Aqueous Corrosion and its Control Prof. V. S. Raja Department of Metallurgical Engineering and Materials Science Indian Institute of Technology, Bombay

Lecture – 10 Forms of corrosion: Uniform v/s localised corrosion

This is the 10th lecture in the series of this course MM 713 on Aqueous Corrosion and it is Control. In the beginning, we said that we will have this course divided into 2 half. The first half corresponds to the thermodynamics and kinetics of electrochemical corrosion. The second half corresponding to various forms of corrosion which are prevalent in the industries actually. You may call it as a form of corrosion or you may called it as a mechanism of corrosion in broad sense.

Now, this is a very practical relevance and importance for controlling corrosion, for developing new materials or to developing some design aspect of it. From all aspect of it you need to understand the corrosion as it occurs in the industry in various components. So, broadly if you look at the Fontana book it says about 8 forms of corrosion, but you go along you will see that, that is not there no sanctity here.

You can have we can call as 9 forms 10 forms or even more. Because you notice that the way you will control corrosion could be different may not be classified as 8 different ways. It can be classified as more than even 9 10 as you see. So, the 8 forms of corrosion we still follow, but you should have a open mind to say that it is not in strict sense there are 8 forms of corrosion. Before we get into the 8 forms of corrosion you need to broadly understand how the corrosion would occur in reality.

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So, corrosion in reality suppose I expose a metal to the environment and you have you know some environment is exposed to this. Suppose there is an environment here the corrosion occurs. What is the corrosion here? You will have a anodic reaction and you will have a cathodic reaction.

Of course, the rate of anodic reaction must be equal to rate of cathodic reaction that I think we all well aware of it. Suppose assume that this is a metal and corrodes as let us say M^{n+} plus n electrons and there has to be a cathodic reaction. I generalize this cathodic reaction as some species. They accept these electrons and they get this here and you call this is a anodic and you call this as cathodic.

We give some illustrations of what are the possible cathodic reactions at later stage. Right now it is sufficient to discuss that a corrosion reaction involves anodic reaction where electrons are released and a cathodic reaction where the electrons are accepted. Now, look at this sample here from this point of view. You can have assume that the metal is very pure assume that it is the best pure metal let us say best possible pure metal and assume that it is single crystal for some reason just assume that it is a single crystal you know ok.

So what will happen now? You will have a anodic reaction occurring on the surface, cathodic reaction occurring on the same surface it will occur very randomly right. Instantaneously, you might find in other place can behave as anode a place can behave as a cathode here.

Now, if this anode and the cathode the locations are fixed what happens? The corrosion becomes quite nonuniform ok. The corrosion becomes more at the anodic side. The cathodic side the corrosion is not going to occur and you call that as what? You call it as localized corrosion.

So, localized corrosion if you look at; if you look at the nature of the place like A and C and you now if I look at this and this is going to be the cathode, this is going to be the anode here and with respect to time they almost remain as a cathode they remain as an anode here. They are not going to change with respect to time at all and that is what you call as a localized corrosion right. So, you will have dissolution occurring around this anode and no dissolution occurring around the cathode here. Visualize that the anode and the cathode assume that the location A I also called this location A.

Suppose I look I call a location 1 location 2 I just re-designate that as location 1 or location 2 and assume that location 1 it goes like this. This is time, this is the nature. So, this is the cathode and this side becomes anode here. But sometimes it remains as a cathode it becomes an anode becomes a cathode and cathode and this form of corrosion we call them as uniform corrosion.

So, in uniform corrosion each location can act as a cathode and anode and they vary with respect to time. So you lead to a reasonably I would say uniform corrosion all through the surface. So, broadly then I would like to classify corrosion as 2 types. Those where occurring in a uniform manner all throughout the surface and those where the anode and cathode are fixed with respect to time.

They do not really change with respect to time. So, they are called a localized corrosion. So, these are the 2 broad categories of corrosion that you must be having. This is very important. The way you prevent corrosion depends upon what do you understand more detail about what is localized corrosion. Of course, the uniform corrosion is fairly simple not that complicated.

Now, you will ask the question why is that in one case the anode and the cathode sides are fixed they are not changing? What are the factors responsible for the location on the steel surface or some metal surface where the anode becomes you know stable with the time the cathode become stable with respect to time? Let us given an example here and see why

you get into anode and cathodic side. Let us take a practical example an engineering example where you use bimetallics.

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You use bimetallics sometimes let us say you may use let us say steel. So, you may use let us say the stainless steel we may use what happens in this case. In this case, the steel become permanently anode the stainless will become permanently cathode here. This is one type of localized corrosion and we call them as bimetallic corrosion we also call or you can called as galvanic corrosions. Please notice here the anode and cathode are my macroscopic. They are quite macroscopic they are not microscopic right.

