

Corrosion, Environmental Degradation and Surface Engineering

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Lecture – 12 Corrosion - Part I

Welcome to the ninth lecture of the course, Corrosion, Environmental Degradation, and Surface Engineering. The topic of this lecture is surface degradation mechanisms due to corrosive action. As I have illustrated with a symbol, the first obvious question is: what is corrosive action? Most students have been studying this topic since grade six. If we've been learning about it since grade six, why deliver another lecture on corrosive action?

It's important to understand that corrosion is a chemical reaction between a material and its surroundings that causes degradation. Corrosion has serious implications because it reduces performance, increases maintenance costs, and compromises safety. Safety is particularly crucial due to its impact on structural integrity and strength. In one of my earlier lectures, I mentioned that the total annual cost of corrosion and corrosion resistance in India exceeds 1.5 trillion rupees, which is much higher than the entire educational budget. This highlights the importance of this topic.

Furthermore, while corrosion has been taught numerous times since grade six, we must consider the different environments. Corrosion-induced surface degradation is not just about corrosion itself but also how it is influenced by the environment, operating temperature, and the chemical reactivity of the material.

So, if I want to really learn about corrosion, I cannot just concentrate only the chemical reactivity of the material, the environment, or only on environment or only on the temperature. In essence, corrosion involves a combination of all three elements. Most of the metals have corrosive resistance; let us take the example of stainless steel. Most people believe that stainless steel is impervious to corrosion, meaning it will never deteriorate. However, we can consider and demonstrate that corrosion also causes degradation in stainless steel. So, it is important that we know what kind of environment, what temperature, and how it influences.

Another thing is that we use the word material instead of metal, because most of the definitions use the word metal. They say there is a chemical reaction between a metal and surroundings. Well, in this case, we have used a material, not a metal, reason being the non-metals like a polymer, ceramics, and composites, when subjected to specific environmental conditions, can go through the process of corrosion degradation. Let us take an example. If there are certain polymers in ceramic, they may swell, soften, or dissolve when exposed to acids. To choose appropriate material for certain applications, it is necessary to apply relevant protection measures. It is also necessary to understand the behavior and degradation of most materials. This is why this course is important. I will cite a few examples.

Let us take the example of sodium, a highly chemically reactive material. You cannot leave it in the open because it immediately reacts with water to form other products, such as salts. For instance, it can quickly react with chloride to form sodium chloride or other compounds.

Therefore, sodium cannot be found easily in an open environment. Whenever sodium is exposed, it immediately reacts with the surroundings.

If I make something out of sodium, I need to really think about how to do that and what kind of measures are really required. Let us take another example: gold and platinum. Now we say these are the noble metals, the reason being that they are non-reactive, and most of the time they remain in pure form in nature. So we can take advantage of these metals, and then we can observe that most of the electrical contacts are routinely coated with gold, or, may be, the gold-like material in industries, to stop or prevent oxidation. Another interesting thing is that we have been mentioning corrosion, but there are some metals, which have built in resistance to corrosion in the form of a sacrificial layer to protect the underlying material.

In such cases, corrosion products, such as oxides, hydroxides, or salts, form a thin, adherent, insoluble, and quickly renewable layer. When I say it is thin, I mean it does not significantly change the dimension of the material, which is advantageous. This layer remains adherent to the surface, meaning it does not cause delamination easily. It is also insoluble, so it does not dissolve readily.

Moreover, this layer has the property of quick self-renewal. If it is damaged at some location, it immediately renews itself. This layer possesses all the good properties, making such metals ideal for repeated use. However, we need to understand how these materials can degrade under certain circumstances.

These aspects are crucial. We classify these materials as passive materials because they protect surfaces from further deterioration. Passive materials rely on their preventive corrosion products, like oxides or hydroxides, which provide some level of security to the surface and prevent further corrosion.

However, not all corrosion products are protective. Sometimes, we assume that oxide formation is beneficial, but this is not always the case. Rust, for example, is a well-known corrosion byproduct of iron or steel. While rust formation is common, it is not a good byproduct because it indicates a problem with material degradation.

To understand the problem related to rusting, we can concentrate on this slide, but we have shown three figures. In figure one, we have shown a jaw coupling, and you are able to see there is some sort of brown-colored iron oxide on this jaw coupling. The second figure is an inner ring of a roller bearing, and we are able to see the marks on it. The third figure is a bearing of an engine bearing, but we are able to see very high levels of corrosion as well as rust on this kind of bearing. So, rust as such can act to prevent further corrosion, but it does not always appear. That is why we say rusting causes an increase in the outside dimension. Now the dimension is also increasing because of the rust; it is not going in a few nanometers or microns; it sometimes increases beyond that. And another problem with the dust is that it gets a dislodge, because the porous nature and the weak tendency to get a stick over the surface it will cause a dislodging. Now if this kind of a jaw coupling if we run at the higher speed, we will find some sort of a rare debris particles are coming out of this surface also.

In this case, because there is a sliding along with the high load, there will be some sort of corrosion, and there is an awareness rate. So, they will get mixed together, and this heavily depends on corrosion and wear. So in the case of an environment where there is water, rust is getting formed on the surface, and wear is also happening, which causes a major problem with the surfaces. So that is why we say that in the case of the rust, we need to really think carefully, the reason being that there is already humidity, but if there is some sort of industrial vapor or acid in this situation, some sort of corrosion of the material will act because there is an environment or corrosive environment. The corporate environment itself is corrosive, and then there is a formation of oxide. We should be sometimes happy with oxide, but whenever there is wear or some other associated mechanism with that, then this kind of product will be problematic.

