Cathodic Protection Engineering Prof. V. S. Raja Department of Metallurgical Engineering and Materials Science Indian Institute of Technology, Bombay

Lecture - 02 Cathodic protection engineering: External corrosion of pipelines

Welcome to corrosion Protection Engineering lectures. We have so far discussed two important aspects, that is related to aqueous corrosion and the electrochemical aspects of electrochemical corrosion.

(Refer Slide Time: 00:35)



Today, we should be looking at the External corrosion of pipelines. Today's lecture will focus on the types of corrosion that affect the external buried structures. We will be looking at the role of the soil on the corrosion, microbes, metal surfaces, external structures in the vicinity of these buried structures and the applied stresses. How they affect the external corrosion of pipelines?

(Refer Slide Time: 01:09)



Pipeline corrosion is unique in one aspect, because the pipeline faces two types of corrosion; one, externally depending upon the environment be it a soil or in offshore sea water; two, internally the kind of commodities are the products the pipeline really transfers, and the nature of corrosion in both the cases externally and internally are different, both of them affect the life of the pipelines. The protective measures are different.

The cathodic protection as we discussed in the last class, is concerned with the prevention of corrosion of the external surfaces. The internal surfaces corrosion will be dealt with separately. So, when you talk about pipelines or even the tanks for that matter, we have to be very specific about what surfaces are we dealing with.

US office of pipeline	e safety (year 2002)	
Accidents:		
Total	: 81 (20 different causes)	
 Internal Corrosion 	: 14 (17.24%)	
Third party excavation da	mage: 13 (16.04%)	
External Corrosion	: 7 (8.64%)	
Flood	: 4 (6.17%)%	
% of Cost damages :	: ~\$ 24.4 million	
Internal Corrosion	: 15.23%	
External Corrosion	: 16.95%)	
• Third party excavation da	mage : 4.36%	
Flood	: 17.84%	
) Fil		

So, today we will be talking about the external corrosion of the pipelines, and also applicable to other buried structures. If you look at the year 2002 data of the US office of pipeline safety, it lists the following. It surveyed the number of accident occurred on the pipelines, in that year in the US they had about 81 cases of pipeline failures for 20 different reasons actually.

I have listed 4 of them here, which are prominent in natures in terms of the number of cases, they are the largest. Internal corrosion the pipeline stands the top most with 14 cases which accounts for 17.2% of the overall failures. The third party excavation damage is about 13 numbers which again accounts for close to about 16% of the failures.

The external corrosion you notice that it is little less than that, about 8.6% of the failures which are about 7 in numbers. The natural calamity such as flood accounts 4 numbers which are about 6.17%. But, look at the cost of the damages due to the four reasons which are listed above. The internal corrosion cost significantly about 15.23% of the overall cost of 24.4 million US dollars.

The external corrosion interestingly the number of cases were only 7, it constitutes only 8.64%, but in terms of the percentage of cost of damages it accounts close to about 17%. The third party excavation though they are large number in terms of 16%, it constitutes only 4.36%. The flood of course, in natural calamity you see about 17.84%.

What is to be noted is the cost due to corrosion is much higher than the natural calamities and also the man inflicted damages such as excavation. So, that is the reason why we should be worried about the corrosion control of these pipelines.

API grade pipeline steels Grade **Chemical Composition** Yield Tensile Yield Elong API 5L X80 Strength Strength $\sigma_y = 80 \text{ ksi}$ $\sigma_{uts} = 95 \text{ ksi}$ NR 0.029 0.21 0.015 0.025 0.161 1.76 0.014 0.019 0.000 0.003 0.111 0.09 0.37 4.6 0.38 Tensil %e = 20 Si Mn Nb Ti min Ratio (ksi) (ksi) (max) API 5L 0.16 0.45 1.65 0.020 0.010 0.07 0.05 0.04 52 66 0.93 21 X52 API 5L 0.16 0.93 0.45 1.65 0.020 0.010 0.07 0.05 0.04 56 71 19 X56 API 5L 0.16 0.45 1.65 0.020 0.010 0.08 0.05 0.04 60 75 0.93 19 X60 API 5L 0.16 0.45 1.65 0.020 0.010 0.09 0.05 0.06 65 77 0.93 18 X65 5L 0.17 0.45 1.75 0.020 0.010 0.10 0.05 0.06 70 82 0.93 17 0.15