So, here the anode and cathode are macroscopic in natures right is easily identifiable I can identify this. I give another example where you have a passive metal generally that can lead to what is called as pitting or called pitting corrosion. An example stainless steel in chloride medium. What is the characteristic of a stainless steel? Generally it is passivate right.

So, that is a passive film on the surface and it is possible that at some place the film damage occurs film damage occurs. When the film damage occurs what happens. This becomes now an anode this case right. The surrounding area becomes what the surrounding area becomes the cathode here.

So, they become the cathode. So, anode will continue to remain as the anode and the cathode will remain as cathode with respect to time and this leads to one type of localized corrosion which is called as pitting corrosion.

Please look at this is microscopic is microscopic in nature at least to start with you know it may become macroscopic with time as the pit grows. You can able to see with the magnifying glass sometime you can see with the naked eyes and this is the other form of what is called as microscopic form of corrosion which is called as pitting corrosion.

We can have the other type of microscopic corrosion. We know that most metals in engineering applications. We do not use single crystal, do you? What kind of material that you use the single crystal.

Student: We may use.

You use normally polycrystalline metals right. We use a polycrystalline metal. So, what is the difference between a single crystal and a polycrystal.

Student: Grain boundaries.

Grain boundaries. So, generally you will have in the metals polycrystalline metal that you use ok.

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Doby crystalline metals COFEE Grain boundary has high energy Anode Grain a cathode MM 713 L 10 / SH43 rganular corrosion Microscopic form of localised Corrosion

You will have grains and so you have grain boundaries. You have it in polycrystalline materials metals and alloys you have this. What is the difference between a grain boundary and the grain generally? What do you think?

Student: Periodicity(Refer Time: 15:58).

So, you have a in within the grain they are quite periodic you know and within the grain and in the grain boundaries they are random. They are strained because the orientation of the atoms in one grain is different from the orientation of atoms in the other grains at the interface it tries to optimize try to adjust itself. So, it is strained. So, the energy of the grain boundaries what happened?

Student: (Refer Time: 16:27).

So, grain boundary has high energy. Am I right has high energy. So, when you have high energy what happens that becomes now anode and the grain becomes cathode and you call this corrosion as intergranular corrosions; that means, it is more complex than what I have depicted here we will see this again in details ok.

Now, look at this the anode and cathode are fixed with respect to time grain boundaries will continue to dissolve with the time and the grains will remain as a cathode with respect to time. So, you have the other form of localised corrosion.

Again please notice it is again a microscopic form of corrosion. So, again it is microscopic form of localised corrosion. Now, we will see the other form of corrosion which is a localised, but a relatively a macroscopic form of corrosion a macroscopic form of corrosion right.

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Metals are are joined Riveting MM 713 L 10 / Slide 4 air-line gap (Environment different from Out Side Crevice Crevice corrosion Macroscopic

Let us look at a situation where the metals are joined. One of the easy ways of joining metals is what by?

Student: Riveting process.

By riveting process right. So, you do riveting ok. What you do in this case? Take one piece you take another and use a rivet to secure that. Now, you see here what you get is a there is an air line gap and the environment inside this is different from that on the outside. When I say outside means outside the this gap here and you call this as and this place is called as the crevice. This is also called as; this also called as crevice and so it leads to one form of corrosion called as crevice corrosion.

Please look at this is macroscopic. Is it important in industry? They are not important. Metals are joined like that they are joined with rivets maybe joined like flange joints corrosion in the flanges in the rivet could be different.

So, you need to understand the mechanism. We need to find if you know the mechanism you can also find a remedy of measures ok. You can also try to know how to improve a point further ok. So, we will look at the mechanism of what is called as the crevice corrosion. This is another form of localised corrosion ok.

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qu-m. (Brans). 1.11.1 713 L 10 / Slide 5 m-> Preferentially dissolves Selective Leaching Atomic Level Flow condition of an Environment Turbulence. _____ Erosion Cavitation Damage

Now, let me just go into the other form of corrosion. We use alloys. An obvious example of alloy you know that is copper zinc. What do you call this alloy?

Student: Brass.

The brass right. In this alloy, you see that copper is noble and zinc is relatively active. So, what will happen now? The dissolution behavior of zinc would be different from the dissolution behavior of copper. So, you have yet another form of localized corrosion right. This happens at what? This happens at the atomic level.

They do not happen at the microscopic level. They happen at the atomic level in air. For example, if you take an alpha brass, it consist let us say somewhere between you know 15 to 35 weight percent of zinc quite homogeneous right. You really do not have too much of micro cycle features except the grain boundaries. A corrosion occurs.