Chlorides, oxides, and sulfides can form and may be porous, not adhering completely to the surface, leading to failure or enhancing the likelihood of failure. This is why we say that when corrosion and mechanical sliding are combined, they cause a significant increase in wear rate. If we consider wear alone, it may not cause extensive damage, and similarly, if corrosion alone occurs but the material becomes passivated, it will not cause much of a

problem. However, when these two factors are combined, they significantly enhance the wear rate. This phenomenon is like saying 1 and 1 do not make 2, but rather 1 and 1 make 11.

Therefore, it is crucial to consider these factors when designing products for long service life. Additionally, the wear debris particles that come from this thin layer can act as abrasive materials, further contributing to the wear and degradation of the product.

Not only does it result in corrosive wear, but it also leads to corrosive abrasive wear, significantly enhancing material degradation. This is why it is important to understand this topic, comprehend the underlying science, and develop mitigation solutions based on that understanding.

Having worked in the bearing area for over 20 years, I can say that bearings are the most prevalent sub-assembly found in almost all machinery. Bearings are common in both mechanical and non-mechanical machines, and even in human joints, we find numerous bearings. If these bearings deteriorate, performance decreases significantly, necessitating replacement. This is why the cost of bearing deterioration is very high.

The cost of bearing replacement is high for several reasons. First, the bearing itself has a replacement cost. Second, there is downtime and productivity loss. When a bearing fails, it causes unscheduled downtime, requiring the machine to stop for bearing replacement. This downtime results in productivity loss, potential missed deadlines, and significant financial losses.

Furthermore, in certain conditions, bearings can corrode due to water ingress, acid formation, or gas exposure. Corroded bearings increase friction because the dimensions change, causing resistance. This increased friction leads to higher energy consumption and operational expenses.

Frequent maintenance due to bearing issues also incurs labor costs, oil changes, and other associated expenses. Lastly, safety is compromised when bearing corrosion occurs. This affects not only the safety of the apparatus but also the safety of the employees.

We can say corroded bearing failure could result in accident injuries and damage to the other component, not only that bearing component, but because of the failure, maybe the quite possible gear box attached to that also may fail. So, the number of failures will increase if there is some sort of failure of the bearing. So, that is why we can say the bearing cost failure is really significantly high, and we should avoid it, and most of the time it is because of water increase because of corrosion or related phenomena. Now, how to avoid all this naturally? There is, as I mentioned, some material that has a passive nature. What is that? That has been explained in this slide. We use the word passivation. What does passivation mean when it comes to creating a protective oxide layer? As I mentioned in the previous slide, not all materials will naturally form a protective oxide layer. There will be the formation of an oxide layer, but it is not necessary that it will be protective; naturally, we need to understand what.

Here we can start with aluminum. Aluminum has a very good resistance to corrosion, but you can see here if the aluminum is submerged in hydrofluoric acid, of which 10 percent is a higher oxide. We can find some sort of scratch, and this scratch is because of the corrosion. So first thing is that aluminum is not a corrosive resistant completely. It gets corroded, but it makes a layer, which is why we are using passivation—this passive layer—to prevent further corrosion. So, what we can say in short is that, due to the development of the protective oxide layer, we can use aluminum oxide on the surfaces of the aluminum surface. Aluminum alloys are widely used in industries, and we can say they have exceptional corrosion resistance. In the true sense, they do not have a resistance of 1 or 2, maybe a few microns or nanometers of layer thickness, which will be a corrosive layer.

So, it is not aluminum itself but aluminum oxide that forms on the surface, creating a passive layer. Once this layer is formed, the underlying substrate is no longer exposed to oxygen, making it impermeable. This means that oxygen cannot reach the substrate, preventing further corrosion.

We can say that this oxide layer serves as a barrier. It acts as both a chemical barrier and, in a way, a physical barrier. This barrier prevents the underlying metal from further corrosion or oxidation. From this perspective, aluminum appears to be corrosion-resistant. However, it is not completely corrosion-resistant in the true sense, as it is not a noble metal like platinum or gold.

That is why we say it is good, but it is a low-cost solution, and if we are not worrying too much about a significant change in the dimension, or maybe in the few nanometres or a few microns, then aluminum is a good solution, but if we do not want any change in a dimension, then we need to go for a noble material. So, aluminum is not a noble material; it gets corroded, but because of the passive nature of that layer, it is useful to us. Another reason we use the word "self-healing" is that if a product oxide layer is damaged or removed for one reason or another, for many reasons, maybe there is a sudden in-between sliding that occurred or increased significantly, or there was some sort of fluid-induced removal of the layer, that is a possibility. So, we can say that in this situation, aluminum alloys can spontaneously reform the oxidized layer, or oxide layer, in the presence of oxygen. However, we need to see that the presence of oxygen should be there, and maybe if the machine is operating at a very high speed and then oxygen is not available sufficiently to reform the layer, which is getting removed from a surface and then deformation, there is some sort of gap, then again, aluminum will be will not be able to resist the corrosion, and there is a possibility.

So, we need to really think about all those parameters. However, for the time being, we are assuming that if the layer is removed, it will have self-healing properties and will be able to form oxygen, assuming there is abundant oxygen available. However, when we think about a space, naturally, oxygen will not be available, and the self-healing properties will not be available for aluminum. However, for the time being, we are assuming a normal environment and oxygen will be available, and then there will be a repair possibility; we can say the aluminum will repair itself and maintain the corrosion resistance. So, these are the aspects that are important to understand. We picked up this example from a 2006 reference. The paper by Sj, which is mentioned, is available if you want to read it.

Now, we have started discussing passivation and want to emphasize it a bit more. Considering the example of aluminum, we can illustrate the amount of corrosion over time. Initially, some corrosion occurs, but it gradually decreases. The black line, which I have now changed to red, indicates passivation, meaning the corrosion rate is gradually approaching zero. This line represents the total amount of corrosion on the surface, not the rate of corrosion.