(Refer Slide Time: 05:09)

In pipelines, API grade pipeline steels are very normally used for oil and gas applications, these pipelines are cathodically protected externally. I have listed here various grades starting from API 5L X52 to down to X70 grade steels. They vary in terms of the yield strength these in fact, this X52 corresponds to the yield strength given in terms of ksi.

So, these steels, the strength increases from say API 5L X52 to API 5L X70. You also notice there is a gradual reduction in the ductility, as expected when you increase the strength of the steel. But, what is important to notice from the corrosion perspective is that the chemical composition of this different grades of steels are not very significantly different, only a minor differences are taking place. These strengths are achieved by different heat treatments.

So, when the chemical composition of these steels are not changed, the external corrosion is not going to significantly change due to the variation of the strength of these steels. In addition to this API 5L 70 grade steel that I have listed here, there is also very somewhat recently developed steel, which is API 5L X80 whose yield strength is about 80 ksi, the ultimate tensor strength is about 90 ksi.

The elongation is reasonably good over 20 percent, but what distinguishes this API 5L X80 steel from the remaining steels is that there are micro alloyed, there are deliberate addition of some micro alloying elements in order to increase the strength of the steels. And also you see the reasonably good ductility, you can see is close to API 5L X52 grade steels. So, it got a good strength as well as good ductility.

Again you notice that the elements which normally affect the corrosion of the steel such as chromium, nickel; there is not significant amount in order to change the corrosion behavior or corrosion resistance of these steels. And therefore, there are different ways we should control corrosion, all the pipeline grade steels we can say comfortably that they are not resistance to corrosion of the soil.

(Refer Slide Time: 08:25)



Now, if you look at the external corrosion of these steels. The corrosion is you can recall back the discussion we had earlier, there are oxidation reaction which is anodic reaction, where iron is getting oxidized to Fe^{2+} and $2e^{-}$, there are cathodic reactions I listed two of them here. One is simply reduction of water leading to hydrogen, other case the oxygen present in the environment may be soil, maybe in the water also giving rise to cathodic reaction.

The point we are trying to look at here is that the corrosion involves a anodic reaction and cathodic reaction and these reactions occur on the surface in differing manner. In the case of uniform corrosion, where the corrosion is very uniform across the metal, the anodic reaction

and the cathodic reactions which are listed above, they occur equally all through surfaces over a time period.

Even though, at a given time they are spatially separated, but over a time period they even out in terms of the rate of reaction occurring on different locations. But in reality such a uniform corrosion may not occur in structures which are buried in the soil. It is possible that the cathodic reaction and the anodic reaction are separated spatially leading to a form of corrosion called localized corrosion.

So, we will be now discussing what are the factors that, affect the localized corrosion. As we discussed in one of the earlier lectures the localized corrosion is much more insidious, they cause unexpected damages to the structures than the uniform corrosion. So, we shall now understand what are the different forms of localized corrosion the burial structures are really facing.

(Refer Slide Time: 10:45)



One of the reasons the buried structures cause localized corrosion is the differential aeration. We have shown here pictorially two different cases on the left side this differential aeration arises because of the fact; the soil there are two types of soil, a soil which is loosely held especially that is surrounding the pipeline and then at the bottom of it you have a soil which is very packed, very highly dense.

So, when you have a loose soil, the permeation of oxygen in the soil becomes quite higher and so, you have large amount of oxygen content in the loosely packed soil as compared to the densely packed soils.

