Corrosion Failures and Analysis
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Lecture - 05
Forms of corrosion: Uniform corrosion (Part 2)

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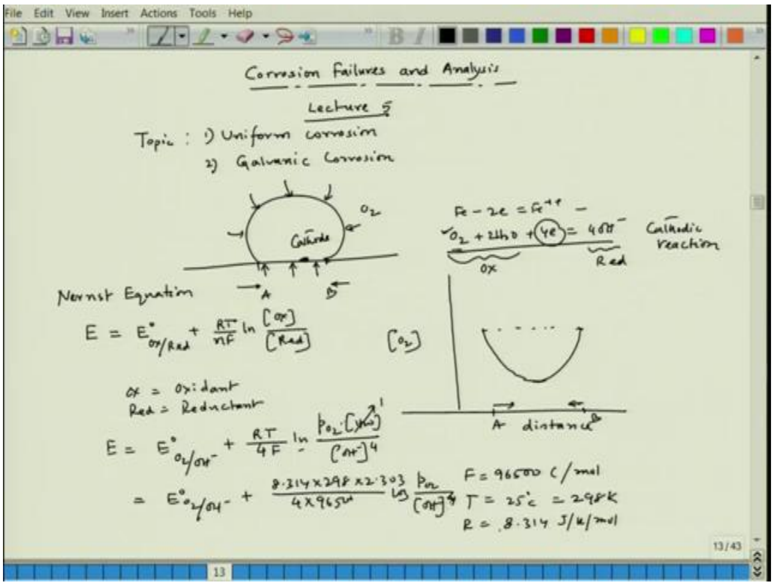

Corrosion Failures and Analysis

Lecture 5

Topic : 1) Uniform corrosion
2) Galvanic Corrosion

$Fe - 2e = Fe^{++}$

$\underbrace{O_2 + 2H_2O}_{Ox} + \boxed{4e} = \underbrace{4OH^-}_{Red}$ Cathodic reaction

Nernst Equation

$$E = E^\circ_{Ox/Red} + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]}$$

Ox = Oxidant
Red = Reductant

$$E = E^\circ_{O_2/OH^-} + \frac{RT}{4F} \ln \frac{p_{O_2} \cdot \cancel{[H_2O]}^{1}}{[OH^-]^4}$$

$$= E^\circ_{O_2/OH^-} + \frac{8.314 \times 298 \times 2.303}{4 \times 96500} \log \frac{p_{O_2}}{[OH^-]^4}$$

F = 96500 C/mol
T = 25°C = 298K
R = 8.314 J/K/mol

Hello, everyone. Welcome back to the Corrosion Failures and Analysis course. Today, we have lecture 5 and today's topic we will continue on Uniform Corrosion and then we will get to Galvanic Corrosion. So, if we recall what we have discussed in the uniform corrosion that there are influence from different environments it could be SO_2 or SO_3 based environment which prevail in petroleum refinery.

There could be situation of atmospheric corrosion where we have O_2 as well as H_2O moisture and on that regard we have checked one situation like rain water droplet. If it stays on iron surface what sort of corrosion mechanism we have and then we can also have the effect of marine environment where we have dissolve oxygen of course, moisture or water and as well as we have chloride ions.

And, we have seen the kind of corrosion that happens and if it is happening over the entire surface without having any preferential location, then it will take place in uniform pattern. But, another information, let me share that though we talk about uniform corrosion, but there could be situation of galvanic effect.

In fact, without galvanic effect having corrosion is difficult to think of just let us get to this same example what we had for rain water corrosion or rain droplet. So, if this is the surface, this is the droplet and what we have seen? That initially everywhere we have both the reactions, this reaction as well as this reaction.

So, cathodic and anodic reactions are taking place over the entire iron surface apart from the this part. Because if I consider only this electrolyte portion the droplet which is in contact with the iron surface so, these are the two reactions that take place. Now, initially it is over the entire surface, but since this dissolve oxygen is consumed because of this cathodic reaction.

So, the oxygen level in that droplet would go down the oxygen concentration will go down. Now, if oxygen concentration goes down so that depletion of oxygen needs to be met by the diffusion of oxygen or the migration of oxygen from the atmosphere. And, the migration as I have told you the migration is happening because of the diffusion effect so, it is a time consuming process.