So, this is a passive case. However, in a few cases, like when we consider some sort of rust that is active, it does not get prevented, and they stopped at all. So, the rusting in the situation is active corrosion, and in this active corrosion, if this layer continues, it will continue on the linear curve, or maybe the non-linear curve, depending on the time it will continuously increase. And you can see that now there is a gap. If the passive layer has been made, then it will always be a better one, and if we are not able to think about or provide a passive layer, then this active corrosion will be a major problem, even if it can eat away complete material. So, we can express this in a word: the most corrosive film passivates, or ceases developing beyond a certain thickness. So, once it reaches the thickness, it stops corrosion, or maybe the layer is sufficient, and then it acts as a barrier for further oxygen, and it does not allow oxygen to react with the surface, which is important.

Sometimes people think that a discolored or reddish surface should be cleaned, but this is a major mistake. Cleaning the surface can remove the protective oxide layer, potentially increasing the coefficient of friction and leading to more corrosion.

Understanding the science behind this is important. Additionally, passivation can halt the rusting process. In some cases, environmental factors, such as reduced moisture or pressure on a component, can stop corrosion naturally. This phenomenon, known as self-passivation, prevents further corrosion without external intervention.

However, in the corrosion films, brittle porous is normally used to mean a surface or layer that is getting formed because the corrosion is brittle or porous. If the material is porous, then naturally, oxygen will keep passing from the top surface to the middle surface to the bottom surface. In this situation, then this sacrificial or short-layer lifetime corrosion film will be lost, and it is not going to give us a good solution naturally. If this is the case, we need to think about how to generate other barriers and how to generate additional barriers. So, we do have a number of processes that we call chemical passivation. We can think about a conversion coating, or we can think about some physical barrier.

So, there are two chemical routes, one physical, and maybe there are many because this is a research topic and people keep doing a lot of research in this area to prevent corrosion in many ways. Let us see what the meaning of chemical passivation is. We are using the word nitric acid or citric acid solution. If used, it can stop the corrosion. Initially, it will corrode the stainless steel, but further, it will not allow more and more corrosion. And in the number of lubricants, this kind of chemical is added to the lubricant itself to make a single passive layer on the working surface to prevent corrosion or further corrosion of that. So, we are intently making or inducing corrosion on the surface to prevent further corrosion. So, that is a science, and we need to understand it because we require a perfect balance. Naturally, concentration is important, and with time, that concentration will keep duplicating.

So, naturally, we need to change that lubricant. That kind of media may change after 6 months or 9 months, depending on the working conditions. So, this is what we are showing here in the case of stainless steel. When you think about the nitric acid or citric acid that can really passivate the surface of the surface of aluminum and stainless steel, then they make a top layer as a chromium-rich oxide layer. So, earlier, when I started this lecture, I said very clearly that many people assume stainless steel is corrosion resistant. Whatever you do, it will not really cause corrosion. We need to think about how to prevent the corrosion of stainless steel naturally. Here, one of the treatments has been mentioned: nitric acid or citric acid. We need to use a solution to do so. The layer is formed, and then there is a chromium-rich oxide layer on the surface that prevents further corrosion of that. Now, coming to the conversion coating, we say another possibility to prevent corrosion is that we can do phosphating.

That means that if a steel we put some sort of phosphate, or sometimes also solid lubricant on it, or even aluminum we do anodizing, which is a common process. So, I am assuming the aluminum is a good layer, or maybe it is corrosion resistant, but we do anodizing. So, further that the layer should not get corrosion, only the top layer, which because of the anodizing has some sort of firm formation and adheres to the surface, should be avoided. In this case, the anodized layer is thick and not thin the way we indented, but slightly thicker and stronger, and then it has much more resistance compared to the other oxides. That means aluminum itself has a layer, but that layer, which we are mentioning in this case, is not sufficient to prevent corrosion, or when the corrosion is severe, it is not as good as an anodized layer.

So, that means, if there is some sort of corrosion environment and aluminum itself is not able to handle the situation or create the kind of oxide layer that stops corrosion, then we can consider anodizing. Aluminum can act as corrosion-resistant in ultra-mild cases, but in more severe cases, such as exposure to certain acids, we should consider anodizing to increase its resistance. Anodizing is a conversion coating method that generates a barrier to stop the corrosion of aluminum itself.

Now, you have come across various physical barriers. We know that we can apply paint on materials or sometimes use a polymer film layer on the surface to shield it from corrosion. These are examples of physical barriers where another material is applied to the surface. If the layer is chemically attached, such as through a covalent bond, then we can say these are chemical layers. If it is only a physical addition to the surface, then it is a physical barrier.

This topic is very interesting because it helps us understand corrosion better. We must consider not only the material but also the temperature and the environment to determine if a material will be corrosion resistant. All three factors together will indicate whether the material can sustain corrosion or not.

Now, let's try to understand a few more phenomena, such as intergranular corrosion. In one of the previous lectures, we mentioned that most brittle materials fail because of weak grain boundaries, and the same applies here. If the grain boundaries are weak, corrosion can dominate. To illustrate, surface corrosion can penetrate deeper into the material. This is intergranular corrosion, which progresses along the grain boundaries because they provide a path for the corrosion.

So, not only surface corrosion, but weak boundaries can also facilitate corrosion progression inside the material, potentially leading to pitting corrosion. Intergranular corrosion (IGC) affects the edges of grains, which are the boundaries between crystals in a polycrystalline material.

An example of this is stainless steel, which is considered corrosion-resistant but can be vulnerable to IGC. The reason is that corrosion resistance decreases particularly at the grain boundaries. We need to consider the grain formation and boundaries in materials known for corrosion resistance and determine if these boundaries are also resistant to corrosion. If not, appropriate treatments are required.

During processes like cooling or tempering, stress relief can cause precipitations near grain boundaries, weakening them and leading to IGC. This problem is common in many alloys during cooling, where corrosion plays a major role. At higher temperatures, recrystallization or resoftening can occur, weakening grain boundaries and leading to local pits, crevices, or larger cracks, contributing to IGC.

