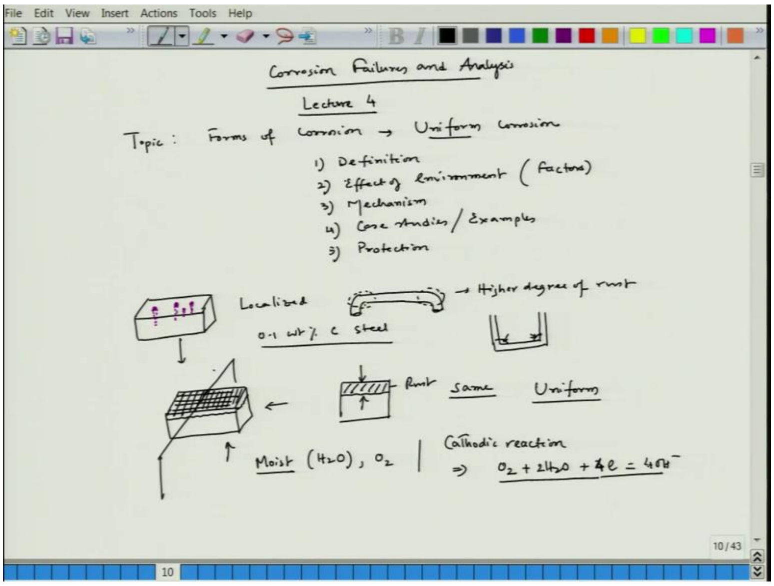
Corrosion Failures and Analysis
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 04
Forms of corrosion: Uniform corrosion (Part 1)

(Refer Slide Time: 00:18)



Corrosion Failures and Analysis

Lecture 4

Topic : Forms of corrosion → Uniform corrosion

1) Definition
2) Effect of Environment (factors)
3) Mechanism
4) Case studies / Examples
5) Protection

Localized

0.1 wt% C steel

→ Higher degree of rust

Rust Same Uniform

Moist (H_2O), O_2

Cathodic reaction

⇒ $O_2 + 2H_2O + 4e = 4OH^-$

Welcome back to the course Corrosion Failures and Analysis. And this is lecture 4 and the topic Forms of corrosion and there today, we will talk about Uniform corrosion.

Now, as I have told you there are 5 segments; first segment is definition, second is effect of environment or I would say factors. Third is mechanism, case studies or examples and fifth is we will talk about protection, fine. Now, if you see the name itself the uniform; for example if you have an object like this, the corrosion can happen like.

This for example, there could be possibility of a small corrosion point, those are forming ok and it can stay on the surface or it can progress through the body, through the body. So, now, in the rest of the parts you do not see much change. But, so that time it is of course, it is basically localized, fine.

Let us say I have a rod like this, fine. See this rod if you leave it in environment, you will see that this portion would have higher degree of rust and remember both I am talking about, let us say 0.1 weight percent carbon steel, ok. Now, both the cases it is localized, so here it is localized here.

So, if you have a kind of a container and if this container the edge is very sharp, you will see that corrosion will be localized here. Now, as the name suggests localized; that means it can never be uniform. So, uniform as the name suggest; for example this example if we take, if we experience corrosion. Let us say the top surface only, the all the surfaces are let us say lacquered or having a plastic coating.

Now, this corrosion the top surface will have almost uniform corrosion if we expose it to the environment ok; it is a flat surface, notch not much of undulation and it is exposed to the environment.

And if you see the cross section wise, you will see that the cross section also you have if you cut through, if you cut it across like this; if you cut it like this, this cross section if you see look from this direction, you will see the cross section would look like. So, this is the last part and the depth is almost all throughout same, ok.

