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Lecture – 14 Anodic protection engineering

Welcome to the last lecture of this course Cathodic Protection Engineering. In this lecture, we shall cover Anodic protection, and then we shall provide an overview of the lectures delivered so far.

If you look at it anodic protection, in fact, does not have much in common with the cathodic protection engineering which is the main objective of this course. If one wish to find any similarity we can say that both are electrochemical techniques which are employed for preventing corrosion on metallic structures. There ends the similarity.

In fact, typical cathodic protection engineers, they may not find this lecture very relevant. Then the idea of including this lecture in this course lies not only this lecture being academic, but also considered to be important to plan personnel where anodic protection engineering is important in some cases.

(Refer Slide Time: 01:32)



Now, let us look at today's lecture Anodic Protection and Overview of this course. This lecture as I told you before has two parts, the part-I involves understanding the principles

of anodic protection, then we should examine what are the applications these anodic protection can be applied in the field, and what limitations one faces when anodic protection is applied to various engineering structures. Then we will conclude this lecture by giving an overview of the course we have seen so far. So, let us look at the first part the anodic protection of structures.

(Refer Slide Time: 02:31)



Let us start with giving a perspective to anodic protection where it started with and how it becomes a technology. The anodic protection has its origin in the discovery of passivity of metals by Lomonosov in the year 1738. Later it was Michel Faraday who suggested that the film formation is the main reason for passivity of metals.

However, the anodic protection as an engineering concept can be attributed to C. EDELEANU who first published a paper in nature in the year 1954. He has shown using a potentiostat that the alloy 304 stainless steel held at different potentials in sulfuric acid undergoes different rate of corrosion. What is shown here in the left side this diagram is the variation of the corrosion rate with the applied potentials.

As you notice that in sulfuric acid, the corrosion rate increases as you increase the applied potentials. It reaches a maximum value, and then the corrosion rate decreases, it remains almost steady over a potential range. And beyond a critical potential the current the corrosion rate increases.

So, the corrosion rate seems to be related to the applied potentials. In fact, this forms a basis for the anodic protection of engineering structures. And it became a technology in the year 1970. If you see later this curve has a resemblance to anodic polarization curve wherein you plot potential versus current density that you will see in the next slide.

(Refer Slide Time: 04:35)



So, let us look at the principle of the anodic protection. What is plotted here is a well known potential versus the log i diagram; wherein, you notice that as you increase the potential as you increase the potential, now the metal source increase in current reaches a critical value, and then it remains constant up to this point, and then again the current increases.

This is a schematic of a polarization diagram of a passivating metal which shows active dissolution here, and then passive dissolution here, and a trans passive dissolution over here. Now, if you immerse this metal in an acidic solution or any corrosive medium, it attains the corrosion potentials defined by a cathodic kinetics and given by this particular line here. You can see this.

The cathodic kinetics, this is the equilibrium potential for the cathodic reaction, and as it polarizes towards negative potentials the current increases. You notice that at this point the cathodic current density is equal to anodic current density, and the metal exhibits a potential called as E_{corr} .

And correspondingly there is icorr which is called the corrosion current densities. Now, it is possible to reduce the corrosion rate of this metal by rising this potential to somewhere here in this region right. So, let us look at the difference between the anodic protection and the cathodic protection, how it these two things are appearing.

Suppose, if you are interested in cathodically protecting these structures, you bring down the potential from E_{corr} to a relatively more negative value in which case one has to apply a current density is given by this value that is the i protection that is the current required to protect cathodically is the difference between the cathodic current density and the anodic current density.

Please notice that this difference in the current is quite significant, because it is in the large scale right. Let us look at how the anodic protection is done. In the anodic protection, you rise the potential of the metal from the corrosion potential to the more positive value to hold the metal in the passive region right. And the current required to anodically protect this metal is given by the difference in the current density between the anodic current density here and the cathodic current density here.

Please notice again that it is in the large scale, the current required to protect the structure anodically is much smaller because the current is the difference between the passive current density and the cathodic current density at that particular potential. So, there is a huge difference in terms of the current requirement for the anodic protection and the cathodic protection of the engineering structures.

What is more important is that even though the current required to protect the structure anodically is small, the it is necessary that the system should able to provide a current, so that it can overcome this current which is called as critical current density. We will see this later.

(Refer Slide Time: 09:06)



So, we looked at the principles of the anodic protection and the cathodic protections. And it is necessary to understand how they are different in practice. Cathodic protection is a thermodynamic concept, and so it is applicable to all systems. You can simply bring down the potential towards a negative value, a corresponding decrease in the corrosion rate occurs.