IGC is a major problem in many industries, including oil and gas, chemical processing, and maritime industries. For example, in the maritime industry, ships and boats must consider IGC because it can significantly impact their structural integrity.

To elaborate, Lee et al. conducted experiments on low alloy steel (500AW) to test its corrosion resistance. They performed immersion tests in a solution with a pH of 4.5, simulating an acidic environment that promotes corrosion. After various durations (0.5, 1, 2, and 3 hours), they observed the corrosion using SEM images. Up to 1-hour, noticeable corrosion was minimal, but after prolonged immersion, precipitation phases at grain boundaries became more apparent, indicating the onset of corrosion.

So, in figure C, we are able to see the depth. In figure D, we are able to see the depth. There is a possibility of the kind of pit formation; there is a possibility of some sort of pit as well as the grains, and then we are able to visualize the kind of 3D. That is why we see the ferrite grain and ferrite in the pearlite area both continuing to get corroded. So, there is a inside now the depth is also coming it is not only surface, and that is what I mentioned in intergranular corrosion there is a depth which is also getting corroded or maybe the vertically, there is a instead of horizontal split of the corrosion there is a vertical deep corrosion you know it is on a surface. And then what we say is that this kind of surface is more and more visible, and then here the precipitation phase, which is what we are using, iron carbide, or Fe_3C , is becoming more and more dominant at the surface. So here, at least in this image, I am able to see much deeper things, and if depth is increasing naturally, a big chunk will come out, as has been shown in the next image. You can see here that E has been shown after 12 hours, F after 24 hours, G after 48 hours, and H after 72 hours, and now here you can see a complete depth, which has it there, and maybe if

you are able to see these are the increasing from 2 D to 3 D, and finally, a chunk comes out, and then which is the deep is visible in this case. So, what we can say here is that after 48 hours of immersion, it started to show up on the sample surface due to the precipitated phase, or the Fe_3 phase, and the grain boundaries, and after 72 hours, the precipitated phase of the grain boundary came off.

It is completely dislodged from the surface, increasing in size, and causing numerous dents. This kind of initiation leads to other associated phenomena that will cause failure. To show this schematically, we can represent it with figures indicating a piece of steel. The solution contains HSO_3 and hydrogen, and what we show is precipitation. The blue color indicates precipitation, while the black color shows the path of pit formation.

Here, we can see deeper pit formations. This schematic representation, though not accurate, is based on what we learned from SEM images. The information is taken from a reference that provides complete details about the experiment, the techniques used for sustainability, and the repeatability of results.

This is a good example to explain what IGC is and how it can damage materials. If not considered, the surface might not show much failure, but the corrosion can spread vertically or deeply, leading to significant material failure in a short time without much notice.

Now we have a given kind of overview of what is the need for corrosion and what is the need for this topic, but let us look at some sort of important, what you say is the most prominent type of corrosion, which is corrosion, and their mechanisms. So, we are not going to cover all kinds of corrosion; maybe you go through the number of books, and there are handbooks also that cover corrosion in, say, a number of classifications. We are not going to cover all kinds of corrosion, but most prominently which oil is causing us a kind of surface degradation. We will try to discuss a few mechanisms in this. So, what we say in this case is basically the main, bigger domain of the three main types of chemically induced corrosion: one is called aqueous, the second is high temperature, and the third is biochemical and biological. As I said earlier in my lecture, we will not be dealing with biology. So, biochemicals have been removed from our course, and biological corrosion has also been removed from our course.

So, we are not going to discuss those. Now, remaining with aqueous environments, one of the popular types of failure is rusting, which happens in most iron or iron alloys. Aqueous environments also cause swelling, as mentioned earlier, which occurs in ceramics, cements, or concretes, and is known as the softening process. This happens in aqueous or water environments.

Another factor is the high temperature. As we know, when the temperature increases, energy increases, and the chances of chemical activity increase. This can lead to oxidation, sulfurization, chlorination of metals, and even some ceramics, as well as solvation or formation of salts. These are the major classes of environmental impacts. Different environments, such as those with acid formation, saltwater, or water itself, can damage both metal and non-metal surfaces.

From an economic point of view, as mentioned in an earlier lecture, corrosion causes more than 1.5 trillion in losses to India every year. Aqueous oxidation of metals at room temperature or slightly higher temperatures, and high-temperature corrosion are significant issues. The breakdown of materials caused by chemicals, including water, results in huge economic losses. Therefore, understanding the prominent types of corrosion, their mechanisms, and prevention methods is essential.

Let's look at the classification of corrosion. Corrosion can be classified into microbial and fungal corrosion, which we will not cover in this course. However, in the broader domain, corrosion can be divided into five categories: uniform corrosion, galvanic corrosion, pitting corrosion, crevice corrosion, and stress corrosion cracking (SCC). These are the types of corrosion we will cover in this course.

Uniform corrosion occurs uniformly across the entire surface of a material, and rust is an example of this type of corrosion. Aqueous corrosion is also a form of uniform corrosion. Galvanic corrosion, on the other hand, generally requires two different materials. While one material is sufficient for aqueous corrosion, galvanic corrosion requires two different materials to act electrochemically. If you remove the electrolyte or the media in between, galvanic corrosion will stop. The presence of an electrolyte is crucial.

Pitting corrosion does not happen in one go; it takes multiple cycles and hours to cause pitting failure. This will be discussed further, emphasizing repetitive conditions. Localized crevice corrosion occurs in small holes, passages, or surface damage where oxygen or corrosion inhibitors cannot reach. Even with lubricants that contain inhibitors, this type of corrosion can occur. It can happen beneath the surface or beneath deposits, following available passages.

Lastly, stress corrosion cracking (SCC) is caused by the interaction of specific media in a corrosive environment under tensile stress. This stress tries to crack or elongate the surface, and the weaker areas under tension will crack. As the surface cracks, the underlying areas are exposed to the corrosive media, leading to continuous deterioration.