So, the area where the pipeline comes in contact with the packed soil, the oxygen content becomes less. As a consequence, this contact point becomes an anode, because the oxygen content is less over here. The remaining areas of the pipeline, you have significantly large amount of oxygen content that becomes a cathode.

We will talk about the reason in the next slide. All I would like to point out here is there are regions where the pipeline faces less amount of oxygen content and there are regions, where the pipeline faces higher amount oxygen content. This is causing us differential aeration corrosion, this arises mainly out of the soil properties; loose and densely packed soil the pipeline encounters.

There is another situation, where the pipeline is surrounded by things like rock or maybe a concrete block for example, they come in contact with the pipeline. So, at that location the oxygen fugacity or the partial pressure of oxygen is reduced significantly as compared to surrounding areas.

So, very similar to the previous case you have you know differential aeration or differential oxygen content that renders one place anodic, the other place cathodic actually. So, this is one type of localized corrosion, we call them as differential aeration corrosion.

(Refer Slide Time: 13:21)



Let me try to explain to you what causes the differential aeration corrosion, from the electrochemistry point of view. What we have seen in this? This is the kind of say; is a schematic of the anodic polarization curve of let us say steel buried in a soil.

What you see in this diagram is the metal passivates (it shows active dissolution) and then a passive dissolution and then a pitting or a transpassive dissolution taking place. This is the anodic polarization behavior of the steel.

Now, the corrosion potential you know is arising out of the intersection of the cathodic reaction with the anodic reaction. In this case the cathodic reaction is the oxygen reducing along with their I think is the water here, so H₂O is something missing here, this H₂O here ok. And this H₂O, oxygen, electrons released from the metal giving rise to hydroxide.

Look at this two cases when the oxygen content is significantly higher, the cathodic reaction rate is significantly higher here. On the other hand when the oxygen content is less as you notice within the crevice the cathodic reaction rate (kinetics) becomes slow and so, you will find that the corrosion potential, in the case of the where the oxygen content is very low it becomes lower. It intersects the active dissolution portion of the anodic curve and so the metal dissolves at higher rate.

When the oxygen content is higher you notice that the corrosion potential lies in the passive regions. So, in metals where you have situation of high oxygen content and low oxygen

content, the low oxygen content areas not only corrodes at a higher rate it exhibits relatively anodic potentials. And, the areas where oxygen content is more it exhibits cathodic potentials there is a sort of galvanic cell happening. So, this is a kind of localized corrosion occurring in the pipelines.

(Refer Slide Time: 15:51)



There are situations where the pipelines surfaces would have some metallic impurities, such as let us say copper or sometimes you have mill scales. The mill scales are the scales that are formed during hard rolling of the steel sheets, normally the mill scales are removed. The mill scales are not removed, they remain on the metal surfaces.

You can have impurities such as maybe a copper, or sometimes I would say deliberately there may be like a copper cables to which are grounded for example, onto the metal surfaces.

Now, these you know the impurities such as copper and noble metal or the mill scale, they exhibit a potential which is relatively noble as compared to the unrusted, clean or a bare steels. The bare steel exhibits about -0.5 to -0.8V with respect to copper saturated copper sulfate electrode. Whereas, the one with mill scale it shows about -0.2V.

Similarly, if you are going to have a copper on the surface it has about -0.2Vt with respect to copper saturated copper sulfate electrode. Sometimes you may have stainless steel fittings this is all called bimetallic corrosion.

So, in such a case the mill scale and the copper or the stainless steel fittings or even the rusted places where you have seen before, they act as a cathode and they are unrusted or sometimes you make a scratch maybe something like dented places, they become the anode. So, there is going to be localized corrosion occurring.

