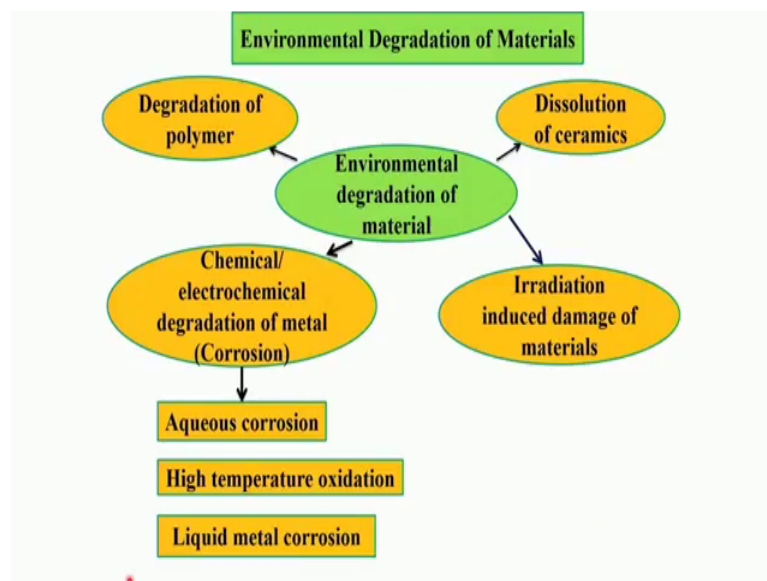


**Surface Engineering for Corrosion and Wear Resistance Application**  
**Prof. Jyotsna Dutta Majumdar**  
**Department of Metallurgical and Materials Engineering**  
**Indian Institute of Technology, Kharagpur**

**Lecture - 12**  
**Corrosion – I**

Hello. We are going to start the degradation of materials because of Corrosion and its protection.

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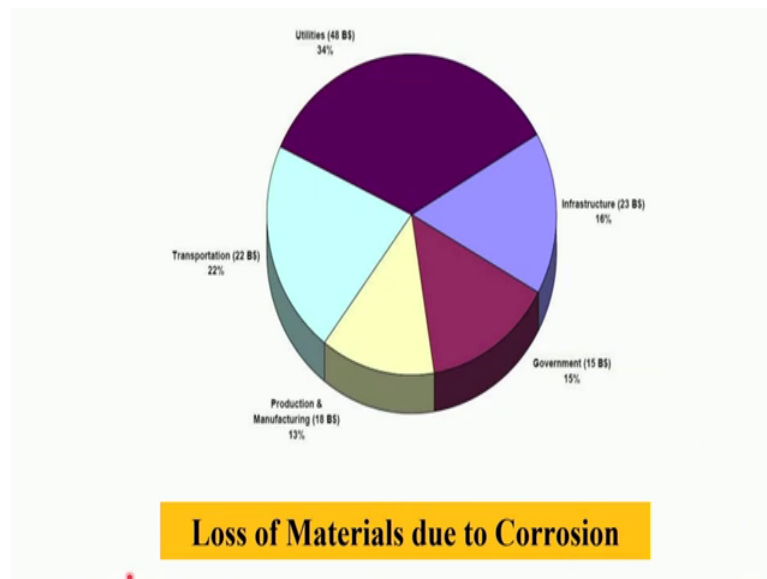
Now, corrosion is a kind of environmental degradation of materials. Now if you quickly go through the different types of degradation of materials, because of its interaction with the environment. You will find that, if you talk about polymer the term which is used is degradation of polymer this usually occurs because of absorption of the moisture from the environment or by the attack due to degradation of its structure, because of attack with the environmental light or UV radiation.

So, usually there is degradation of polymeric structure. If you talk about ceramic material there is either dissolution or maybe dissociation of ceramics at very high temperature. There is also irradiation induced damage of materials, but on the other hand if you talk about metallic materials usually the term which is commonly applied is corrosion. This is nothing, but chemical or electrochemical degradation of materials. Now if you quickly go through the different types of corrosion you will find that, they may be classified into

three categories one is aqueous corrosion, then second one is high temperature oxidation and third one is liquid metal corrosion.

Now, corrosion is a kind of degradation which is very much dependent on the surface, structure particularly surface micro structure and composition and it may be prevented by the process of surface engineering. So, in order to know which kind of surface engineering technique may be applied for prevention of corrosion, it is very much important to know the different types of corrosion and the surface micro structure and composition or surface structure, which are required for prevention of corrosion and the surface changing tool you should apply it for the modification or structure change on the surface. In the next few slides I will just briefly discuss about different types of corrosion which is the metric materials usually face.