So, this is what I plan to divide into 5 categories. However, I have encountered numerous references and books that suggest a more comprehensive classification of classes. I am just taking one of the examples in this one of the reference book says that it should be the general corrosion. General corrosion and uniform corrosion are largely synonymous. Galvanic corrosion, we are also going to explain localized corrosion instead of localized corrosion. I will go for pitting and provides the corrosion to separate categories. Then there is another one; they divide something like flow-assisted corrosion, and instead of thinking of flow-assisted corrosion as a single device or mechanism, I will consider this as a erosion corrosion.

So, we have already considered erosion in earlier classes. Once we complete this, we will cover this topic in lecture 11, where we will discuss the synergetic effect of different mechanisms of surface degradation. This topic will be further explored in lecture 11, focusing not only on corrosion but also on the combined effects of various mechanisms. Corrosion naturally occurs if any mechanism causes it, and if there is a fluid with some velocity impinging on the surface, it will take away the protective layer.

Creating a special class for corrosion or erosion-corrosion, or in this case, flow-assisted corrosion, may not be necessary for daily discussion. Another term used is environmental cracking, but we refer to it as stress corrosion cracking. This is because, under tension, we require an environmental corrosion film. However, if not subjected to tension, cracking will not be as easy unless the material itself is inherently weak, like rust, which makes it prone to cracking soon.

So, we are covering this aspect within the broader context of aqueous corrosion or uniform corrosion.

So, we will not repeat it here. Last time, they mentioned high-temperature oxidation. So, in the earlier lecture, I said the oxidation was just a subclass of the corrosion, and then, naturally, at high temperatures, everything will change; even uniform corrosion will increase, galvanized corrosion will increase, pitting will increase, and stress corrosion will increase. Therefore, I believe that creating a separate category for high-temperature oxidation may not be as significant as it seems. So, that is why we are going to stick to the classification into five categories. Now, if I want to express it in some other words, we can say the most frequent type of corrosion is general corrosion. As such, we are using the word uniform corrosion, and then what is really happening in this case is that surfaces will get rougher and rougher.

So, general corrosion, uniform corrosion, and aqueous corrosion can be kept in the same category, and it is necessary that people juggle with the words I am using. These are the kinds of synonyms. Localized corrosion

typically occurs in isolated areas where the rest of the metal surface is untouched. This is only some specific area, and when we cover the two topics of pitting and crevice corrosion, that is what we can say: pitting and crevice corrosion, which we are going to deal with, are equivalent to localized corrosion. When we say chemical, as they grow and attack the surface or metal, the corrosion is going to be infected by microbes as well. However, we will not be covering the microbes of microbiologically related corrosion; we will not be considering them in this case. Next, I mentioned that high-temperature oxidation occurs at high temperatures, where the interaction is predominantly between the metal and reactive gas or molten salts. However, this is not going to be classified as a separate category of corrosion. High temperatures will enhance the effects in every class we cover, so it is not necessary to consider this as a separate category.

I also mentioned that environmental cracking is caused by the combination of corrosion and some additional phenomena, such as tension or wear. Again, we will not consider this as a separate category. Instead, we will focus on cracking under tensile stress conditions. If cracking occurs due to other reasons, such as mechanical sliding, it will be covered under wear.

We do not want to increase the number of categories, as we assume the five categories or subcategories are sufficient to cover corrosion comprehensively. These five categories can be used to understand various corrosion phenomena. However, we need to focus on the basics and how corrosion occurs so that we can apply this knowledge to improve product design.

Let's start with the first category: general corrosion. In this case, we particularly want to emphasize rust, which causes many failures.

What we say in the rust we required chemical action, we require material, we require environment. If the environment is not there, this kind of rust will not occur. If the material is not there again, it will not occur. If there is no chemical action again, it will not occur. So, we require all, and then sometimes we use the word rust, sometimes we use the word corrosion, and sometimes we use the word oxidation.

Again they can be played in manner. Now here we are showing some sort of the alloy of iron that the clean surface is started surface. Now in this situation we are showing that this surface can get oxidized in presence of oxygen, and it will make a iron oxide or ferric oxide. Now this ferric oxide in presence of water it will give a hydrated ferrite oxide, and that is what a red color has been shown over here. So, if I want to define a rust we can say the rust is a byproduct. So, red color what has been shown in this case or the brown color which is been shown on the surface, which is kind of the porous and they can be removed easily rub easily and then the powder will come out of this.

We say it is a corrosion byproduct as such. So, we mean that when we use the word rust, it is just a byproduct of the oxidation, and in the presence of water, the product comes out. So, this corrosion byproduct develops in iron or iron in steel, or it may be alloys of iron. Now rusting is aqueously assisted; it happens in the presence of water. If you remove the water, this complete action will remain only here. Ferric oxide has a reasonably good oxide surface.

However, if additional phenomena occur, it becomes problematic. Otherwise, it is not problematic if you do not touch the surface or remove the iron oxide layer; the life of the component will be in the hydroxide state. However, because of the hydrogen or hydrated ferrite oxide, it completely gives a path for deeper corrosion, similar to what we mentioned about IGC. So, rusting is an aqueous-assisted form of corrosion characterized by the formation of outer layers predominantly made of hydrated iron oxide, typically with a reddish-brown color. Additionally, there is magnetite, which is darker and forms an inner layer. On top of this surface, there can be another layer of magnetite, closer to the metal surface, with a porous top layer as mentioned in the case of rusting.

We require a chemical, material, and environment for the process. If you remove water, this type of corrosion can be significantly reduced. To explain why water is crucial, I am using this sketch. Assume this is an iron or iron alloy bulk with an iron oxide layer on the top surface. However, there are salt crystals or some sort of contamination and irregularities on the surface. Irregularities on the surface can lead to cell formation, which I will explain. This oxide layer, salt, and the top surface in water or electrolyte will act as a cathode. The cathode formation around the contaminants will be more dominant. A cathode transfers electrons to oxygen, which come from the bulk iron.