So, the anodic reaction is now centered around this area, a cathode reaction is centered around all these noble areas. So, that causes the localized corrosion occurring on the metal surfaces

(Refer Slide Time: 17:59)



There is yet another form of corrosion, which is called as microbiologically influenced corrosion. Microorganisms exist in the soil and these organisms, they colonize the metallic surfaces and wherever they colonize the metals become anode. And the remaining area becomes the cathode and in fact, the current from these colonized areas enter into the soil and comes back to the pipeline, and it returns back again to the anode.

So, localized anode formation is part of microbiologically influenced corrosion. Microbiologically influenced corrosion becomes very important, because about 20 to 30% of failures are due to microbiologically induced corrosion. The presence and activities of the microorganisms such as bacteria and fungi, they leads to corrosion of metallic structures. The steel in fact, is very highly prone to microbiologically induced corrosion.

Let us look at the role of microorganisms on the corrosion of metallic structures. The microorganisms do not directly damage the metallic structures; they are not involved in corroding the structures. The byproducts of the metabolic reaction that happens on the metal surface, they interact with metal and causing the corrosion. They also in fact, introduce crevices, pitting under the deposits, enhancing the corrosion of the metals.

There are several types of microorganisms that cause the corrosion. I have listed here three predominant type of microbes which are responsible for corrosion, they are anaerobic type, aerobic type and the acid producing type. Among these three the anaerobic type bacteria are very commonly present in the underground pipelines.

What does the a microbe really do say a anaerobic microbe, what does it really do? In this case called as sulfate reducing bacteria, it reduces the sulfate into sulfides. And these sulfides further interact with the corrosion product such as Fe^{2+} and form iron sulfide. And again it generates H^+ ions in the process these localized area consists of iron sulfides, which can depassivate the metal. In fact, in this area even the hydrogen can enter into the metal much more.

The other type of bacteria called the aerobic bacteria, predominant among them is iron oxidizing bacteria, it oxidizes Fe^{2+} to Fe^{3+} , enhances the reaction on the metal surface. Please look at this is an oxidizing bacteria, this is reducing bacteria. So, it requires oxidizing atmosphere, the other one requires reducing atmosphere.

There are other bacteria such as nitrifying bacteria, they produce acid and it can increase the corrosion of it. For example, it can convert the iron sulfide or hydrogen sulfides back into sulphuric acid and cause the corrosion of metallic structures.

(Refer Slide Time: 22:18)



I would like to explain, the role of microbes on the electrochemical corrosion behavior of the metals. We shall use the Evans diagram to explain how the microbes affect the electrochemical corrosion behavior of the metal.

The electrochemical kinetics for the cathodic reaction in this case H^+ combining with electron giving rise to hydrogen and a metal getting oxidized to metal ions both the kinetics are given here. This point wherein the rate of oxidation is equal to rate of reduction corresponds to the corrosion potential or the natural potentials. And you also have the i_{corr} which is the corrosion current density.

Now, if you have microbes it can alter either the anodic kinetics or the cathodic kinetics. In this case I have represented here, in a simple way the altering the anodic kinetics. Please look at this the slope which we normally called as Tafel slope is decreased significantly, because of the microbe. As it is decreased the corrosion rate is increased from this point to this point. And the corrosion potential has decreased from a higher value to a lower value.

In fact, when you talk about cathode production, we will see that we apply much higher negative potentials, in order to prevent the microbial corrosions. The reason being that wherever you see a microbial active place, it's very likely you have higher corrosion rate followed by lower corrosion potential or natural potential.

(Refer Slide Time: 24:08)



Now, we shall talk about the role of soil. What I shown here is a pipeline that goes through two different types of terrains, wherein the pipeline goes through a marshy land which is wet land here. And if it goes through marshy land and because it is a wet and that becomes an anodic area where the corrosion becomes higher, the remaining area becomes a cathode.

(Refer Slide Time: 24:42)



You can also have soil of different chemistry, you can have a clay soil, you can have a sand soil, you can have soils of different chemical compositions. For example, chlorides one place, sulfates in some other place, you can also have different pH of the soil.