So, then there will be if I consider from this end to this end and if I try to draw a kind of semantic oxygen concentration level as a function of distance and let us say this is A position, this is B position, this is A and this is B. So, oxygen concentration at A location would be the maximum and here I am not talking about gaseous oxygen I am talking about dissolve oxygen.

Now, this oxygen would decrease and B position also having close to the environment. So, B position also will have the same level of oxygen content dissolve oxygen content. So, this will also decrease and around center position it will have to be the minimum oxygen level.

Now, if we consider this reaction this cathodic reaction and, if I try to see the Nernst equation for this reaction, the generalized Nernst equation talks about E naught ox by Red; that means, plus RT by n F ln ox concentration of ox and concentration of Red and here ox is basically oxidant and Red nothing, but reductant. So, this is Nernst equation.

$$E = E^{o}_{Ox/Red} + \frac{RT}{nF} ln \frac{[Ox]}{[Red]}$$

Now, here in this reaction the oxidant is basically this part is ox and this part is Red ok reductant. So, now I can write this E equal to E naught ox by Red and here I can write O 2 OH minus since OH minus is the reductant plus RT whatever the temperature we have here n is 4 here. So, 4 and this is 1 faraday ln ox is oxygen concentration I can write in terms of partial pressure of oxygen and H_2O if we consider this water to be pure then I can write this I can take it as one and then concentration of OH minus to the power 4.

So, this will be my form of that potential. So, that means, wherever I for example, at this location I have this reaction this cathodic reaction oxygen reaction. So, this part is cathode let us say at some random time. I could see that this particular reaction is taking place here.

So, this will be cathode. So, this cathode is distributed, anode is also distributed because this is also taking place over the entire surface in the beginning of the operation where oxygen contained in that particular bubble or in one particular water droplet is same everywhere.

Now, because of these reactions oxygen content is depleting as we go inside the bubble. Sorry, not inside the not bubble, it is a basically droplet. Now, if we see this equation, so, then E naught O_2 OH minus plus you can write let us say 314 into 298 Kelvin 4 into 96500, F is 96500 Coulomb per mole of electron 298 temperature is ambient temperature is 25 degree Celsius which is 298 kelvin and R universal gas constant 8.314 Joule per Kelvin per mole ok.

If you put that and then if you want to convert this lawn to log so, then you multiply 303 log pO_2 by OH minus whole 2 whole 4, ok.

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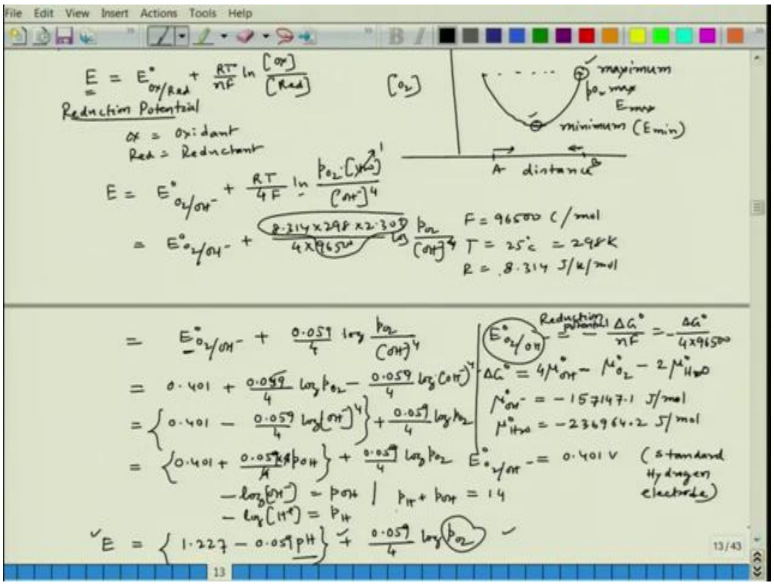

$$\underline{E} = E^\circ_{Ox/Red} + \frac{RT}{nF}\ln\frac{[Ox]}{[Red]}$$

Reduction Potential

Ox = Oxidant
Red = Reductant

$[O_2]$

$$E = E^\circ_{O_2/OH^-} + \frac{RT}{4F}\ln\frac{p_{O_2}\cdot[\cancel{H_2O}]^1}{[OH^-]^4}$$

$$= E^\circ_{O_2/OH^-} + \frac{8.314\times298\times2.303}{4\times96500}\log\frac{p_{O_2}}{[OH^-]^4}$$