If the electrons come from bulk iron, it acts as an anode. So, we have a cathode, an anode, and water acting as an electrolyte. There will be continuous electron loss and deposition, creating a battery effect. Consequently, the bulk iron becomes invisible, and the orange rust increases in depth, eventually consuming everything, as shown in this figure. The crack formation happens because this layer is relatively weak and porous, allowing water to penetrate and form pits.

This mechanism shows how pits form. For instance, an iron alloy subjected to rust can develop deep pits. In this case, water or an aqueous solution functions as an electrolyte, facilitating electron movement. Removing the electrolyte would stop or significantly reduce corrosion. However, in the presence of water, corrosion rates increase, forming small electrochemical cells that accelerate the process, especially where discontinuities like pits or cracks exist.

This process happens faster when oxygen, electrons, and iron are present. Initially, the oxide surface is thin, but the process accelerates over time, becoming non-linear. I showed a diagram with passivation and active zones. The process is not linear but increases rapidly because the cathode area continuously increases while the anode area decreases.

We'll explain the impact of this with examples later, but a smaller cathode dimension is preferable to keep corrosion rates in check. A larger cathode dimension increases rusting and corrosion significantly. The bulk iron acts as the anode, and anode formation occurs beneath crystals or contaminants, leading to oxidation and electron loss, allowing material to dissolve into the solution.

This shows how crack formation and pit formation involve iron and possibly sulfide ions. Overall, this mechanism explains how wear and rusting rates increase over time. Initially slow, the process follows a non-linear curve due to increasing cathode areas and decreasing anode areas.

Continuing this topic, rusting relates to aqueous corrosion because, without water, rusting reduces. When exposed to water, metal surfaces develop a thin layer of water molecules due to wettability. To avoid rusting, use metals that do not allow water to stick. Many people coat metals to prevent water from spreading, keeping it as droplets.

Assuming water spreads as a thin layer, ionization of water molecules occurs, forming hydrogen and hydroxide ions. Metal surfaces also ionize, discharging electrons into the surrounding water. The positively charged metal ions attract negatively charged hydroxide ions, forming insoluble metal hydroxides. This process depletes the metal surface, making it uneven. Uneven surfaces are problematic, especially with rolling or sliding motion, resulting in pitted surfaces.

Now this is the case of the water now here in the aeroplane. It is showing you that is going to accelerate under this circuit in this is a common normal case, as such, now in the case of the acid in the case of the salt, which is very corrosive, then because of the change in environment, the corrosion rate of the metal will increase significantly. So, speed up, right? Maybe we are talking about a few kilometres per hour, but now we go with a

much higher speed, the same thing as the corrosion rate. Whatever it took time earlier, it will take $1/10^{\text{th}}$ of the time. So, what we are saying is that because of the chemical process between metal and electrolyte, it happens more quickly. Now, this was only the acid environment; now we are talking about the temperature as well. So, if you increase the chemical activity of the electrolyte, corrosion will increase; if you increase the temperature because energy is going to increase, the corrosion rate is going to increase; and lastly, if you really reduce the pH value, which may be somewhat related to acid formation, if you reduce the pH value, then the corrosion rate will also increase. So, if the pH value is decreasing, the temperature is increasing, which is going to really increase the corrosion rate.

So, we need to carefully consider the environment and the solution we are using, and how we can implement barriers to prevent corrosion or rusting in those cases. That's why we emphasize utilizing corrosion-resistant metals, applying coatings like paint or anodizing, or using corrosion inhibitors commonly found in grease or lubricants. These measures help prevent aqueous corrosion, reduce rusting, and increase the lifespan.

This is what we aim to explain. Sometimes, there's a need to clarify the difference between rusting and aqueous corrosion. Hence, this slide is specifically designed to illustrate the distinction between the two. Aqueous corrosion and rusting occur under different conditions, with slightly different mechanisms. Rusting is defined as the corrosion of iron and its alloy steel.

Rust is a byproduct, as I mentioned earlier. This is an oxidation reaction that occurs when iron and oxygen combine to form iron oxide. In this case, the iron atom loses an electron to generate the iron II ion. This is the iron II aqueous II iron now that has been mentioned that interacts with the waters to form iron hydroxide, because we know that the hydrogen and the water also make a hydrogen ion and an OH ion, and then the hydrogen hydroxide is free, and then there is a positive charge and a negative charge, so naturally it will make some sort of iron hydroxide. Another one is that iron III ions are also formed, the reason being the oxidation of iron by oxygen.

So, there is one interaction with the water and another interaction with the oxygen. So, this rust will not be there as such, but because of these two, we assume that it is a hydrated form of iron, and that is what has been mentioned. So, this is a form of rust. If I don't have this product, all others can be aqueous corrosion. So, that is why we are kept in a special category of rust, the reason being that it happens very commonly with iron, and iron alloys have been extensively used for the number of products. Now that the time has changed, it has reduced to some extent, but otherwise, there are a large number of alloys related to iron, and that is why this kind of separate category for rust is important.

So, if I do not get this kind of Fe_2O_3 or maybe with water molecules, then we can say the rust is not going to be there. Now, coming to corrosion, we can say aqueous corrosion is a more generic term, or rust is just a subdomain or subcategory of this that refers to the various metals and non-metals as well. So, it is not only the metals; non-metals can also come, and then there is another environment, a water-based environment. So, water is there, and the metals may be different. I can bring zinc, I can bring copper, and I can bring some sort of polymer that will act in aqueous corrosion but will not be part of the rusting. The rust we want to keep as a special one that iron oxide with water molecules in this case or hydrated iron oxide.