So; that means, you can have differential soil concentrations, that leads to one area becoming anodic, the remaining area becoming cathodic. The current flows between two places, as you see here the area that is marked over here is called as anode. And current leaves this pipeline here, goes through the electrolyte and goes to the cathode again the current goes back to the anode here.

So, these are the different types of soil natures can cause corrosion. We can similarly what we have done in the case of microbial corrosion, explain using the Evans diagram how the electrochemical behavior of the steel changes because of soil chemistries. I have just listed here the electrochemical kinetics of the anodic reaction of the metal, you know the soil 1 and the soil 2.

You can see clearly that the Tafel slope changes. As the Tafel slope changes the natural potentials or open circuit potentials or Ecorr you can call it the change. As a consequence you see there is a change in the corrosion current densities. So, because of two different potentials existing in these two locations and one place becomes anode, the other place becomes the cathode.

(Refer Slide Time: 26:30)



There is yet another form of corrosion which is very important in the pipeline; the external corrosion of pipeline called as stress corrosion cracking. I will just talk about the basics of stress corrosion cracking. The stress corrosion cracking occurs, when you have a metal

exposed to the environment and this metal is subjected to a tensile stress, because of the design considerations.

Now, when you talk about stress corrosion cracking, it is very important to know what are the factors that affect stress creation cracking. I have listed here the different factors with respect to material, environment and the design. When it comes to material, the chemistry, the chemical composition of the material, the crystal structure of the material, the microstructure of the material, they all can affect the stress corrosion cracking.

In the environment, you have different type of chemical species present, the pH or I would say even the temperature of the pipeline then affect the stress corrosion cracking over the metals. In design, the stresses; it could be a residual stresses happening, because of the weldment or because of pick up stresses that is happening or the stresses because of the process conditions may be hoop stresses, can affect the overall stresses present on the metal structures. So, it is very important to know how these pipelines will behave with respect to stress corrosion cracking.

(Refer Slide Time: 28:17)



Now, why this stress corrosion cracking is very important? It is important because almost all grades of steels that we listed before, they be it welded ones or be it seamless stainless steels; they are prone to stress corrosion cracking. If it is a welded one the heat affected zone with coarse grains are more prone to SCC than the base metal.

The stress corrosion cracking in relation to the pipelines, there are two types of stress corrosion cracking. One is associated with the high pH and the cracking mode in this case is intergranular actually and it is associated mostly with bicarbonates and carbonates solutions that are surrounding the pipelines. And you know that when you have bicarbonate and carbonates the pH of the solution is about 9. And the high pH stress corrosion cracking increases with the raise in temperature; it is a temperature dependent process.

There is again one more type of stress corrosion cracking which is near neutral or low pH stress corrosion cracking. This type of cracking is differentiated from the high pH stress corrosion cracking in terms of the mode of failure; it is transgranular cracking in nature.

And as stated here, it occurs at the low pH about 6.5, the solution consists of carbon dioxide. As opposed to the high pH stress corrosion cracking, the low pH or near neutral pH SCC is less temperature dependence. Now, we have two types of SCC we have seen they are affecting all grades of these steels, we have seen earlier.

(Refer Slide Time: 30:20)



Now, how significant they are? Are they really that severe? I have shown here what are the parameters that the stress corrosion cracking can really affect. The stress crossing cracking can occur below the yield strength, it can occur below the fracture toughness. So, it becomes difficult for the engineer to design the structures.

Stress corrosion cracking, because of that the steel loses its ductility, it becomes like a brittle. So, stress corrosion cracking is a real problem from the point of your structural integrity of the pipelines, which you should be worried about. What are the other characteristics of stress corrosion cracking?

The stress corrosion cracking occurs in stages, they are initiation; occurs at different locations actually and small small nuclei of cracks form, they coalesce and then they grow. And these large cracks further join together and then the crack growth it becomes very large and ultimate failure occurs.