What will happen in this case? In this case, zinc preferentially dissolves and you call this as selective leaching and it occurs at the atomic level. You need to find a solution otherwise you cannot use brass, you cannot use these kind of brasses in seawater application for example, you cannot use them. So, we need to understand the mechanism.

What is happening there? How do I improve upon the selective leaching or selective dissolution of zinc in the bass? If you remove zinc from of the brass, what happens? It becomes quite porous the strength becomes so weak. So, structure cannot be holding the

pressure right stress levels you cannot do that because this is a other form of localised corrosion occurring at the atomic levels.

So, we have talked generally about problems related to the alloy you know. There is a grain boundaries passive film damage or a selective leaching we talked about intergranular corrosion talked about, we talked about what happened in the rivet and all. There can be a situation where the environment can cause a special kind of localized attack under the flow conditions environment ok.

It can cause a lot of turbulence right. So, when cause lot of turbulence what happens. What happens when you have turbulence? It impacts the metal surface. When impacted what happen there is a metal loss. So, there is a mechanical damage plus the corrosion process localised places and you call this as.

It is a very interesting form of corrosion right. It depends upon the design, it depends on the environment all this, it depends on the geometry of the system. It goes for example, is it a circular you know cross section or is it rectangular cross section through which the electrolyte is moving. There is other form of corrosion.

This is also other form of corrosions which is called as other localize corrosions. A variation of that we also have a cavitation damage, but these are all macroscopic. The material is not a problem not really fault I would say more often. The fault we cannot say fault it is a requirement. You know you need to have high velocity in the pipeline that is not a fault like that this ok.

So, how do you really handle the corrosion problems in that cases this is different? So, you have flow induced corrosion. We call it carbonation damage, we will call it erosion corrosion we call it. There are several names given to given to that we will try to understand this in detail and so that we can find a solution to the particular problem. Now, I can have a variation of what are all we have seen.



Suppose I have a sample, I have a structure maybe and that I apply a stress and it is exposed to the environment applied stress applied stress. This stress can be tensile and you can have a tensile stress and it can be static with respect to time and you call this leads to a failure called as stress corrosion cracking very prevalent industries. I can have a stress which can be alternating stress. It can be; it can be tensile, it can be competitive, it can happen like this or it can be tensile tensile and such kind of problems leads to corrosion fatigue.

In stress corrosion cracking again that can be sub classifications. You may call hydrogen induced cracking you may call it. Even when you have a fatigue, you can have hydrogen involved in the process mechanisms they become complicated and the solution to that problem is different from a normal stress corrosion cracking. That is why I said you can have several mechanisms and depending upon situations and the solution for these problems are not exactly the same.

So, to summarize I would say you can broadly say that corrosion occurs in the 2 manner. A uniform corrosion, other is a localised corrosion. The difference between these 2 can be broadly again said as the uniform corrosion the anode and the cathode locations. They keep alternating with respect to the time and so the corrosion becomes uniform.

In the localised corrosion, the anode and cathode they become rigid with respect to time and so there is going to be localized attack. Attack can be simply a dissolution process. It can be assisted by a mechanical means such as erosion, cavitation or it can be assisted by a tensile stress or fatigue stress can lead to cracking. So, the localised forms of corrosion are even more dangerous as compared to what is called as the uniform corrosion. So, these are broadly the classifications of that. So, far have any of you any kind of questions.

Student: What sort of scenario besides that a metal or a part of metal will act as cathode or anode and how do we determine the scenarios?

See it is a interesting question. To make a metal as anode and to make a metal as a cathode it requires a specific properties you know. Momentarily, at that particular location the energy has to go up right then that location becomes an anode and the remaining places becomes a cathode.

Assume that I have let us say aluminum and it is 99.9999 some 6 9s purity. There is no alloying elements. So, energy of aluminum all the aluminum atoms are same. I do not think there is much of difference unless you associated with dislocation or vacancies all kinds of stuffs actually ok.

So in the absence of that every atom in the lattice would have similar energies. So, you have equal probability of acting as a cathode and as well as an anode here. Momentarily, these atoms can become anode because after all what. After all, you see electron wave you know the energies are not going to be same all the time you know.

There can be lattice vibrations can happen or momentarily the oxygen atom can go to the surface can lead to that. So, the various reasons you can render the particular place as an anode and then cause dissolution. Of course, you dissolve a metal, you release electrons the electrons have to be accepted by some other species other places you get an cathode.

So, all this variation that occur on the metal surface are mostly statistical or probabilistic issues. They are not really atomic issues. When I say atomic or deterministic means they have a character. The character of these metal all through is similar. Momentarily stochastically they are changing and so they become anode and cathode with respect to time. You get a uniform corrosion taking place.