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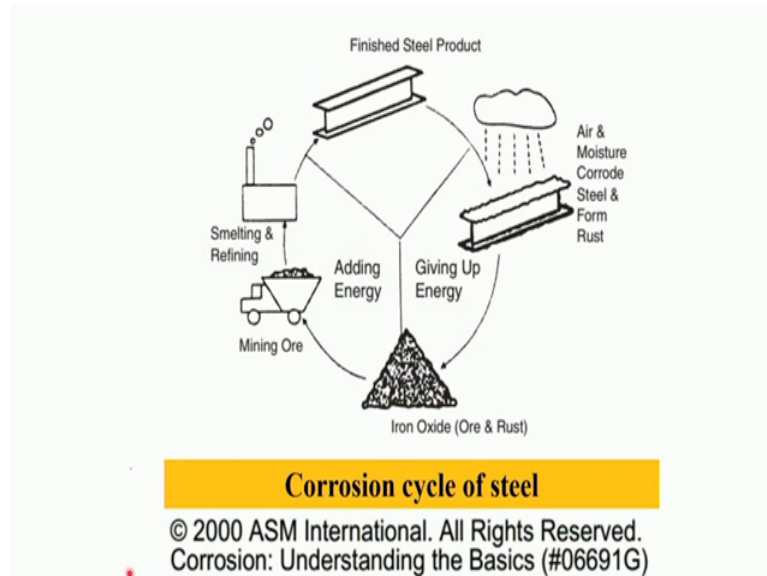


Now, if you quickly go through the loss of materials, because of corrosion you will find that there are different sectors where different types of damages occurred by corrosion. Maybe if we just quickly go through different sectors like, in the utility sector it is 34 percent, infrastructure 16 percent, government sector it is 15 percent, production and manufacturing sector 13 percent. And in the transportation sector it is 22 percent.

Now if you quickly go through these different sectors and different ways you will find that these usually occur in aerospace, automotive, or maybe atomic energy sectors. So, you

will find that different kind of corrosion usually occurs in different sectors and their mode also vary to a large extent.

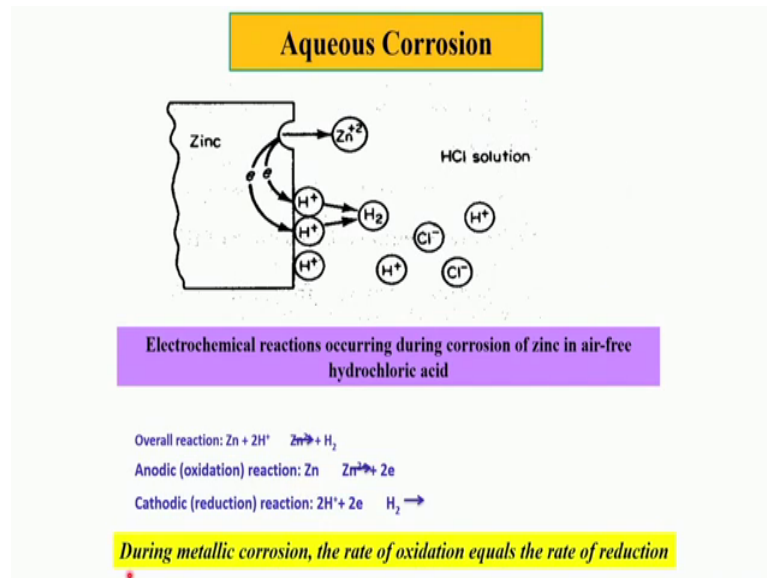
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Now, corrosion is a natural phenomena, because you will find that metallic materials are metallic state is really very much non stable state. So, when you keep the metallic material in environment, you will find that, there is formation of oxide scale on the surface naturally when there is oxidation phenomena that particular oxides get released into the environment by giving up energy.

Now, again by adding energy you basically extract the metals by different routes like pyrometallurgy or hydrometallurgy or electrometallurgy routes. So, you will find that this is a corrosion cycle of different materials, this is the case for steel, but it can be extrapolate to extrapolate it to aluminum, titanium or maybe aluminum magnesium these all different types of metric materials. So, corrosion is the natural phenomena. So, it is very much important that you try to avoid the corrosion so that, you can save lot of energy loss because of the corrosion.

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If you quickly go through the different processes of corrosion as I mentioned you that corrosion occurs in 3 different ways, one is aqueous corrosion second one is dry corrosion or high temperature oxidation third one is liquid metal corrosion. Now in the next few slides I will discuss about, different types of corrosions that are experienced by metallic materials in practice. So, this is the case for aqueous corrosion where, zinc if it exposed to hydrochloric acid solution. So, naturally there is the process of corrosion where, zinc converts to its zinc ions and this is the anodic reaction and cathodic reaction.

That is nothing but, hydrogen ion it changes to hydrogen molecule hydrogen molecule. So, in one case there is release of the electron which is anodic reaction and other cases there is acceptance of the electron which is called the cathodic reaction or reduction reaction. So, in equilibrium basically the rate of anodic reaction is equal to that of rate of cathodic reaction.

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THE ELECTRODE POTENTIAL			
<p>□ The potential developed by the electrode in equilibrium is a property of the metal of electrode → the <i>electrode potential</i></p> <p>□ It is measured by the potential developed by the electrode in a solution containing an unit concentration of the ions of the same metal with reference to the standard hydrogen electrode as the counter electrode (whose potential is taken to be zero)</p>			
Standard electrode potential of metals at 25 °C.	System	Potential in V	
	<i>Noble end</i>	Au / Au <sup>3+</sup>	+1.5
		Ag / Ag <sup>+</sup>	+0.80
		Cu / Cu <sup>2+</sup>	+0.34
		H <sub>2</sub> / H <sup>+</sup>	0.0
		Pb / Pb <sup>2+</sup>	-0.13
		Ni / Ni <sup>2+</sup>	-0.25
		Fe / Fe <sup>2+</sup>	-0.44
		Cr / Cr <sup>3+</sup>	-0.74
		Zn / Zn <sup>2+</sup>	-0.76
		Al / Al <sup>3+</sup>	-1.66
<i>Active end</i>	Li / Li <sup>+</sup>	-3.05	

Now, if you just quickly go through the tendency of the different metallic materials to corrosion, you will find that, they vary a lot it depends on the typical free energy change associated with the process of corrosion.