Now, if you look at the two types of stress corrosion cracking most IGSCC, the intergranular stress corrosion cracking failures occurring at high pH. They are due to hoop stresses; the crack characteristics are longitudinal in direction. And they occur you can see very nicely at a stress level 46 to 76 % of yield strength.

No residual stresses are found wherever people noticed high pH IGSCC failures. In the case of near neutral pH SCC, there are features which are localized, which assist the failures; these features are corrosion say is corrosion, gouges, weld toe and these are the ones which leads to stress concentration leading to the failures. So, the high pH stress corrosion cracking, the neutral pH stress corrosion cracking, they have different characteristics in terms of the damages.

(Refer Slide Time: 33:01)



There is other form of corrosion which is called as stray current corrosion, we shall be discussing stray current corrosion in detail, later and we also talk about how to control stray current corrosion. We shall give a small introduction to stray current corrosion so that you can complete the understanding of external corrosion of pipelines.

The stray corrosion occurs primarily because the cathodically protected structures, be it a pipeline or a storage tank when it encounters another metallic structure. And stray current corrosion is again predominant, when people use ICCP system.

And, in this case, the impressed current cathodic protection system, we use a rectifier; the driving force for the cathodic protection becomes very large. And the current that leaves the anodes goes to the soil most of the current while it may enter into the pipeline of interest or the structure of interest, which is cathodically protected, a part of the current enters a foreign pipeline.

And when the current enters the foreign pipeline or foreign structures and this current travels across the pipeline, because the pipeline provides a low resistance path. The current so entered has returned back to the source, so when the pipeline crosses the other pipeline of interest which is cathodically protected.

Close to this vicinity the current from the foreign pipeline enters the soil and then re-enters the host pipeline. You know that the current wherever it leaves, it is an anode and wherever it enters it makes the structure cathode.

So, the foreign pipeline has two characteristics where the current enters the pipeline it is made as a cathode there is no corrosion occurs. But, in the foreign pipeline where the current leaves and enters the soil it is made as a anode and so, the corrosion occurs over there. The current density at these locations are significantly large the damage can be quite significant.

So, this is one form of corrosion that can happen when you have foreign structures surrounded by the structure of interest in host structures. And we will talk about this in detail later as to how to prevent the stray current corrosion of the structures.

(Refer Slide Time: 36:18)



I shall come to the last topic of today's talk. How much of the metallurgical factors affect corrosion? With respect to external corrosion we see that. In the external corrosion with respect to uniform corrosion, even for that matter localized corrosion the various pipelines, various grades, do not significantly change the corrosion rate.

The metallurgy does not affect the corrosion, they behave almost the same because the corrosion resistant alloying element like chromium nickel are not significantly added to it.

So, we need to have control measures. What are the control measures given? Coatings and cathodic protection are given without which all types of all grades of pipelines will suffer external corrosion. There are of course the two types of cracking we see later which could be hydrogen embrittlement, stress corrosion cracking and hydrogen induced cracking.

But, these type of failures are very much dependent on the grades of steels. And they are also largely affected by the cathodic protection, if done in a reasonable manner in a correct manner, stress corrosion cracking can be controlled by cathodic protection. But, if you are going to have hydrogen embrittlement, then cathodic protection can be a problem. we will see that later too. (Refer Slide Time: 38:07)



Before we close this lecture, I would like to summarize, what we have seen so far. We have seen about nine different reasons for the localized corrosion of the buried pipelines, with respect to external corrosion.

They involved bi-metals, lack of oxygen content, differential concentration of the soil, metal impurities, mill scales, damaged surfaces because of the scars, bacterial corrosion, stress corrosion cracking, stray current corrosion. They are all different forms of localized corrosion happening on the metal.

We also saw that the chemistry of the pipeline steels generally used are not significant enough to alter the uniform corrosion or the localized forms of corrosion excepting the stress corrosion cracking over the pipelines.

Thank you. We hope to see you in the next lecture.