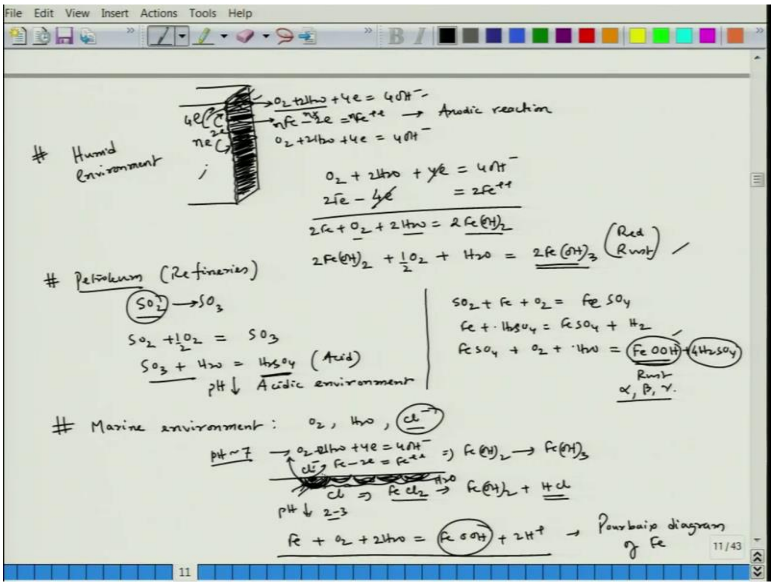
For example if it has gone 0.5 micron. So, it will be more or less 0.5 micron in on an average, ok. So, there is no localized tendency of the corrosion front to get into the material. So, then of course, this is called uniform fine, this is called uniform corrosion. Now, this uniform corrosion let me just show you one example; ok I will come to that example, before that let us talk about how this uniform corrosion can take place.

Now, if we talk about the environment, normal environment which is moist, let us say the Kanpur environment; moist we have now summer time this time onward, this time we have lot of moisture outside, we have oxygen and this is mostly neutral environment. So, the cathodic reaction that can happen is, this cathodic reaction can happen.

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

So, we are not discussing what is cathodic reaction; so cathodic is basically nothing, but wherever electron is accepted that is cathodic and wherever electron is released that is anodic reaction. So, this cathodic reaction can happen over the surface.

(Refer Slide Time: 07:16)



\# Humid environment

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

$nFe - 2e = nFe^{++}$ → Anodic reaction

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

$4e$, ne, $2e$

$O_2 + 2H_2O + \cancel{4e} = 4OH^-$

$2Fe - \cancel{4e} = 2Fe^{++}$

$2Fe + O_2 + 2H_2O = 2Fe(OH)_2$

$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O = 2Fe(OH)_3$ (Red Rust)

\# Petroleum (Refineries)

$SO_2 \rightarrow SO_3$

$SO_2 + \frac{1}{2}O_2 = SO_3$

$SO_3 + H_2O = H_2SO_4$ (Acid)

pH ↓ Acidic environment

$SO_2 + Fe + O_2 = FeSO_4$

$Fe + H_2SO_4 = FeSO_4 + H_2$

$FeSO_4 + O_2 + H_2O = FeOOH + 4H_2SO_4$

Rust

α, β, γ.

\# Marine environment : O_2, H_2O, Cl^-

pH ~ 7

$O_2 + 2H_2O + 4e = 4OH^-$ ⇒ $Fe(OH)_2 \rightarrow Fe(OH)_3$

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

Cl ⇒ $FeCl_2 \xrightarrow{H_2O} Fe(OH)_2 + HCl$

pH ↓ 2-3

$Fe + O_2 + 2H_2O = FeOOH + 2H^+$ → Pourbaix diagram of Fe

So, if you see this surface, let us say cross section wise, let us say this surface is exposed. So, let us say O_2 plus H_2O plus 4e equal to 4OH minus that reaction is taking place and electron is taken here.

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

Now, these 4 electrons need to be supplied to the segment to the segment. Now, that supply would come from the surrounding, where iron would release 2 electron then form F e plus 2 and these 2 electron will go there to the cathodic side. Similarly here also one this reaction can take place and here also another this multiple number of reactions can take place. So, n multiplied by n n.