So, we find that when the as I mentioned you that metallic state is the unstable state. So, whenever it corrodes naturally there is a decrease in free energy. So, you will find that this particular free energy change is usually negative. So, the negative Gibbs free energy change is the basically driving force for the corrosion. Now when you just expose the metallic materials in any solution in aqueous solution you find that there is a potential which is developed by the electrode in equilibrium and which is called the electrode potential. And usually the standard electrode potential is the measure of the tendency of materials metallic materials to corrosion.

For example, if the metallic material or the electrode is exposed in a solution containing and in a unit concentration of the ions of the same metal with reference to the standard hydrogen electrode. As the counter electrode this is called as standard electrode potential. So, you will find that there is standard EMF series which is available and, which acts as the guideline for the choice of materials for different application. And which gives you the information about the activeness or nobleness or how proven the metal is to corrosive environment or to corrosion.

So, this is the typical EMF series where, you will find that the gold is on the top of the series and basically magnesium is magnesium zinc aluminum those are in the bottom and lithium is the least one. So, this particular potential gives you information about the that potential developed in the electrode surface whenever it is exposed in the solution containing one unique concentration of the ions of the same metal.

So, this is typically a kind of ideal series which gives you an approximate information about the relative corrosiveness of different metric materials in the standard solution; and naturally under ideal condition that is in at 25 degree Celsius.

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Role of Environment on Corrosion				
Type of atmosphere	Deposition rates (mg/m <sup>2</sup> d)		Steady-state corrosion rates (µm/year)	Comments
	SO <sub>2</sub>	Cl <sup>-</sup>		
Rural	<20	<3	5-10	Measured at various places in Scandinavia and Eastern and Western Europe
Urban	20-100	<3-50	10-30	
Industrial	110-200		30-60	
Marine	<10	3->100	10-40	Measured after 4 years of exposure at various places in Scandinavia*
Arctic	<10	<3	4	Measured after 4 years of exposure, Gällivare, northern Sweden

\* Corrosion rates at higher atmospheric temperatures, such as in the tropical zone, may be several times higher.

Temperature and normal pressure, but you will find that actual corrosion rate varies and it depends on the kind of environment you are exposing and the actually what kind of material materials composition is. So, now, this is the case where it also depends on environment to a large extent.

So, we will find that, this is the effect of environment on the corrosion behavior of the steel you will find that that whenever the contain the atmosphere contains sulfur dioxide or chloride then the corrosion rate is like this is the case for steel whatever it is in rural environment or urban environment.


Or in industrial environment marine environment or arctic environment, you will find that depending on the environment the corrosion rate also varies and you will find that in

industrial environment corrosion rate is maximum. So, actual corrosion rate in practice depends on where you are exposing the component in which environment what is the composition in the environment and other factors too.

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Alloys used in service are complex and so are the electrolytes (difficult to define in terms of  $M^+$ ) (the environment provides the electrolyte)

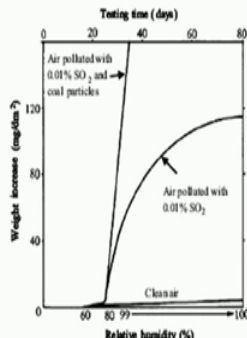
Environment	Corrosion rate of mild steel (mm / year)
Dry	0.001
Marine	0.02
Humid with other agents	0.2



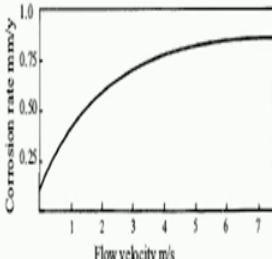
So, again this is the measure of the corrosion rate in different environment, in case of steel you will find that in that dry environment it is a quiet low, in marine environment it is quite high and humid and other regions where there are a lot of sulfur dioxide and chloride there the corrosion rate is maximum.

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### Parameters influencing corrosion rate



**Effect of Relative Humidity and Air Pollution on Atmospheric Corrosion of Iron at 25 °C**



**Corrosion rate as a function of flow velocity of steel in sea water at 25 °C**

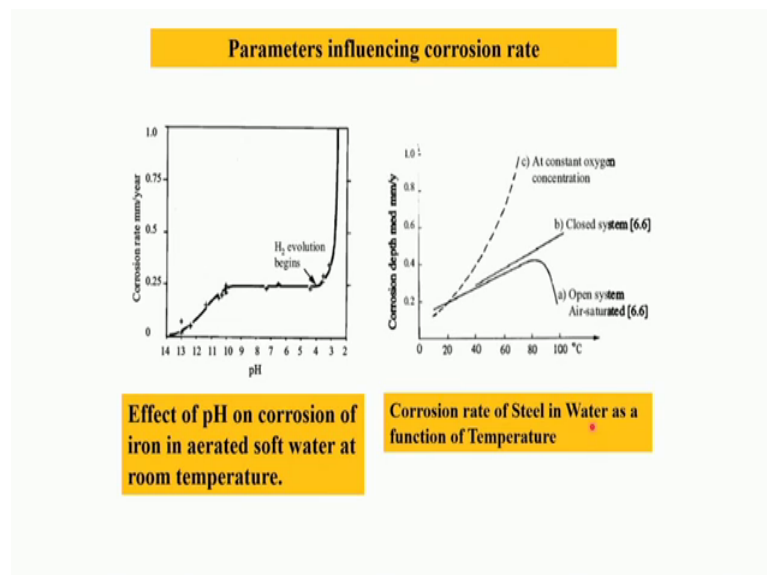
Usually the parameters which influence the corrosion rate their relative humidity, you will find that as you go on increasing the relativity usually the corrosion rate increases.