So, we know in this case, as I mentioned, that it includes a corrosion process involving metals other than iron, which can be aluminum, copper, or zinc. Now that this aqueous corrosion can be defined, we can say it works on the concept of electrochemistry. There will be anode formation, and there will be cathode formation. This is the same as the way we have discussed rust. However, that iron is been removed now we can bring some other metals like in this case zinc alone can be used, copper alone can be used now can be mixed also.

Now this is the next slide on this. What we say is that in aqueous corrosion, there is a naturally occurring sort of initiation. Initiation happens only when there is an electrolyte, and in terms of the water with some sort of

dissolved iron, that is what acts as an electrolyte, and surfaces of materials are also important. There is an electrochemical process the way we started we say the electrochemical process is important for us, that is why we say as a different regions of metal surface having varying potential, even the metal reactivity is different their potential difference will be there, and then that is why we say that there will be two surfaces. One is an anode, where the metal will get dissolved; it will lose electrons, and then ions will be formed. The other surface will act as a cathode, where the reduction takes place, or electrons are joining the oxygen as such. So, these are the creation of the cathode, the creation of the anode, and the exchange of electrons, or balancing of electrons. We use the word balancing of electrons because that is what electrochemical action means, and then there is the presence of an electrolyte, particularly water, and some sort of dissolved ions, whichever there are, that will be called aqueous corrosion. So aqueous corrosion is a bigger domain, and then what we are trying to show you can see in this surface as such anode and cathode are shown as the same surface.

One is acting as a cathode, which is losing material. So, this is a portion where the loss of the electron happens, and this is a surface where the electrons are getting captured, or with oxygen, and the reduction phenomenon is happening over here. So, there is oxidation here; there is a reduction over here on the same surface, and we can show this reaction as such. In this case, we are showing a kind of zinc that loses an electron. So the zinc ion here now goes to the cathode, and there is some sort of water ion there, and it acts without it, and then it makes some sort of this ion. So, this is a continuous phenomenon, which is why we see the reaction of the anode, metal loses electrons at the anode and that electron gets dissolved in the electrolyte, and then finally, metal ions get formed or produced. Meanwhile, in the case of the cathode, because there is an imbalance to make a balance, naturally electrons need to be absorbed, and then that is how the reduction reaction occurs, so the cathode and this act with oxygen and maybe with some sort of associated ion there at the cathode, and it will cause a balance of this.

Now, this involves zinc, as I mentioned earlier. Another material commonly used, especially in ships, is aluminum because aluminum tends to undergo passivation. When passivation occurs during aqueous corrosion, it's beneficial. However, if it doesn't happen, it raises concerns. Many textbooks attempt to explain aqueous corrosion using diagrams depicting copper and zinc. In such diagrams, zinc loses electrons while copper gains them, leading to surface damage due to material loss. As zinc loses electrons, iron may come into play, dissolving into the electrolyte, and the chemical process continues.

However, a question arises: Is this not galvanic corrosion? In my opinion, whenever two separate metals or materials are depicted in such diagrams, it resembles galvanic corrosion more closely.

However, in this case, the medium can be water. So, I can say the galvanic is part of the aqueous corrosion. However, we aim to clearly distinguish between the two types of corrosion: aqueous and galvanic, which we intend to store separately. What is the difference between galvanic corrosion and aqueous corrosion? In my opinion, aqueous corrosion, also known as uniform corrosion, is a type of corrosion that affects the entire surface of a metal. The process is repeated until the metal is entirely corroded, or it is protected by some sort of passive layer, or some additional barrier layer, or something like that, and then environmental variables like temperature, acidic nature, pH values, or some sort of contamination can really increase aqueous corrosion. So, these are related to aqueous corrosion. In relation to galvanic corrosion, we say galvanic corrosion occurs when two different metals or alloys are electrically linked or submerged in an electrolyte. So, even if I can operate with a battery, I can also create a potential difference there; I can start galvanic corrosion, or if I understand it, I can understand why in some materials we find galvanic corrosion.

So, that's why we want to keep it separate because there is some chemical activity of the materials coming into the picture, and properties of electrolytes are also involved, leading to more applications of galvanic corrosion in industries. We will try to keep this in a separate category.

Now, in this case, the metals are the same as what we have considered aqueous corrosion. In this galvanic scenario, one metal operates as the anode and the other as the cathode. The metal acting as the anode gets

oxidized or corroded, losing material, while the cathode receives electrons, thus maintaining conductivity in the whole cell.

To summarize, I can say that aqueous corrosion can occur without the presence of a second metal, while galvanic corrosion cannot. So, galvanic corrosion necessitates the presence of two separate metals and alloys, and that is why I am giving these two in a two-separate category. I do not want to be in the same category. Then comes the aqueous corrosion, which is caused by the chemical properties of the environment. So, more emphasis is generally given to the chemical properties of the environment as such. Whereas, in galvanic corrosion, we want to place more emphasis on the electrochemical potential difference between the metals and the presence of some water in the electrolyte.

So, here more emphasis will be given to metals or materials that have a potential difference. Aqueous corrosion will gain more emphasis on the environment. There are some differences, which is why we want to keep them in separate categories. Let's look at what galvanic corrosion means in our view. We say galvanic corrosion happens when two different metals or materials alloy with different electrochemical potentials. If they have the same electrochemical potential, I will not categorize them as galvanic corrosion, or if they have a very marginal difference, we will not classify them as such.

There is some difference, so that is why we say that there is something we want to keep in a separate category. When they come into the electrical contact because there is an exchange of electrons, the way in aqueous or a sink, the same thing happens, but we are using the word electrical contact with each other and there is a presence of electrolytes. So, we say galvanic corrosion happens when two metals or alloys with a different electrochemical potential come into electrical contact with one another while an electrolyte is present. When these different metals are coupled, they are made in the form of a battery unit, and an electrochemical cell is created, causing electric current to flow. These are important for us, of course. In rust, the same thing happens; in aqueous corrosion, the same thing happens, but we want to give in this weightier region, being the two different metals. Now here we are saying to differentiate that the more active, the less noble we are trying to give a degree to what kind of activity and how more reactive this is.