F = 96500 C/mol
T = 25°C = 298 K
R = 8.314 J/K/mol

$$= E^\circ_{O_2/OH^-} + \frac{0.059}{4}\log\frac{p_{O_2}}{[OH^-]^4}$$

$$= 0.401 + \frac{0.059}{4}\log p_{O_2} - \frac{0.059}{4}\log[OH^-]^4$$

$$= \left\{0.401 - \frac{0.059}{4}\log[OH^-]^4\right\} + \frac{0.059}{4}\log p_{O_2}$$

$$= \left\{0.401 + \frac{0.059\cancel{\times 4}}{\cancel{4}}\,p_{OH}\right\} + \frac{0.059}{4}\log p_{O_2}$$

$-\log[OH^-] = p_{OH}$ | $p_H + p_{OH} = 14$

$-\log[H^+] = p_H$

$$E = \{1.227 - 0.059\,pH\} + \frac{0.059}{4}\log p_{O_2}$$

$E^\circ_{O_2/OH^-}$ Reduction potential $= -\frac{\Delta G^\circ}{nF} = -\frac{\Delta G^\circ}{4\times96500}$

$\Delta G^\circ = 4\mu^\circ_{OH^-} - \mu^\circ_{O_2} - 2\mu^\circ_{H_2O}$

$\mu^\circ_{OH^-} = -157147.1$ J/mol

$\mu^\circ_{H_2O} = -236964.2$ J/mol

$E^\circ_{O_2/OH^-} = 0.401$ V (standard Hydrogen electrode)

So, now if we multiply this part and divide with this you would get E naught O_2 by OH minus plus 0.059 by 4 log pO_2 divided by OH minus whole 4 I can. So, this value I can find out would be minus delta G0 by nF delta G naught rather 4 into 96500. And, that delta G naught would be mu0 of OH minus mu naught of OH minus mu naught the standard chemical potential O 2 minus 2 mu naught H2O.

$$E = E^o_{Ox/Red} + \frac{RT}{nF}ln\frac{[Ox]}{[Red]}$$

$$E = E^o_{O_2/(OH)^-} + \frac{RT}{4F}ln\frac{p_{O_2}.[H_2O]}{[OH^-]^4}$$

$$E = E^o_{O_2/(OH)^-} + \frac{8.314\times298\times2.303}{4\times96500}log\frac{p_{O_2}}{[OH^-]^4}$$

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$$E = E^o_{O_2/(OH)^-} + \frac{0.059}{4}log\frac{p_{O_2}}{[OH^-]^4}$$

$$E^o_{O_2/(OH)^-} = -\frac{\Delta G^o}{nF} = -\frac{\Delta G^o}{4\times96500}$$

$$\Delta G^o = 4\mu^o_{OH} - \mu^o_{O_2} - 2\mu^o_{H_2O}$$

$$E^o_{O_2/(OH)^-} = -0.401\ V$$

$$E = 0.401 + \frac{0.059}{4} log p_{O_2} - \frac{0.059}{4} log(OH^-)^4$$

$$E = \left\{0.401 - \frac{0.059}{4} log(OH^-)^4\right\} + \frac{0.059}{4} log p_{O_2}$$

$$E = \left\{0.401 + \frac{0.059}{4} p_{OH}\right\} + \frac{0.059}{4} log p_{O_2}$$

$$log(OH^-) = p_{OH}$$

$$E = \{1.227 - 0.059pH\} + \frac{0.059}{4} log p_{O_2}$$

In order to understand this you have to follow corrosion part 1. So, there we have in detail under analyzed why these things come. So, now, these values I can put it. So, these values mu naught OH minus equal to minus 157147.1 Joule per mole mu naught would be equal to minus 236964.2 Joule per mole. So, if you calculate as per this E naught O2 by OH minus you should get 0.401 volt and this is with reference to standard hydrogen electrode which is the reference electrode.