It also depends on the kind of species which are present in the environment for example, this is the case where corrosion rate of the iron at different environment is shown. In clean air it is minimum as it is polluted with point o 1 percent sulfur dioxide then it is a little higher even much higher than that of clean air. And whenever it is polluted with point o 1 percent sulfur dioxide and coal particles, you will see that corrosion rate is maximum.

So, corrosion rate is usually measured in terms of weight gain, as a function of time or temperature of different environmental parameters.

So, in case of environment where there are particle coal particles dispersed, you will find that the corrosion rate is maximum because of the fact that the coal particles they get deposited on the surface and as a result of deposition of coal particle the absorptivity of the surface increases. So, much amount of humidity is absorbed on the surface which increases the corrosion rate to a large exchange.

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If you see the effect of flow velocity you will find that, as you go on increasing the flow velocity again the corrosion rate increases to a large extent. Similarly the effect of pH is shown here. So, you as you go on increasing the p H you will find that, corrosion rate



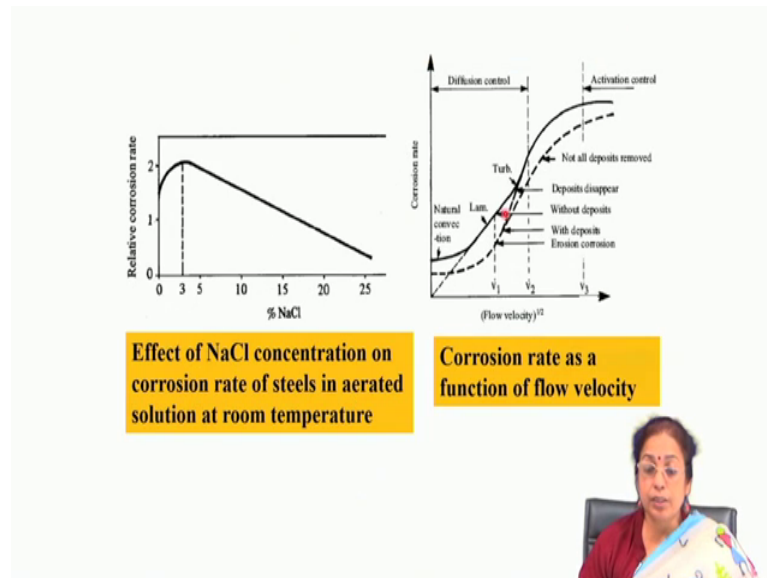
increases and then at a particular level it is quite steady and then after a certain value it increases to a large extent because there is hydrogen evolution, which starts and as a result of which the rate of corrosion increases to a large extent. Again corrosion rate is also dependent on the oxygen concentration, in open system where there is a saturation in air.

Then there you will find that the corrosion rate actually increases up to certain temperature and then, after that it decreases the effect of temperature is very important because corrosion is also a thermally activated process, as you go on increasing the temperature you will find that the rate of corrosion increases. And it also depend on the it depends on the kind of air which is there how much concentration of air is there whether it is open system or closed system. In open system if you see you will find that after a particular temperature the corrosion rate or depth of corrosion decreases.

This is because of the fact that at a maximum temperature there is strong oxide layer formation passive layer formation and which, basically protects the surface from corrosion as a result of which as you go on increasing the temperature, you will find that there is decrease in corrosion rate.

On the other hand in closed system you will find that increases and in that particular environment where there is a constant oxidation constant oxygen concentration there you will find that corrosion rate goes on increases. Because of the passive layer breakdown, there is formation and breakdown of the passive layer because oxygen concentration is not enough for the passive layer formation.

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Similarly, it is also dependent on the sodium chloride, whenever there is chloride content in the environment as you go on increasing the chloride content it increases. And at a particular certain value of chloride content you will find that, there is a the corrosion rate actually decreases. Similarly flow velocity has also the effect whether it is a laminar flow or it is a typical convective dominated flow. So, everything actually play very important role to determine the rate of corrosion.

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So, actually the environment plays a very important role, to determine the kinetics of the corrosion. And few examples of corrosion are shown here like this is the white rust on seaside, road railing, say will find that these all are steel structures. So, you will find that there is rusting of steel and it is quite severe in seaside road rolling, because of the presence of chloride in the environment. And there is rust formation and this was actually zinc coated steel.

So, usually what happens is that, whenever you just expose it in the savior chloride containing environment, there is there is a white rust formation and that white rust also get removed from the surface. So, even though zinc protects the surface from the sacrificial action were still there is corrosion on the surface of the underneath the iron underneath my steel. Similarly this is the case for copper where copper sink drain having suffered complete perforation after cleaning by local plumber.

So, they use all kinds of a solutions like sulfur sulfuric acid solutions or cleaning purpose and then after that due to the involved reaction with the environment there is sulfate formation and then, you will find that there is a corrosion on the structure.