On the other hand you can have a composition variation right. Suppose you take a steel. What a steel consist of any of you? Typically, we see in the microscope.

Student: (Refer Time: 33:54).

What do you see?

Student: (Refer Time: 33:57)

You get you get up for right matrix and you may get a cementite a cementite of course, located in the pearlite right. So, your 2 phases you have ferrite phase and cementite phase. Cementite phase is what is rich in carbon and the ferrite is very lean in the carbon content chemically they are different.

So, you have one making an anode other becomes a cathode. So, there can be composition variation that can make the alloy locally anodic and cathodic can happen. It can happen in many of the alloy systems because in fact, the metallurgists we develop alloys with different phases that is why it gives you strength aluminum alloy is.

Another example you increase the strength of aluminum alloys because of what. Because by adding the elements like copper, zinc, magnesium and do heat treatment and get the strength but these precipitates are chemically heterogeneous. So, you can also have that is more deterministic that is not a time bound process.

So, you can have corrosion taking place along the precipitates. So, if you have to have a uniform corrosion the one of the general criteria would be that you will have mostly a homogeneous alloy systems or even you may have heterogeneous alloy system they are not too much biased as anode and cathode. They may be only marginally they are going to different. So, it can able to vacillate with respect to time actually.

So, in even in normal steels you know you will see generally you get uniform corrosion the ferrite and cementite are not going to cause so much of it atmospheric corrosion, but you go to laboratory and then you are going use the etchant like picral or whatever you are going to use it. You can nicely reveal ferrite you can reveal cementite because that etchant is a chemical etchants. It just etches out separately. That is essentially what is that it is a localized corrosion then only you can able to see phases.

So, localised corrosion would depend upon differential you know a tendency to corrode can happen because of various reasons that we have been seeing all along like this only. So, generally pure metals are more prone to uniform corrosion than pitting all kind of stuff. But, then you can have a crevice corrosion nothing to do it with the metal. I can have a purely austenitic stainless steel I can get a crevice corrosion why because it forms crevice externally it is forming there. So, you need to understand from the context in which these forms of corrosion are occurring.

So, we will discuss also in detail what are the mechanisms governing mechanism for various localized forms of corrosion. Coming back to the point here actually if it is a very uniform metal and if the alloys generally not cold worked grain boundaries are not too much any difference you will see a uniform corrosion.

In fact, I used to tell people if you take a very high pure aluminum of 99.99 5 9s purity they call it and then you ask to etch it you will not get the grain boundaries revealed at all ok. But, on the other hand, you are going to have a small amount of copper you etch it and grain boundaries are very much revealed actually.

So, the purity of element is very important in seeing whether there is a uniform corrosion and localized corrosion at all. I hope I have answered the questions actually. Any anybody else have any questions? Ok. So, there are no further questions let us move on to understanding the various forms of corrosion ok. What are the various forms of corrosion? First let us discuss the so called uniform corrosion.



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You have just now seen in a uniform corrosion one of the most important criteria is uniform corrosion is that the say anode, the cathode, they shift with respect to the time actually here. In the semantic manner I did not draw a nice sinusoidal curve ok. In a semantic manner, you will have the location anode and cathode can takes place. There are several examples. One is if you look at the rooftop of steel sheets the this steel sheets you will see around actually the uniform corrosion.

Most of the atmospheric corrosion of steel structures you will see them as uniform corrosion. So, you can say generally atmospheric corrosion steel see that. It could be even the steel, it could be in hydrochloric acid, it can happen in I am sorry steel in sulfuric acid, steel in hydrochloric acid, steel in phosphoric acid.

Even in water generally they undergo a uniform corrosion ok. In all these cases you will get you might have seen pipelines around you know steel bars lying in the open atmosphere when it rains. They are all practically uniform corrosion.

Some confusion however arises you know I have seen when you interact with the industries they say they look like pitting. What do you mean by that is look at the surface? The surface is not atomistically uniform. When you say uniform please do not mistake that it is going to be very smooth. You may have a rough surface you know. If you touch it you will see the roughness that is not considered to be pitting.

When you talk about a pitting we will discuss in detail what it is may be pitting, when do you call it is a pitting all we can talk about. Shear roughness shear within quotes nonuniform corrosion is not considered as a pitting corrosion. No, it is not considered as a pitting corrosion.

So, that you know you should able to make the distinction between what a pit is, what a rough uneven corrosion is not considered as a pitting corrosion. Now, when you talk about uniform corrosion we seen what it is then we have to look at the what are the factors that control uniform corrosion.

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Factors controlling Uniform corrosion (i) Nature of the environment (ii) Temperature IIT Rombay Nature Nature of Anodic & Cattodic reactions

First and foremost is the nature of the environment ok. This is one factor that you can say. The second is the temperatures. The third is the is a the external variables like velocity. Of course, it also depends upon the alloy nature ok.

