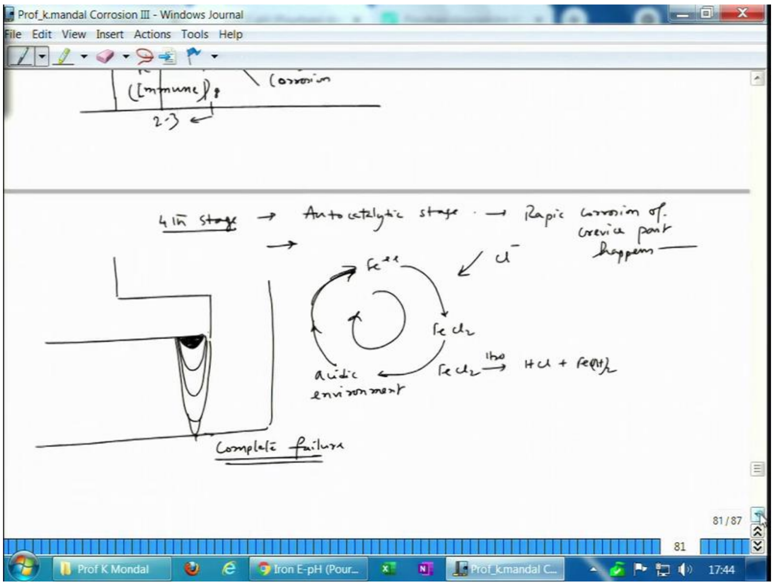

So, that means, this one continues in a cyclic manner and then it reaches to auto catalytic stage, the rapid corrosion of crevice part happens. So, that constitutes the all the stages of crevice corrosion the mechanism part.

So, now, if you have this crevice so, here initially the crevice started and then immediately the localized one it will keep on dissolving and let us say the thickness was this. This was the thickness of the wall of that particular iron structure. So, finally, it will reach to the other end and then it is a complete failure complete failure.

So, this is the four stages of crevice corrosion. So, now, we will stop here before stopping.

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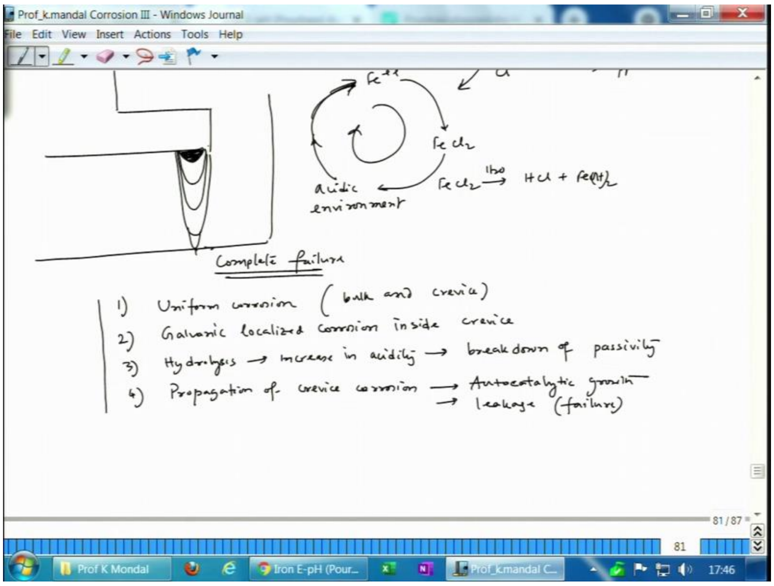

1) Uniform corrosion (bulk and crevice)
2) Galvanic localized corrosion inside crevice
3) Hydrolysis → increase in acidity → breakdown of passivity
4) Propagation of crevice corrosion → Autocatalytic growth
→ leakage (failure)

So, let me just mention all those four stages. 1st stage is uniform corrosion bulk and crevice. So, then we have galvanic localized corrosion inside crevice. 3rd stage is hydrolysis increase in acidity and breakdown of passivity and 4th stage is propagation of crevice corrosion and autocatalytic growth. So, these are the four stages and finally, it lead to finally, failure complete leakage; leakage or failure ok.

So, let us stop here. We will discuss some of the protection measures as well as some of the case studies industrial case studies of course, taken from some of the book sources and then we will complete our discussion on crevice corrosion. Let us stop here.

Thank you.