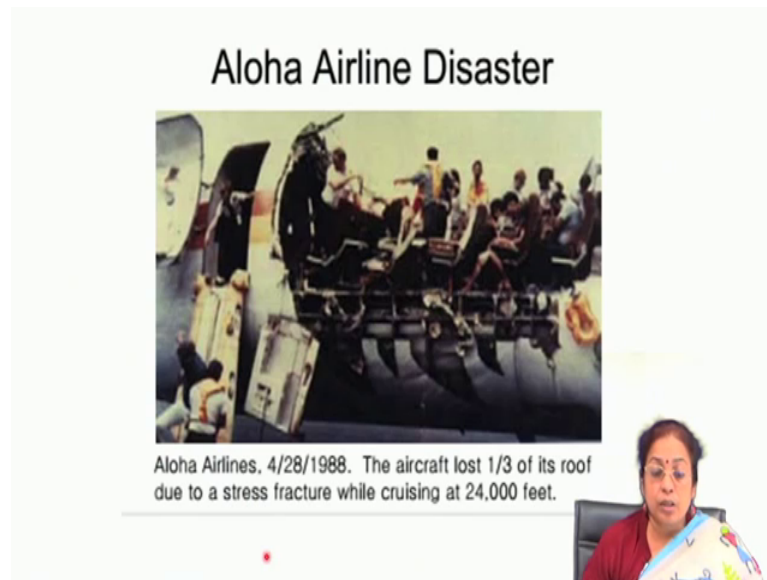
This is a typical example of the typical example of the crevice corrosion associated damage of the pillar structure. You will see that the structure started that corroded by crevice attack and the corrosion is so, severe that it has fallen from the route actually.

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So, like that there are several other cases for corrosion like there is common copper or mineral, malachite formation, greeny structure because of the corrosion attack. In corroded brass plate because of the selective leaching and then corroded ashtray with typical rust color so made of cast iron.

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So, similarly this corrosion damage can be so severe that, this is the case for a fatigue corrosion which caused the day like the base station of the a aloha airline structure. So, you will find that the structure, because there was that typical accident in 1998. So, the aircraft lost one third of its roof, due to stress fracture while cruising at 2000 2400 feet.

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## Corrosion Rate

- There are three main methods that are used to express the corrosion rate:
  - a) Thickness reduction of the material per unit time.
  - b) Weight loss per unit area and unit time.
  - c) Corrosion current density.
  
- Corrosion rate (mils per year) =  $534 \frac{W}{DAT}$ 
  - W = weight loss
  - D = Density
  - A = Area of specimen
  - T = exposure time



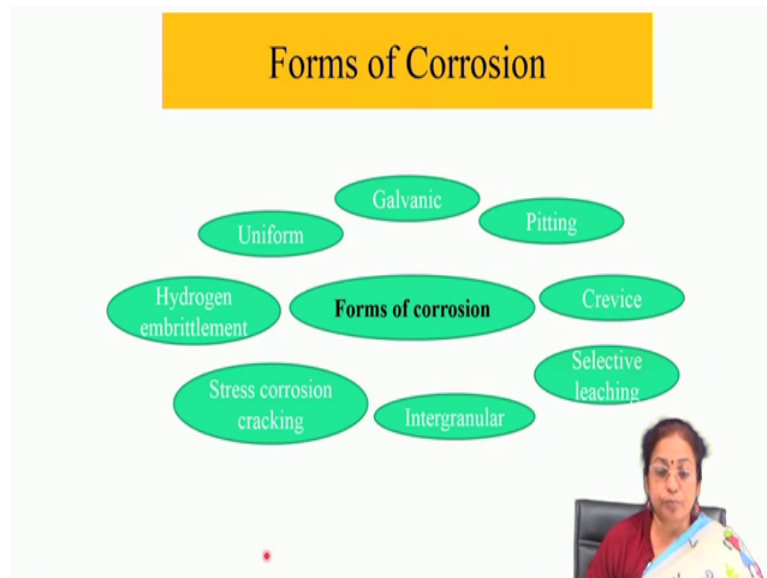
So, these corrosion can be quite dangerous phenomena, causing the attack and subsequent damage of the component to a large extent. And it is also very very much severe in aerospace automotive and marine sector. And so, you have to be very much careful and our main objective is to minimize the corrosion to a large extent.

Now, if you talk about corrosion rate corrosion rate can be measured by three different ways; like thickness reduction of the material per unit time or weight loss per unit area per unit time or corrosion current density. So, thickness reduction of the material per unit time and weight loss per unit area these are very important time standard approach..

And usually people go on doing standard coupon testing for the measurement of the corrosion behavior in simulated environment. But you can also accelerate the rate determination by typically electrochemical testing where, corrosion current density is taken as a measure of the typical corrosion rate.

And corrosion rate can be easily calculated by applying typical Faraday's law. And corrosion rate mils per year can be a corrosion rate is usually presented in terms of mils per year which is nothing, but  $534 \frac{W}{DAT}$  is not nothing, but weight loss by density into area of area of the specimen into the exposure time.