So, let us look at one after another how they affect the uniform corrosion of a metal. Let us take the nature of environment. First and foremost I would give pH as important variation. Actually even before that I think it is better to talk about what are the type of anodic reactions and the cathodic reactions involved in the metallic corrosion.

So, let us first get into the nature of anodic and cathodic reactions. May be it is coming covering there only. Let us look at it. Suppose I have a metal.

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Nature of reactions
Anodic

$$M \longrightarrow M^{M+1} + ne (a nodic)$$

 $Cathodic
 $H^{+} + e \longrightarrow L^{+} + 2$
 $O_2 + 4H^{+} + 4e \longrightarrow 2H_2O(Acidic) - (2)$
 $O_2 + 2H_2O + 4e \longrightarrow 4OH^{-}(meutral or - (3))$
 $D_2 + 2H_2O + 4e \longrightarrow 0H^{-} + L + 2 (water)$
 $H_{20} + e \longrightarrow 0H^{-} + L + 2 (water)$
 $H_{20} + e \longrightarrow 0H^{-} + L + 2 (water)$
 $M^{2+} + e \longrightarrow M^{2-} + Oxidant) = (5)$
 $M^{+} + e \longrightarrow M^{-} + Oxidant) = (5)$$

So, let us look at the nature of reactions then only you will able to appreciate all this nature of reactions. Let us take an anodic reaction. I generalize as

$$M \rightarrow M^{n+} + ne$$

this is anodic reaction. Let us look what are the cathodic reactions possible. Cathodic reactions are say 1.

The simple hydrogen ion production process and giving rise to hydrogens molecule.

$$H^+ + e \to \frac{1}{2}H_2$$

It can be oxygen in acidic conditions can react with H plus and electrons give rise to possible. This is the acidic conditions right.

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O$$

You can number this cathodic reaction as 1 as 2. You can also have the oxygen here in a neutral medium. It can combine with this electron you can form it is neutral or alkaline. You look at in both cases it can happen.

$$O_2 + 4H^+ + 4e \rightarrow 40H^-$$

You can also have simple water accepting the electron simple. This is called water reduction 4 right.

$$H_2O + e \rightarrow OH^- + \frac{1}{2}H_2$$

You can have like any kind of you know oxidant for a, you know you can have let us say M x plus can combined with some electrons can become M x minus 1 plus can happen actually ok.

$$M^{x+} + e \rightarrow M^{(x-1)+}$$

This can be some oxidant. Can you give an example for this you guys have seen already?

Students: Ferric ions.

Ferric ion right, the ferric ions converted into ferrous ions. You can also have one more. Let us say a metal ion can combine with this electron can give rise to metal.

$$M^+ + e \rightarrow M$$

See this is noble metal. I think this is a important slide for you ok. Why it is important? Suppose you go to industry and you are given and one guy says sulfuric acid is present. We are storing sulfuric acid in a tank. So, it is corroding. If you look at these equations what do you think are relevant here in this.

Look at these equation right look at these equations. Tell me corrosion of stainless steels in a sulfuric acid tank we saw these reactions are relevant here. Of course, forget about the anodic reaction that is going to happen. Let us look at the cathodic reactions. What all the reactions which are relevant? Tell me.

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Student: (Refer Time: 49:43)
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First is relevant.

Student: Second.

The second may be relevant then is the third relevant is relevant a third one?

Student: I am (Refer Time: 49:59).

I want answer ok. Is the fourth relevant fifth relevant? We do not know 6 relevant we do not know. Now, let us look at one after another. First is little obvious sometimes can be less obvious. If I am going to use 99.9 weight percent sulfuric acid you might find that the first reactions sulfuric will not be there we will see later because sulfuric acid cannot dissociate into H^+ plus sulphate ions $(SO_4)^{2-}$ if even it is a highly concentrated for I mean do not worry about it ok.

Let us assume it is a dilute sulfuric acid do not worry about that concentrated sulfuric acid. So, first question you are going to ask is that what is the concentration of the sulfuric acid. Is it concentrated dilute? Assume or it is dilute. Now, there is equation number 1 is relevant 2 is relevant the 3rd is certainly not relevant.

Now, the 2 is relevant or not you have to check. Is the tank is deaerated is it open to atmosphere. You have to ask these questions you know all industry guys I mean how (Refer Time: 51:15) the tank is not going to talk to you right nor the environment is going to talk to you now you need to apply your mind and see what happens.

So, we need to look at now we need to just look at it. Now, of course, we can see that system is closed system no aeration, but for sure then what happens. You may use a DO meter dissolved oxygen meter to say that there is a oxygen content present here. The question number the one 5 depends upon how does the iron dissolve.