So, now, you put that value 0.401 I am not getting into this because this has been in detail analyzed in corrosion part 1 plus 0.04059 by 4 log pO2 minus 0.059 by 4 log OH minus by 4 to the power 4, ok. So, now you see that let us say this I will take it as, ok. Now, I can write it as p OH pO2, ok.

Now, you see this this is pOH means log OH minus minus is nothing, but pOH and one can do this small calculation pH plus pOH is nothing, but 14. So, and pH is nothing, but log H plus ion activity equal to pH, ok. So, you can do the calculation you will see that this value would come 1.227 minus 0.059 p H.

You do that calculation you will get that and here since I am converting into this pH. So, it will be there will be a 4 multiplying factor 4. So, this 4, 4 would get cancelled. So, you will get this. This is one part and the another part is pO2. So, this is the final expression. Now, let us see what is happening there. So, now, here oxygen content is maximum, here we have minimum, maximum and minimum.

So, now, if we apply this particular formula; this particular formula this particular formula so, what do you think about the potential of that particular cathodic reaction at this point and at this point? Definitely since oxygen pO2 would be the maximum here and if the outside atmosphere is 1 atmosphere it will be same as that. So, that time not same as that because it has to be as per the fraction of oxygen present in that particular atmosphere ok, but it will be maximum.

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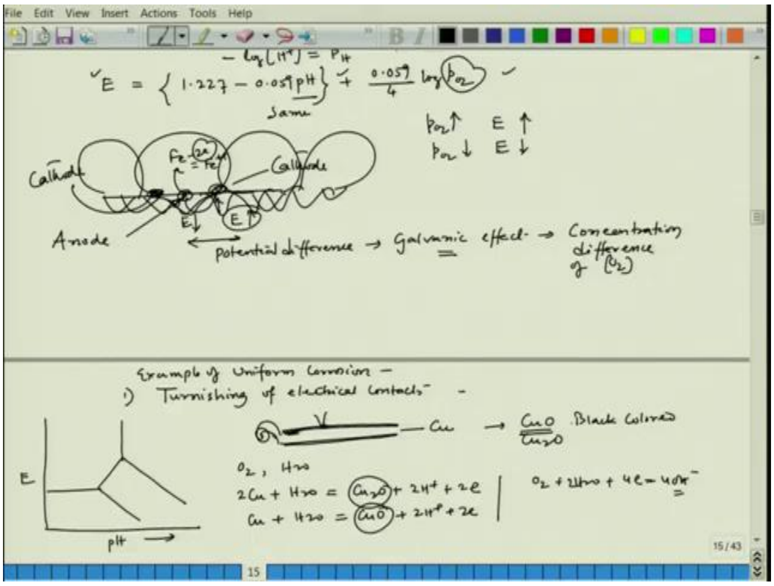

$-\log[H^+] = pH$

$E = \{1.227 - 0.059\,pH\} + \frac{0.059}{4}\log p_{O_2}$

Same

$p_{O_2}\uparrow \quad E\uparrow$

$p_{O_2}\downarrow \quad E\downarrow$

$Fe - 2e = Fe^{2+}$

potential difference → Galvanic effect → Concentration difference of (O_2)

Example of Uniform Corrosion –

1) Turnishing of electrical contacts –

— Cu → $\underline{\underline{CuO}}$ / Cu_2O Black Colored

O_2, H_2O

$2Cu + H_2O = Cu_2O + 2H^+ + 2e$

$Cu + H_2O = CuO + 2H^+ + 2e$

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

So, now if this is this is same, the p H is same fine. So, now, only change is this one. So, if pO2 increases E this E would increase because there is a positive sign and if pO2 decreases E decreases. So, now, and this is about reduction potential remember we are talking about all reduction potential and this is nothing, but reduction potential and here the calculation this is also reduction potential, ok. So, now here E would be max and here E would be min.

So, now, whenever we have this situation then we can see that the center the surrounding part. So, if I draw this this part having E to be very high and this part having E to be low. So, there is a potential difference and this potential difference would lead to a galvanic effect.