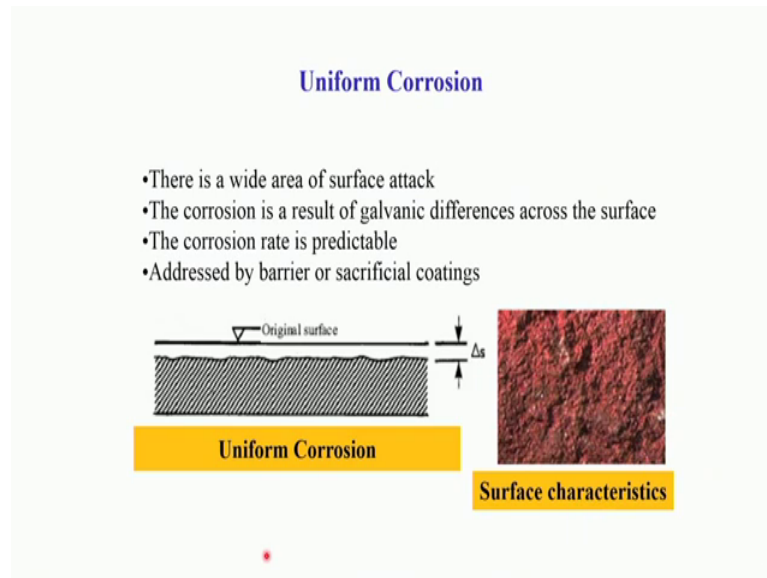
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Now, quickly go through the different types of corrosion it is very important to know that, the which mode corrosion occurs; because depending on the mode in which the corrosion occurs you will find that different major preventive measure needs to be taken.

So, this is the ways were different 8 or 8 different ways standard different ways that by which the corrosion occurs. So, they are like uniform or environmental or general corrosion, then galvanic corrosion, pitting corrosion, crevice corrosion, selective leaching, intergranular corrosion, stress corrosion cracking and hydrogen embrittlement. Now in these next few slides I will discuss about the degradation of the materials by different types of corrosion.

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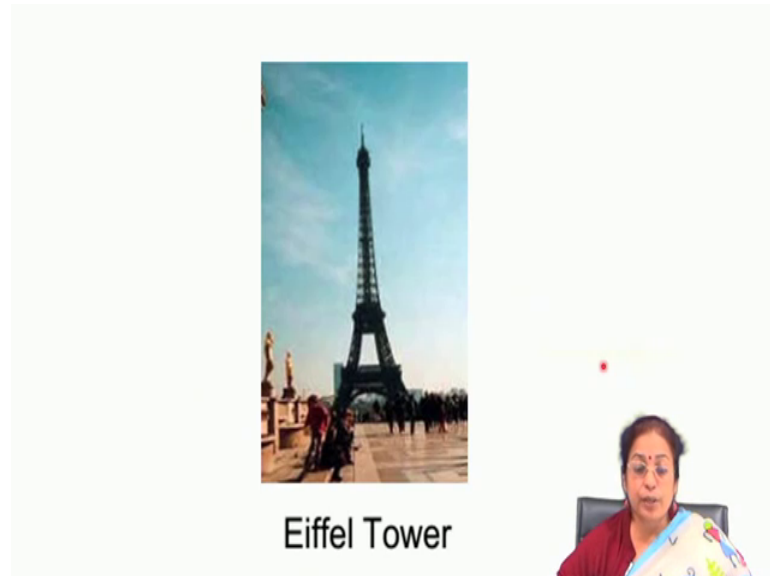
Now, if you are coming to the uniform corrosion you will find that uniform corrosion is the simplest form of corrosion. So, this is a kind of corrosion which usually occurs in normal environment, when the material microstructure and composition is quite homogeneous there the rate of corrosion attack is uniform all throughout the surface and you call it as a uniform corrosion.

So, usually this is a easy or simplest form of corrosion and you can easily measure by measurement of the thickness loss or by measurement of the weight loss because of the corrosion. So, you will find that this particular kind of corrosion rate is very easy to understand because corrosion rate is you usually in uniform, all throughout the surface and you can easily predict it because you calculate or measure the corrosion rate for a particular length of time. And then you can extrapolate it to know the lifetime of the component by this particular kind of corrosion.

So, the surface characteristics of the uniform uniformly corroded surface is usually like this, so you will see that corrosion attack occurred all throughout the surface in an uniform in uniform fashion. And there is not much change in the appearance with in different directions or with the different zone or within along x and y or with time actually. With time also it does not change much you will find that there is some rust formation on the surface, because the corrosion layer which used the passive layer which usually forms on metallic surface which protects the surface from corrosion that is not

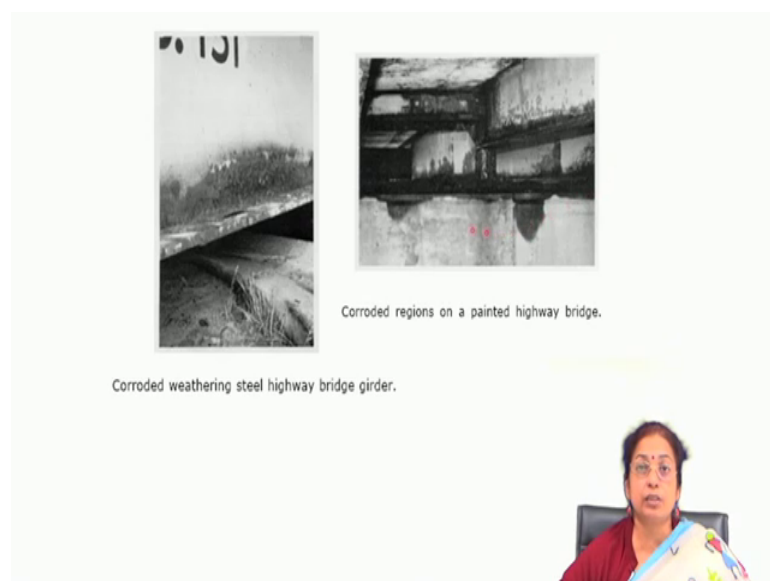
protective. And because of that the material corroded and then corrosion occurs by uniform fashion.