If iron is dissolved and become ferric ions becomes relevant for you; that means, you have to analyze the content of sulfuric acid. The sulfuric acid does not have ferric ions and again I have to rule out the 5 is not going to be there ok. And the noble metal very unlikely to happen unless you have some system carried away with copper ions.

So, an analysis of possible corrosion processes are very important in order to diagnose industrial problems ok. So, you need to have a broad idea, what is likely to happen at all in this case ok. So, this is these are very very important for this. Now, I ask the question to you I have has a question to you. I have a carbon steel and I have a stainless steel. 2 scenario I am giving to you a carbon steel and a stainless steel I am giving to you. Now, you start analyzing the problem which is beneficial which is detrimental what happens.

Suppose a situation where the tank is open to atmosphere where the tank is closed no oxygen content present here. One case stainless steel second metal is steel now. You apply

this principle here you tell me what do you happen what will happen here in this cases. Let us take steel now. Steel the equation 1 is a problem. What are the equation 2 is a problem or not problem. Is a problem no problem?

Students: (Refer Time: 53:31).

Problem of course the 5th is also can be a problem if it is a aerated open. You take a stainless steel what happens number 1?

Student: (Refer Time: 53:45).

I want tell please tell me is a problem or not a problem.

Student: Problem.

It is a problem. What are what is number 2? Maybe problem. Why is that maybe is it going to decide based on who is going to examine the problem or what? Tell me number 2 is it a problem or a no problem. You must have the answer now because you studied already the fundamentals in the first course I mean first start of this course right thermodynamics and kinetics you seen.

You apply this now you tell me the 2 is it a problem for stainless steel or not a problem for stainless steel. Come on I want to have a answer from you ok.

I give answer for you. You defend you I want I hope you will defend me ok. I give the answer for you I say the 2 is not a problem. I say the 2 is better. Can you defend me actually?

Student: Passivity (Refer Time: 54:59).

Passivity right. So, because the oxygen present in the stainless steel tank will passivate. The same oxygen present in the carbon steel tank will be harmful to you actually the value see it is ok. So, you need to be trying to understand this.

Now, what are the things how you know it is very I mean unless you get a comprehensive idea you cannot analyze the industrial problems. But it is very simple you just apply the principles ok. However, complexities they start unravelling one after another, but you need to go in this direction. So, these are all very important equations ok.

So, this is how I want you to learn. This is what I want you to understand these equation from the thermodynamics and a kinetics point of view. So I want you to get clarity in how you approach the problems actually ok. Now, let us get into this and see how we can give solution to the people ok. Now, let me just give one example of let us take the; let us take the equation 1 ok. The equation 1 H plus is related to pH obviously right. So, let us look at the pH.

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Now, the pH affect: If the pH is increased, what will happen to corrosion rate? What do you expect to happen? Of let us say steel in water ok. What do you think will happen? Yeah.

Student: pH is increased (Refer Time: 56:44).

When the pH is increased what will happen to corrosion rate

Student: Decreasing.

Decreasing. Please and you have to be firm and clear about it. Why is when the pH is increasing the corrosion drops? Because H plus ions concentration is decreasing. So, the corrosion rate will increase. So, there are certain things actually ok.

People have also had some equation you know some trend people have found and this is the corrosion rate versus the pH. pH is going this way is increasing reverse way actually and something like it goes actually is a trend actually and see very interesting it increases and remains stable and then you find very very high corrosion rate and the pH is going to be down actually here.

Now, you know the boiler right I am going to now give an example and you are going to give me a solution to the particular problem ok. Let us take the case of boiler corrosion fine. It does not matter I think you guys know about boilers. What for people use boilers anybody? Any idea?

(Refer Slide Time: 58:00)

Boiler Corroston Steam is generated Pure water is used. 1111 713 L JO / Slide 1 Water -> 250 - 280°C Steels, Cr- Mo Steels basics in water treatment PH Oz

Student: Steam generation.

Steam generation right. Steam is used for many purposes. One of the purposes is to generate electricity. The second is also for heating the systems. In a chemical process, industries use steam to heat the reactors you cannot go and use electrical heaters now all ok.

They use steam to raise the temperature of a reaction processes. So, steam is used for 2 purposes. One is you know a generating the electricity in a steam turbine, other is to heat the chemical processes involved actually. Now, let us get into that.

Now, you please go back to these equation and idea is to heat the steam. You are going to generate steam. Steam is generated. For simplicity, I will say they use pure water. Pure water is used because you do not want to form a scale and all people use pure water. Now,

what is the temperature of the boiler actually generally? Anybody has a temperature any idea about it? What is normal temperature of?

Student: First around... (Refer Time: 59:22).