So, now, since here the reduction potential is maximum so, that means, this oxygen reduction would take place around this location and at this location oxygen reduction is minimal. So, now where would that electron come from because the oxygen reduction takes 4 electron, one particular molecule of oxygen.

So, now, the oxygen that electron will come by the dissolution of and this these electron will go there, fine. So, that means, this portion would become preferentially anode and this portion these two portion will preferably become cathode and why this is coming up? Because of oxygen depletion and difficulty in oxygen to get from top surface to the center of the droplet, ok so, that is what this difference is arising.

Initially it is actually happening uniformly, but later on it is actually the corrosion will be concentrated at the center location at the center location. So, that means, initially it started with uniform mode, but gradually it is actually going into the center part. So, it is a localized mode and this is happening because of the galvanic effect and this galvanic effect is coming due to concentration difference of dissolved oxygen, fine.

But, now this concentration effect is actually leading to potential difference. So, now, initially it is uniform later on it becomes localized. Now, question is then still we are telling that this is uniform corrosion because it is not only one droplet. Now, there are multiple droplet forming. So, everywhere we are having such situations. So, that is what we are finally, this thing will be like this corrosion will be unified over the entire segment of that particular surface.

So, it will be uniform over the sections though in an individual droplet we are having localized mode because of this concentration effect. So, now, what I said that the uniform corrosion most of the cases you would see that it will end up in galvanic mode ok we will see lot of lot more examples. But now coming to this uniform corrosion whenever we talked about it we have to see other some of the examples on uniform corrosion ok, fine.

Let us say examples, tarnishing of electrical contacts. Now, whenever we have let us say a wire and there is a plastic cover and this wire let us say copper, ok. Now, copper interesting part is copper has got so many reactions with the environment, ok. Now, copper can go to CuO or Cu_2O.

Now, if there is a puncture somewhere here or if this end part when you do the connection do the connection here the end part the plastic cover is removed and when you do that that particular part is exposed to the environment and, even here exposed to the environment.

Now, interesting part is the part the wire part which is exposed to the environment that might not get tarnished to a great extent, the tarnishing will happen the part which is inside the plastic cover. Why this happens? We will understand later when we talk about galvanic corrosion, but actually these happens and then there could be a reaction and there will be moisture as well as oxygen and there could be reaction like this, ok.

So, this reaction can happen which is basically oxidation reaction and Cu2O is forming. There could be reaction like copper plus H2O, it can go to CuO plus 2H plus plus 2e. So, this reaction can also take place, ok. Now, oxidation reaction could be. So, this is hydrogen generation. So, now, there could be reaction like cathodic reaction this is H2O plus 4e 4OH minus, ok. So, that reaction can also happen.

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e$$

$$Cu + H_2O = CuO + 2H^+ + 2e$$

Now, everything can be clubbed together and we can have a 4 way diagram of copper the diagram looks like this and this pH and this OH do not get confused with the OH minus, OH minus can also be converted into p H ok, H plus ion. So, this reaction product might give Cu 2 O or Cu O which is nothing, but the rust of copper. So, this happens because if there is a possibility of that copper to get in contact with the atmosphere and then the corrosion starts, the tarnishing starts and here this looks like a black colored oxide.

And, this black color oxide you will see that the copper wire if you remove see for example, if you throw some copper wire with the plastic cover on and then after sometime you remove the copper, the plastic end of the copper wire where it is exposed you will see it has become little darkish black colored. You know that is nothing, but this tarnishing of copper it is basically copper oxide is forming and that is happening because of the corrosion effect fine. So, this is one example.

Now, here one important thing I have to inform I have to tell you that wherever the copper is exposed to the environment the corrosion will not be significant there, but wherever the copper is covered up there the corrosion would be more prevalent, ok. So, this happens because of the galvanic effect we will talk when we talk about galvanic corrosion ok.