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Usually if you quickly go through the different examples of uniform corrosion or environmental corrosion you will find that, this is typical case for Eiffel tower where, people just go you will find that at a regular interval of time they go on basically painting the surface for protection against the uniform corrosion.

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Similarly, corroded weathering steel highway bridge girder, then corroded region on a painted highway bridge.

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**Atmospheric contaminants**



**Delamination of plain carbon steel due to SO<sub>2</sub> + Ash deposit outside the boiler area of a coal-fired power plant**

**Addition of 0.1% Cu will help**

So, these are typical examples of the uniform corrosion which occurs all throughout the surface. Similarly this is the case for plain carbon steel which has corroded due to sulfur dioxide and ash deposit outside; the boiler area of coal fired power plant see how corrosion can be severe? But this is more or less uniform or rate of attack is uniform all throughout the surface.

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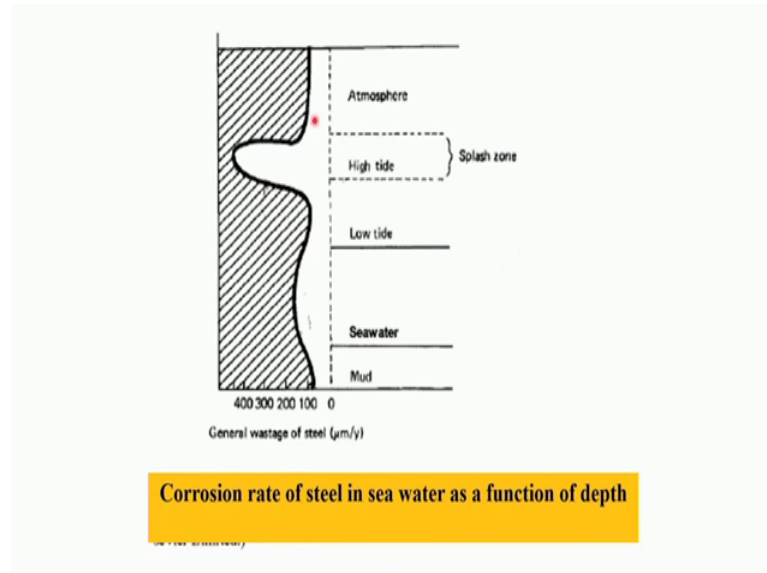
Table 8.1 Typical corrosion rates for carbon steel in different types of atmospheres.  
(Adapted from References [8.1, 8.5].)

Type of atmosphere	Deposition rates (mg/m <sup>2</sup> d)		Steady-state corrosion rates (µm/year)	Comments
	SO <sub>2</sub>	Cl <sup>-</sup>		
Rural	<20	<3	5-10	Measured at various places in Scandinavia and Eastern and Western Europe
Urban	20-100	<3-50	10-30	
Industrial	110-200		30-60	
Marine	<10	3 - >100	10-40	Measured after 4 years of exposure at various places in Scandinavia*
Arctic	<10	<3	4	Measured after 4 years of exposure, Gällivare, northern Sweden

\* Corrosion rates at higher atmospheric temperatures, such as in the tropical zone, may be several times higher.

So, as I mentioned you that uniform corrosion is very easy to measure and it depends on the environment, which the component is subjected to.

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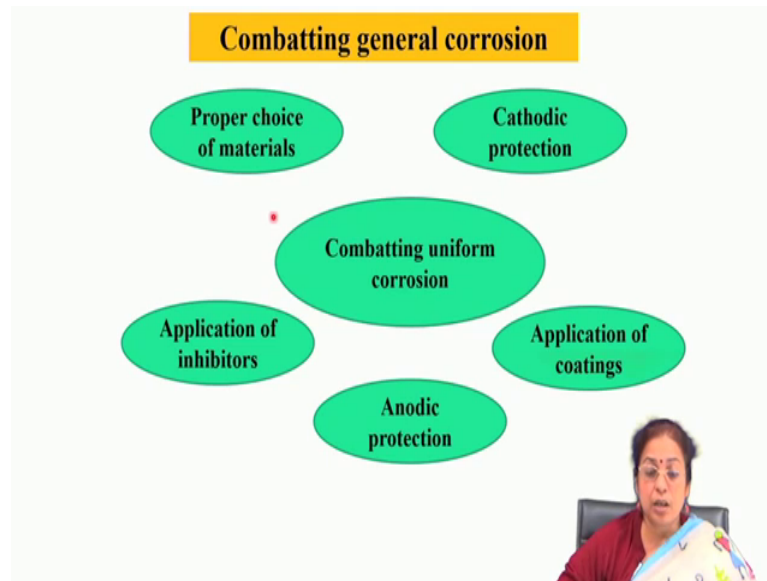


And it is also dependent for example, this is the case for uniform corrosion of steel in seawater as a function of depth, you will find that near to the environment, the attack is more or less uniform, but as you go down you will find that, in the high tide region there is a lot of I mean the attack rate is much higher than that of low tide region.