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

So, now, n number of electrons; so part of it will go there, part of will go there depending on the need of electrons by the cathodic reactions and this is anodic reaction. Now, this portion now is going through a dissolution. Now, if I combine. So, now, we see FeOH whole 2; that can further react with this oxygen and H_2O, it can convert to FeOH whole 3. So, now, here if we balance it, then it will be let us say 2, 2; if I put half, then it is balanced.

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

So, now this is nothing, but the ferric or hydroxide which is rust or red rust, so that red rust forms. Now, question is this particular reaction, since there is no preferential sides over the surface; this cathodic reaction at one point it can happen here, second point it can happen here, third point it can happen here. So, it is basically a kind of the tendency of that particular cathodic reaction could be over the entire surface.

So, if one time one particular place is cathode, the surrounding place would be anode and the second time the surrounding place could be cathode; the portion which was anode cathode earlier that could be anode. So, this rust would form over the entire segment, entire segment I can have rust formation.

So, that time that rust would also progress uniformly in the depth direction. So, this is a kind of situation we would experience. Now, it is a basically a simplistic situation what we have talked about, so where we have moisture, we have oxygen. Now, there could be possibility that there could be presence of SO_2, ok.

Now, for example, in case of industries where we have petroleum product, the handling of petroleum product; there could be possibility of formation of SO_2 and that SO_2 can convert to SO_3, ok. So, that SO_3 conversion would be possible by; if we consider let us say petroleum industries, where we have these are the normal pollutants, ok.

So, there we can this reaction can form SO_3. So, this SO_3 can react with H_2O to form H_2SO_4 and this is now a strong acid.

$$SO_2 + 1/2O_2 = SO_3$$

$$SO_3 + H_2O = H_2SO_4$$

So, the pH would decrease, so it will make acidic environment. Now, we know that if the acidic environment persist, the reaction the anodic reaction can be favored or the metal dissolution can be favored, ok.

So, now, this SO_2 can react with, this H_2SO_4 can react with or this SO_2 can react with iron and can form a $FeSO_4$ or you can write H_2, so this situation can arise. Now, this FeSO4 can then react with oxygen and water and can form plus H_2SO_4, ok. So, this is also possibility. Now, this is also a rust and we will see later that it has different forms alpha, beta, gamma; so these are the forms of Fe FeOOH. Now, when we have these are the, this is basically a rust that is forming and this rust is.

$$SO_2 + Fe + O_2 = FeSO_4$$

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

$$FeSO_4 + O_2 + H_2O = FeOOH + 4H_2SO_4$$

And now, interestingly if you see that H_2SO_4 is forming due to this reaction and after the rust formation the H_2SO_4 is coming back again. So, it is a basically a kind of auto catalytic mode, it will keep on rusting. So, that is what this SO_2 is a very very bad pollutant; because it lead, because it forms acids. For example, SO_2 it can react with H_2 and then form H_2SO_3, ok. So, that is also an acid. So, those are those influence in having accelerated corrosion of iron.

Now, this is one case, where we have presence of SO_2. So, this is also possible in case of, for example, this is in case of where we have refineries, fine; refineries where we have generation of SO_2 or SO_3 and this is the corrosion product, so this is the rust. Now, there could be marine environment. Now, in case of marine environment, we have O 2, H 2 O as well as chlorine ion. Now, here this chloride ion would be a serious culprit.

I am just that giving you the example those reactions; but we will talk about the effect of chlorine ion, when we talk about crevice as well as pitting corrosion. Now, what happens; usually this if this is the surface. Let us say, usually this; this cathodic reaction would take place and here you have small dissolution point, where F e goes to Fe plus 2 and then it can lead to FeOH whole 2 and then finally, it will go to FeOH whole 3.