About normally the water is heated about 250 to 300 degree Celsius. So, you create this thing water is heated in the temperature range of let us say 250 to 280 something like that. The heat flows there to you know to increase the efficiency of the turbine that is not the point. The water is heated within 250 to 280 degree Celsius depending upon the pressure of the boilers.

What material do you think you can use. Anybody? Material of construction, stainless steels. You think nickel base alloys titanium alloys?

Student: Stainless steel.

Stainless steels.

Student: (Refer Time: 60:13).

Somebody saying no you tell me what material you know it. No, they use steels ok. They use steels at base they use chrome-moly steels. You know why they use chrome-moly steels. The chromium and molybdenum is not meant for corrosion resistant they are meant for creep resistance. Please make it very clear. The chromium and moly present in this one generally are not meant for corrosion resistance.

Now, if you look at look around steel just expose to atmospheric condition water corroding heavily right. At that temperature 250 degrees Celsius 280 degree Celsius water. The boilers are supposed to not corroding in fact boilers life is only about 30 plus 25 plus years ok. Some of the power plants they like to run it for 40 years. So, 40 years you are supposed to use the tube not undergoing corrosion at all or minimal corrosion undergoing.

How is that possible? The steel at that temperature not undergoing corrosion. How is it possible? Whereas, the water you see around you know exposed to this you get red rust you see here right flash rust moment rain comes within about few hours you see a flash rust coming right. So, how is it possible here ok? How is that possible? You please take

your notes and have a look at it and tell me how is it possible. So, this is your notes right. Tell me how is it possible that the boiler can be made resistant to corrosion.

Student: (Refer Time: 62:20).

Good. So, you know what are the; what are the cathodic reaction you know what are the anodic reaction. You cannot do much about anodic reaction maybe you can do bit will come back to this later. First look at the cathodic reaction here.

First of all you get rid off you said deaeration why? Because the oxygen is one thing this is causing problem. So, first thing they do is they do deaeration. The oxygen content is kept well below 1 ppb, 2 ppb, 6 ppb line up things you know ok the oxygen content is removed totally.

But, there are different type of boilers they keep oxygen content about 50 ppbs. Let us not worry about it, but we can say that oxygen is removed completely then what happens. You cannot obviously keep the H^+ it is oxygen's enemy number 1. So, how do you; how do you reduce this H^+ ? What do you do for that?

Students: Increase the pH.

Increase the pH. So, you make the pH and slightly alkaline this is going to have you are going to be something like situation 3. But, remove this oxygen from here then what happens now the corrosion rate of in the steel significantly get reduced how do you remove oxygen and all.

let us not discuss right now that is a boiler is separate subject together. But this is how the principle is. The principle is remove the species responsible for cathodic reactions stage 1. So, make the pH alkaline, remove the oxygen content and so the corrosion rate of the boiler stops on the cathodic side. And the anionic side what you can do you can make the metal now passive right.

Now, you have seen the pourbaix diagram before right. What pourbaix diagram is? It is a potential pH diagram. If the pH is slightly alkaline, the metal can form passive films. So, you form the passive films remove these things. So, what happens? This steel can last for 25-30 years at that temperature with the water no corrosion problems at all actually.

So, the basics can be applied in order to minimize the corrosion in the field actually and it is a common practice. You go to any industry any thermal power plant the utility is a very important thing. The water treatment is a separate department all together ok.

They look at the dissolved oxygen content. They monitor the H plus content actually means pH is the monitor rate and then so the corrosion rate is now dropped. Of course, the metal in that case forms a nice magnetic oxide which means a passive oxides that also promotes the corrosion resistance of the boiler steel tubes.

So, that is why basics the fundamentals are very very essential in order to solve the corrosion problems. We go to industry there are so many variations that happens. You in fact, you will not see same problem faced by other industries because after all we have human nature there are so many variations are happening, but the basics the fundamentals are similar all through you can able to find a solution to the problem ok. Do you understood this one actually? Can I move further?

So, when it comes to boiler this things you say that this is so that means, the basics here involved the basics are basics involved in water treatment, pH is increased then what happens. You also oxygen is oxygen level is reduced and both of them leads to passivation and also leads to low cathodic reaction.

Now, it is also important to understand corrosion in entirety. It is very very difficult to know what all the different environments present in industry. There are millions of different environments. See it is very difficult for you to make a tabulation of that actually, but you should be able to analyze the problem you have to able to address the problem ok. I will get into the other kind of environment how the corrosion can change.

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Look at the case of say corrosion of steel in NaCl solution. So, if you take a steel and if I measure the corrosion rate of the steel with the addition of corrosion rate versus if I plot what do you think will happen to corrosion rate. Assume that let us say sea water right you let say take a sea water ok. Now, I want to determine the corrosion rate of this steel in with a different amount of sodium chloride solution. What do you think will happen to corrosion rate?