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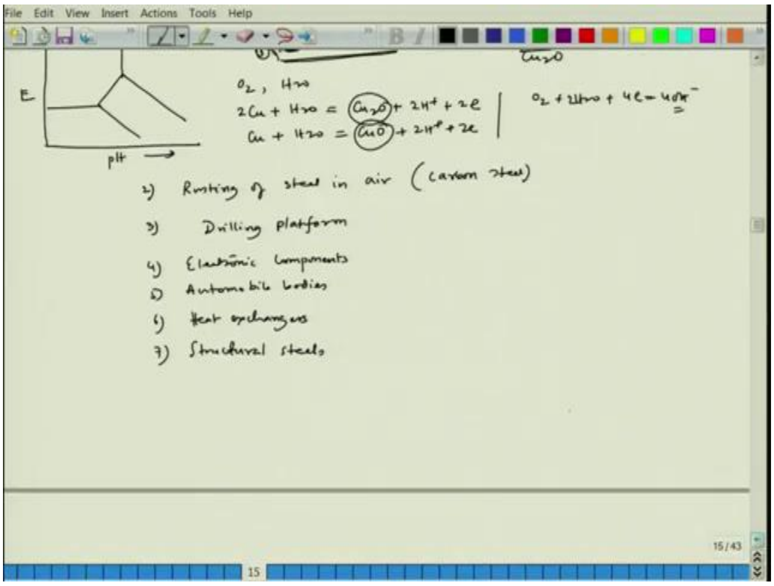

Cu_2O

O_2, H_2O

$2Cu + H_2O = \boxed{Cu_2O} + 2H^+ + 2e$

$Cu + H_2O = \boxed{CuO} + 2H^+ + 2e$

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

2) Rusting of steel in air (carbon steel)
3) Drilling platform
4) Electronic components
5) Automobile bodies
6) Heat exchangers
7) Structural steels

So, now coming to other forms of corrosion other examples rusting of steel in air and here I am talking about carbon steel. In case of stainless steel generally it happens mostly in a localized fashion. But carbon steel for example, some if you go to a sea side if you see a bolts there let us say a jetty there the corrosion is mostly uniform corrosion and over the entire segment you will see the rust has form all over the bolts or nuts whatever you see.

It is a basically carbon steel and there the rust is forming in the air. Also there are effects of there will be effect of chloride ions, but mostly it is uniform ok. Then let us say drilling platform drilling platform or also observe drilling platforms, then you can say electronic components, there could be possibility of automobile bodies.

Interestingly if you see old ambassador car standing on the road aside you will see that the top surface is totally rusted. Ambassador vehicle or the normal vehicle it is basically carbon steel low carbon steel and that is having basically and there is a flat section. So, not much of possibility of having crevice effect. So, it is a general corrosion or uniform corrosion, ok. So, these are some of the examples.

For example, heat exchangers heat exchangers the top surface heat exchangers mostly it is even the inner internal part can be general corrosion, but there are other effects like the fluids are going. So, there could be oxidation if for example, water see this water is flowing and so, this water can have debris with it, ok.

For example, in some of the cases there could be possibility that for the water heat exchanger the water can contain lot of debris or deposits calcium carbonate deposits that might choke the pipe and that debris can also lead to erosion corrosion. So, there are other effects also so, but mostly it is uniform corrosion.

So, and also structural steels; for example, bridge if we have a long beam the corrosion is mostly uniform corrosion. So, these are the examples.

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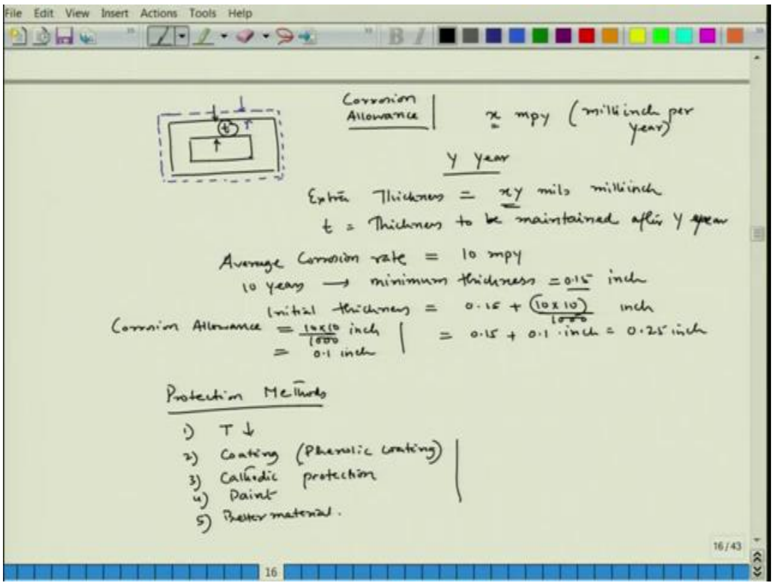