Now, the interesting part is this chlorine is present in that marine environment; that chlorine will try to come is also there. And this chlorine can lead to a formation of $FeCl_2$ and that can hydrolyze, which will form FeOH whole 2 in the presence of H_2O

and HCl, ok. So, this HCl would form here and because of the formation of HCl, the acidity, the pH drops down in this location.

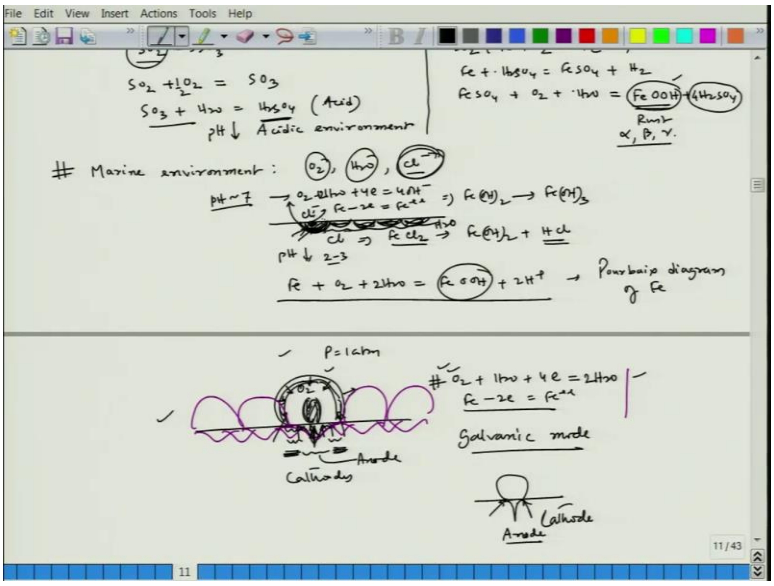
Now, actually the pH to start with, because since this is neutral solution, pH is close to 7; now in that particular corrosion point, the pH goes to even it can go to 2 to 3, so that means it becomes highly acidic. So, the corrosion happens here. So, like that way there would be possibility of corrosion at every location like this and it can lead to an; if you join together, it can go to a uniform mode. If the metal does not have much of dissimilarities in its composition or microstructures.

But this is the example of marine environment, ok. So, there could be another possibility of reaction in presence of O_2, iron plus O_2 plus H_2O; it can also form this particular phase and with 2 hydrogen ion. So, these reactions ok; these reactions these are also part of pourbaix diagram of iron, ok. So, now, this is another product that can happen in the marine environment.

So, initially it starts with this particular corrosion product the way this has been explained. And once that chloride ion is present, the chloride ion will react with Fe and then it will form a $FeCl_2$, it will hydrolyze and then from a FeOH whole 2 and then finally, it will keep on having corrosion in this sections and if this distributes over the entire surface, then you can have an uniform corrosion mode. Now, there could be and this is the effect; for example, here whatever explanation I have given, this is humid environment in humid environment.

So, for example, the Kanpur kind of corrosion can that can happen like this, ok. So, these are the three examples. Now, the mechanism as I have suggested that the mechanism happens like this, the way this happens. But let us consider one a typical example of rain water corrosion or rain droplet corrosion, ok.

(Refer Slide Time: 21:15)



Now, if I see a metal surface which is iron, a small rain water droplet is there. Now, in the beginning, here we have oxygen, dissolve oxygen and this is environment and pressure is 1 atmosphere, fine.

Now, if you see this, in the beginning everywhere you have this reaction taking place

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

Ok as well as this reaction is taking place.

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

Now, after some, since there is no conv, there is no forceful this is a very stagnant droplet. After some time we will see that the oxygen concentration in this regions would be different than the oxygen concentration in this region; why?