We keep adding this. We all know that seawater is very highly corrosive right. So, what do you think will happen? It will keep increasing right. So, you say when you add sodium chloride more and more the corrosion rate would increase. It is not the case ok. Look at the corrosion rate of that.

You see the corrosion rate like this. How do you analyze this problem? You will able to analyze the problem only we understand what is the anodic reaction and what is the cathodic reaction right. What is the anodic reaction of let us say steel in sodium chloride solution? Come on what is the anodic reaction here steel.

Student: If it is (Refer Time: 69:27) steel.

Steel.

Student: Fe²⁺ (Refer Time: 69:29) sodium chloride.

Fe will go into Fe²⁺ fantastic.

$$Fe \rightarrow Fe^{2+} + 2e$$

What is the cathodic reaction here?

Student: Hydrogen evolution (Refer Time: 69:43).

Why hydrogen evolution coming here?

Student: (Refer Time: 69:46) sodium chloride (Refer Time: 69:47).

Chloride you think this will happen? You think this Cl⁻ plus electron becomes Cl²⁻ will it happen?

$$Cl^- + e \rightarrow Cl^{2-}$$

No, do you think that this will happen. What will happen? Sodium chloride does not actively participate in the cathodic reaction actively; does not really at all wherein you must understand that ok. Neither sodium can take nor chloride can take. So, would not occur. So what is the cathodic reaction here?

Student: (Refer Time: 70:35).

So, you forget. So this is the oxygen reaction this is what happens. This is oxygen reaction, reduction reaction with water minus ok.

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

So, this occurs. Now, you must be able to understand this clearly. If there is no; if there is no chloride in the medium only pure water neutral water exposed to air iron will corrode and combined with hydroxide and form what will happen. It will forms ferrous hydroxide right ferrous hydroxide formed on the surface will form reasonably protective I do not say excellent.

So, the corrosion rate of steel in neutral water is less because it can form a loosely protective iron hydroxide ok. That is what will happen these two will happen. What does the chloride do? The chlorides they damage this oxide film. So, the corrosion rate is increasing because they damage the oxide film. Why does the corrosion rate decrease?

Anybody with the chemistry background? When I add more and more chloride what happened to the solubility of oxygen in water. What happen to oxygen solubility? It drops.

Student: Drops.

So, the oxygen solubility if you plot; if you plot the oxygen content if the oxygen content if I plot the oxygen content approximately if you plot like that. I am not saying exactly this is schematic is not I do not take it as the trend at all actually. The oxygen level falls down. So, what happen to the overall reaction. Overall reaction will drop unless the cathodic reaction occurs the anodic reaction will not happen. So, the corrosion rate now drops actually.

Now, these are some examples ok. There are several cases you see like this. The corrosion rate is dropping when you increase the environment like sodium chloride. There are several other example a couple of them I will give you, but you have to keep your.

See if you want to find out you can find out because the library has got all kind of data ok. Only thing is you have know sulfuric acid what happens with concentration oh nitric acid what happens with concentration. You have to just go and find out then you get an answer right. You cannot assume things.

So, you know very well. We have already discussed also earlier right. We discussed already we already discussed also that how the corrosion rate varies with the nitric acid. Did we discuss or not. Corrosion of steel in dilute nitric acid corrosion of steel in the concentrated nitric acid. When the concentration of the nitric acid it is increased significantly what happen to corrosion rate?

Students: (Refer Time: 74:22).

Yeah.

Student: No, (Refer Time: 74:24).

This decreases right; so, changing. So, that means, you have to get a clear picture about how the environment affects corrosion, there is no linearity here. Please understand I am only trying to derive that particular point only; do not jump into conclusions and then say the corrosion is decreasing or increasing. And you know with the concentration temperature; all will not happen at all.

So, there has to be an analysis. I come to the only that particular point. You need to analyze what is happening to cathodic reaction, what is happening to anodic reaction when you change the environment actually. Both cases can change, then automatically you come to an understanding how the corrosion will change if you alter the environment at all actually.

So, that analysis are very very important. Simply you do not just jump to conclusion that corrosion rate will increase when sulfuric acid concentrations is increased. No, do not do that. That is going to be incorrect way of analyzing things. I think I have some more issues. I will tell you in the next class and today I think we will close and we continue in the next class. I think we are going to start were going to have a class on Saturday right. I can do that ok.

So, thank you very much. Please read this. Do not read it just grossly. I think they I know you must read it the way I am just trying to analyze the problems. Each of it you need to be reading as analysis mode not as informational mode ok. If you do at information mode I think you are not going to do justice to the course at all actually; so that has that has to be done.