Corrosion Allowance | $\underline{x}$ mpy (milli inch per year)

y year

Extra Thickness = $\underline{xy}$ mils milli inch

t = Thickness to be maintained after y year

Average Corrosion rate = 10 mpy

10 years → minimum thickness = 0.15 inch

Initial thickness = $0.15 + \frac{(10 \times 10)}{1000}$ inch

Corrosion Allowance $= \frac{10 \times 10}{1000}$ inch $= 0.1$ inch | $= 0.15 + 0.1$ inch $= 0.25$ inch

Protection Methods

1) T ↓
2) Coating (Phenolic coating)
3) Cathodic protection
4) Paint
5) Better material.

Now, when we talk about this uniform corrosion since it is happening over the entire segment let us say if we talk about uniform corrosion. So, let us say this is my body and this is the thickness let us say T and if the corrosion happens uniformly. So, that means, we know that after some time if we know the corrosion rate the average corrosion rate we will be able to calculate how far it has moved inside the body.

Now, that case one can think of allowance or we call it corrosion allowance. So, it is a basically extra thickness of that material to be provided in the beginning so that after certain years of operation the minimum thickness will be maintained because that uniform corrosion is taking place.

For example, if the corrosion rate is x mpy; mpy is what? Milli inch; milli inch per year fine and let us say I want to and this is the average corrosion rate and that we expect that for the next 10 years it will maintain that average corrosion rate. So, 10 year or the y year let us say. So, now, the thickness that is to be provided extra thickness would be x y mils or milli inch, fine.

So, that means, and this is the t is basically let us say the thickness to be maintained after y year. So, that means, I have so, that means, this much of thickness would reduce. So, this is to be added on top of it. So, you add it there. So, this is the thickness you are adding it up.

So, that means, after y years of service this much will corrode. So, remaining thickness will be there and after that we cannot use it. If we cannot use beyond that y years because the thickness will go down below the desirable limit.

So, now, we can calculate this value. For example, let us say I have the average corrosion rate let us say it is basically 10 mpy. Now, I want to serve for 10 years and after 10 years the minimum thickness of that component should be let us say 15 milli inch or let us say ok let us say 15 0.15 inch. This is the thickness I want to maintain.

Now, after 10 years, so, that means, how much remaining corrosion allowance I have to give corrosion allowance how much I have to give. So, that means, the initial thickness to start with should be equal to 0.15 plus 10 into 10 divided by 1000 inch. So, it will be 0.15 plus 0.1 inch should be equal to 0.25 inch.

$$initial\ thickness = 0.15 + \left(\frac{10 \times 10}{1000}\right) inch$$

$$initial\ thickness = 0.15 + 0.1\ inch = 0.25 inch$$

So, the initially I have to start with 0.25 inch ok. So, this is the way we calculate the allowance and this is also called remaining corrosion allowance so, this this part. The corrosion allowances could be equal to this much. So, that way one can calculate what should be the initial thickness to start with, but remember we are doing it considering the average corrosion rate for that many years. This average corrosion rate may be different.

For example, 1 year it could be 10, another year it could be; it could be 20 like this some accidental corrosion. So, those thing can happen, but this way you can somewhat have some protection of that particular material, fine and if we consider protection routes protection methods for controlling uniform corrosion.

So, there are several protection methods one can think of: temperature – operating temperature one can reduce and if we increase the temperature the reaction rate increases. So, that is what if we decrease the temperature corrosion rate would be less. One can use coating that is a phenolic coating.

We have a fantastic case study with this phenolic coating we will talk when we talk about galvanic corrosion. So, there could be possibility of cathodic protection, there could be protection possibility of paint, there could be possibility of having better material.

So, these are kind of general practice people follow, but you will see gradually that what all those protection methods well again come back and discuss why this protection method is thought of, ok. So, till then let us stop and we will continue our discussion in subsequent lectures.

Thank you.