So, a less noble metal will corrode as a result. Suppose there are several materials available, some cheaper and some costlier. When constructing a complete structure, we know that the interior part is more difficult to replace, while the top surface is easier to replace.

I can utilize this understanding to minimize galvanic corrosion by using less noble material for the interior, allowing the outer surface to corrode, which is easier to replace and visible to us. This scientific approach can inform our design process.

Another important aspect to consider in galvanic corrosion is the shape of the surface and its microstructure. Both the surface shape and microstructure have a significant impact on galvanic corrosion, as I will explain. Let's look at this figure. Maybe say figs. 1 and 2, and there are what we are showing: cathode and anode are reversible here. Whatever the cathode, we are making anode here, and whatever the anode, we are making cathode. So, in this case, we see a large anode and a small cathode area showing relatively insignificant attack, which means that the larger size of the anode is preferable compared to the cathode. If this ratio of anode area to cathode surface area is something like 3, 4, 5, 6, or 7, it will always be preferable. In the second scenario, we say the anode is smaller and the cathode is much wider, or something like that. So, a large cathode area and a small anode area show a relatively pronounced attack on the fastener head. In this case, we are showing that the corrosion of this head will be very high.

So, naturally, now that we know the science of which surface should act as anode and which surface should act as a cathode, we can play with the kind of anode we can daily design according to that. So, if I try to

summarize this, we can say that the that the relative surface area of the two metals in contact affects galvanic corrosion. Another one is the microstructure. As I mentioned, the microstructure of a metal surface has an impact on how corrosion forms and is spread. So, if there is a corrosion with deformation, how will it spread? Now here we can say very clearly surface imperfection like scratches, cracks, and roughness that is going to increase the localized corrosion.

If you keep the surface free from scratches, cracks, or roughness, it will have a lower chance of corrosion. This principle is similar to what we've studied in wear phenomena and friction, where maintaining a smooth surface at a nano level reduces wear and corrosion significantly. Any additional manufacturing cost incurred to achieve this can be offset by the substantial benefits gained, like spending a penny to get a dollar.

It's essential to delve deeper into understanding this ionization process, particularly in the context of galvanic corrosion. Ionization occurs primarily at the surface atoms of a metal, as these atoms are loosely connected within the atomic structure. Their fewer bonds with subsurface atoms make them more susceptible to ionization. So, what I mentioned here is that ionization happens only to the items that are exposed, which have a lesser binding with other atoms. So, that is what has been mentioned. Now any impurity present acts as a catalyst. So, it makes the corrosion phenomenon, or it can enhance a corrosion phenomenon significantly.

So, we say that acts as a catalyst for the reaction and speeds up this process. I'm just trying to show an example to indicate that here we are using the term 'grain boundaries' to illustrate the three phases of the surface: top, front, and maybe side.

Now, if you want to just keep a graphene flack on a copper surface, something like a graphene flag can be placed on a copper surface. As such, copper has some resistance, but now graphene comes in, creating a sort of localized defect. If there is a localized defect, it is going to occur because graphene has good wettability. It can adsorb water easily, and then if it adsorbs the water, it is really going to facilitate the ingress of water to the copper inside.

So, copper will not be able to resist, and then there will be phenomena to change it. Now if there is a phenomenon like that and there are some other matters or the kind of galvanic corrosion available, then these are going to create a local defect or if there is some sort of vacancy. So, either we give some path because of impurities, like in this case I am using the word graphene flack on the copper as a kind of impurity, or there is some sort of vacancy. Then this is the transformation or the chain, the shifting of atoms or maybe atom ions is an easier one, and that is what we say, and the reaction will occur at a much faster rate and the corrosion rate will increase. While in this case there is a possibility of selective corrosion also, wherever you want to have a vacancy, we can create one and then make selective corrosion.

So, there are possibilities like that. Now to explain this in more detail, I will just take one reference, and in this case, what we are shown here is something like figures a, b, and c. In this case, whatever I have mentioned on the on the previous slide is the copper, and we are showing here the partial oxidation of copper at the graphene flake edge. The graphene is giving some sort of conducting path, or the path to ingress water inside the copper, and that has been shown here. Now here is what we are saying: this is some sort of edge that has been shown here, and there is a cut C that has been shown here. There is also some sort of patch that has been shown in this case. So, the graphene at the edge has been shown, which is getting partially oxidized because of the oxygen presence there, and from water it comes to, the oxygen will get absorbed in this surface, while at the center has also been shown, the patches are here.

So, it is for some sort of corrosion, and then just to elaborate, something like this has been shown; there are some sort of images, but coming to the D to DG, there has been some sort of schematic oxidation process. What has been mentioned here is the chemical absorption of water vapor. This water gets absorbed chemically with the

covalent bond on the surface, and then there is a really provided some sort of path, and then it should be shown here some sort of different colors, and these are basically water molecules, and then this water molecules has a hydrogen. That is why we are showing that black and white is a carbon, red is oxygen, and green sphere is a hydrogen. So, we are showing here in green and red that the oxygen is there and surfaces, while oxygen inversion has been shown here. Initially, oxygen gets attached to the carbon, and this has been shown over here, and then with the process, it gets inverted inside. Once oxygen gets inside, that is the partial oxygen of the copper.

So, water spreads onto the surface, and with the presence of graphene, it allows for partial oxidation of the copper. If we remove this impurity, it's quite possible that graphene will not have much effect on the surface. This topic will continue in the next lecture, Lecture 10, which will cover surface degradation mechanisms due to corrosion, Part 2. We will begin with this slide and then proceed with the lecture. Thank you for your attention.