And in the mud region, this is the case for the corrosion rate of atmospheric corrosion as compared to that of the inside seawater, you will find that atmospheric corrosion resistance or corrosion rate is more or less same.

And as you go on moving towards the sea in deep inside the sea you will find that corrosion rate changes to a large extent, because of different form of corrosion walking over there. Because the corrosion attack is no more the general corrosion in that case, here it changes from general corrosion to erosion corrosion that is different mode of corrosion.

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We will discuss in the next few slides. Now if you just quickly go through the as I mentioned you earlier the all corrosion, corrosion is ever a desirable phenomena.

So, it is a kind of degradation of the materials and you have to be careful. So, that the degradation does not occur or maybe you can take protective measure. So, that it is minimize the probability of corrosion can be minimized.

Now if you quickly go through the different way by which you can combat uniform corrosion, they may they may be categorized into different types like first of all first and foremost you can most of the cases most of the mechanical or manufacturing sectors or manufacturing engineers they combat uniform corrosion by proper choice of material.

So, if you choose proper materials in proper place you will find that, there will be no corrosion at all. For example, if you take stainless steel if you use in nitric acid containing solution you will find that there is no corrosion at all. On the other hand if you just used 304 stainless steel, in chloride containing solution there will be different types of corrosion. But if you just choose proper material in proper place you will if you just use for example, titanium based alloys in chloride solution it will work perfectly.

So, proper combination of materials is very important so that, you can minimize the probability of corrosion. Other way by minimizing the probability of corrosion is by application of inhibitors, which actually controls the environment you can use different

types of environment cathodic, inhibitors anodic those all things will be discussed again a little in detail.

So, that particular the role of inhibitors some of the inhibitors they basically scavengers oxygen, some of the inhibitors basically reduces the hydrogen content in the environment. Some of the inhibitors actually controls they just get absorbed over the surface and like that it acts as a protective barrier so different inhibitors are available.

So, those inhibitors actually reduces that environment aggressiveness of the environment or protect the surface by forming a very thin film. Another very common way of combating the general corrosion is by cathodic protection, where you basically go on connecting the material of your combination material of your choice with another metal which is having which is more prone to corrode.

So, in that case what would happen is that, your material will be protected your metallic material will be protected by the corrosion of the other metal which basically corrodes and supplies electron to the structure. So, by that process, it basically reduces the probability of corrosion. So, you can as well apply very thin coating, which is made of again the corrosive material which is made of more active material like zinc coating on steel.

So, when zinc coating is applied on the steel. Initially it acts as a barrier coating and gradually when the zinc basically gets corrode corroded or it gets damaged by that case also in that case also, it protects the surface by the process of sacrificial action, so you call it as cathodic protection. So, you can also apply coating different types of coatings are available may be barrier coating or may be and a black cathodic coating, barrier coating or may be that sacrificial coating.

So, different coatings are available in practice which can actually combat the corrosion to a large extent. And also by anodic protection you can reduce the probability of the corrosion, the basic purpose of anodic protection is a little bit reverse than that of cathodic protection, here you basically take out electron from the system in such a fashion that, you basically allow oxidation to occur on the surface. And when there is oxidation on the surface there is formation of very thin protective layer on the surface and that protective layer actually helps in protection against the corrosion.

So, you will find that gradually the corrosion rate of that metallic material decreases. So, that is these are the different ways by which you basically combat the general corrosion. So, you as I mentioned you in this particular class, that it is very important that, corrosion you have to understand the corrosion phenomena, you have to know that different modes by which corrosion occurs; especially when you talk about the aqueous corrosion phenomena.

Aqueous corrosion usually occurs in an environment where there is a suite or acquires the water in the environment, showing there is water in the environment naturally you will find that corrosion is aqueous you call it as aqueous corrosion. Aqueous corrosion proceeds in 8 different ways; depending on the mode by which the corrosion process you will find that their rate also varies and also the appearance of the surface also varies.

So, you have to know the kind of corrosion that the component has undergone and further thing to know you have to do different for example, you can do you can just estimate the corrosion rate in that particular simulated environment by standard coupon testing or you can also do its typical electrochemical testing, like electrochemical polarization technique for knowing the kinetics of the corrosion in that particular environment.

And once you know the kinetics of the corrosion, in that environment naturally you can always take care of that particular corrosion by any of the protective measures as I discussed. Like particularly, if you talk about application of surface engineering in combating uniform in combating corrosion this is very easy. You basically select proper material, apply in the form of coating on the surface and then you will just apply there whenever you apply there coating your surface is protected from the environment. Usually painting is very common way of protecting the surface.

From the general corrosion particularly if you talk about and, apart from painting galvanizing or aluminizing, these are also another two approaches by which you protect the general surface from general corrosion. Like whenever you just think of galvanizing, galvanizing protects the surface by typical sacrificial action as well as by barrier action. Whenever you talk about aluminizing, aluminizing also protects the surface from typical barrier action, if you talk about you can also apply thin coating you call it as thinning.

So, by application of thin coating you basically protect the surface from typical water containing solution distilled water containing solution. And it is very much applied for the development of therefore, just carrying the food carrying cans where you basically face lot of corrosion problems.

But if you just apply thin coating you will find that, the surface is protected from the solution aqueous t solution, which is nothing but, typical water and that tin is very much safe it is non toxic in nature. So, by that process you can save the lifetime of the can to a large extent.

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So, now in the next few slides I will discuss the other forms of corrosion in details.

Thank you very much.