Because the oxygen as the oxygen is depleted because of this reaction, cathodic reaction; this oxygen can only go inside the droplet by diffusion process. So that means a diffusion is basically a time dependent process. So, this particular section and if we compare the surrounding periphery section, the periphery section is closed by its contact in contact with the atmosphere where we have lot of oxygen. So, the oxygen concentration would not deplete much in this annular portion, but it will deplete at the center portion.

Now, once the oxygen concentration goes down in the center portion, the center portion will have depletion of oxygen. So, here no more such reaction can take place; but around this section, outer section this reaction will continue. So, then these parts are cathodes now and the center part is anode. So, if the center part is anode, this dissolution reaction happens in the center part and the center part will dissolve like this, ok.

If the center part dissolves like this, the center part will have a little drop, a little a valley, fine. Now, if the rain drops, then after some time the rain drop happens here, raindrop happens here, the rain drop happens here, rain drops happens here. So, like that way, so this particular corrosion process will continue at every portion and then later here also the rain drops can happen and then finally, it will have an kind of uniform corrosion pattern.

And interestingly I have, I am not getting into the in detail of it; you can guess that there is a influence of galvanic mode. And this is my experience that, whenever we talk about uniform corrosion; it is actually happening due to a galvanic mode, some part is becoming cathode and some part is becoming anode. And after some time if that particular; for example, if the rain drop stays here only, you will see there will be a pit formation at the center of the droplet, around that you do not have anything.

For example, you can do that experience that, that particular experiment; you put a small water droplet and keep on once it dries, keep that put that particular droplet again on that particular same place, you will see that you can have a localized mode of corrosion rather than uniform mode of corrosion.

So, this happens because this section will act as cathode; because this reaction happens preferentially at the annular portion, but central portion it is preferentially anode. So, that time it becomes localized.

But if it happens like this, then all the localized modes are connecting together and will giving you a kind of appearance of uniform corrosion, fine. So, now, so these are the kind of examples, these are kind of effect of different environments. I am talking about three environments one is petroleum or refinery, marine environment, another one is we have a situation of a normal atmospheric corrosion, where a kind of a situation what is exist in Kanpur region or something, where it is a normal no such SO_2 or no such chlorine ion effect is there, fine.

So, now, if we see carefully, we can check out the protection right itself, right now. As you see the culprits of, culprits are nothing, but oxygen SO, H_2SO_4, H_2O, chlorine ion, SO_2; if we get rid of them, definitely you do not have the severity.

But just to take this particular part, that means we have talked about only definition and the effect of different environments. Let us take it to the next class, where we talk about some of the industrial experience as well as examples of uniform corrosion and protection routes or protection methods. Before I end, I would like to show you uniform corrosion what we experience.

(Refer Slide Time: 27:09)

For example, this is a dog bone like of, it is a kind of tensile samples, ok. So, this tensile sample if you see the top part; this was polished, this was actually machined and then kept it in my, I have kept it in my home ok, inside the house and this is lying there for almost 3 months. And if you see the top part and the center part also it is started corroding and the corrosion is more or less everywhere and this is a typical example of uniform corrosion, ok.

(Refer Slide Time: 27:46)

Now, another example let me show you; this is a very old knife, household knife, ok. And this is not used anymore, it is left in the drawer, I just took it out today. And if you see this this surface, this these surfaces; these surfaces you will see that everywhere you have rust ok.

And it is a kind of black rust; it is not kind of a red kind of thing, but the black rust, this is also rust let me tell you, you have to believe me that there are also some red patches also, it is not clear right now, but you can see that there are red rust, ok. So, this rusting is not localized, it has formed everywhere. So, this is also a typical example of uniform corrosion.

So, just I wanted to give you some household examples, ok. In household most of the corrosions are uniform ok, so that let me just explain to you. But another thing I would like you to remember or understand that whenever we talk about uniform corrosions, remember there will be a sense of galvanic effect ok and we will try to connect this both as we continue our discussion. So, till then let us stop our lecture today, ok.

Thank you.