However, anodic protection is possible only when the metals and the corrosive medium, they exhibit a passivity. So, it is restricted to certain systems, where the metals can exhibit a reasonable passivity. As we discussed the metal is made cathode, the metal is made anodic here.

Again the cathodic protection can give rise to complete immunity from corrosion, whereas there is a residual corrosion occurs in those structures which are anodically protected. But in fact in reality even in the cathodically protected structures the corrosion is not completely stopped. And so there seems to be much not much of a problem in adopting the anodic protection of the structures if possible.

As we have seen earlier the current requirement is high for the cathodic protection systems as opposed to just a few micro amperes per centimeter square required for a few tens of micro amperes per meter square required for the anodic protection of metal structures. This in fact is compared to a few milli amperes per centimeter square required for cathodically protecting the structures. The other problem that happens in the cathodic protection is when you are going to make the metal cathode; there is a possibility of hydrogen embrittlement because hydrogen can enter into the metal because of cathodic polarization. This, in another problem as far as the anodic protection is concerned because you are rising the potentials towards a positive direction, the metal has higher tendency to corrode and only thing that resist corrosion is the passive film formation.

If there are any species that can attack the passive film, then there is a great chance of localized attack like pitting can takes place or a crevice corrosion can takes place on these alloys or structures. Now, the other important difference is it is more tolerance towards potential control.

I can have a varying potential ranges. The only thing is the extent of cathodic protection can change. Whereas, in the case of anodic protection there has to be strict control of potentials if you move towards the active directions the corrosion indeed will increase it would not get reduced.

(Refer Slide Time: 12:29)



As we have seen that the anodic protection is restricted to the certain systems. I have shown you a list of them like sulfuric acid, phosphoric acid, nitric acid and nitrate solutions, and organic acid and caustic solutions, and corresponding metals are listed here ok. So, that means, the anodic protection is much limited as applicable to or in contrast to the cathodic protection of engineering structures.



Let us look at the sulfuric acid wherein anodic protection is very much utilized. We have taken sulfuric acid because it is the largest chemical produced the worldwide. And in fact it is an economic indicator how much sulfuric acid is produced is an indirectly an indicator of the economy of a country.

So, it is very relevant that we take sulfuric acid as an example for the anodic protection of the engineering structures. Then the anodic protection of the structures in sulfuric acid plants are the following the storage vessels, process reactors, heat exchangers and transportation vessels for corrosive liquid. So, a limited applications wherein the anodic protection can be applied.

(Refer Slide Time: 14:24)



Let us look at how it is important to have anodic protection with respect to sulfuric acid. This is a typical polarization curve ok. It is a schematic of polarization curve of a metal showing active passive transition. And it illustrates how the alloying elements and the nature of sulfuric acid can affect the passivity. And so how the alloys select and how and so how we need to change the alloy in order to reduce. So, this will illustrate how depending upon the nature of sulfuric acid, we need to change the alloy chemistry.

Let us look at this. Let me now describe this polarization curve here. Again what is very important is the passivation potential and the critical current density. As you notice that unless the system crosses the critical current density, the metal cannot achieve the passivity ok.

So, if you have a cathodic reaction that can substantially increase the reaction kinetics, it is possible that the metal can reach a corrosion potential that will lie in the passive region ok. And so it will exhibit a corrosion current density which is equivalent to the passive current density.

If the concentration of this oxidizer increases, then you notice that it is detrimental, then the mixed potential will lie in the transpassive region, and so the corrosion rate increases. So, in order to reduce the corrosion rate, we need to look for alloys which shows in extended passivity, so that is done by alloying elements using chromium. For example, the alloy 310 shows very high resistance to corrosion over a range of concentration of sulfuric acid.

If I look at the other side, if the oxidizer concentration is very small, the corrosion rate indeed is increasing right. In order to reduce the corrosion rate, we need to suppress the critical current density. And how it is done? It is done by adding alloying elements such as molybdenum and even chromium.

By lowering the critical current density, it is possible to reduce the corrosion rate. So, alloy selection is one of the means of reducing the corrosion of sulfuric acid in a typical plant. We do not really need to do anodic protection all along, but that is an advantage we will see that later.

(Refer Slide Time: 17:40)



So, based on this concept, various kinds of alloys are being considered starting from carbon steel with silicon, cast irons, stainless steels, cast stainless steels, higher austenitic stainless steels means containing higher amount of chromium, nickel and molybdenum, a one such alloy is alloy 20 Cb type alloys. And we also look at iron-chromium-nickel base alloys, nickel base alloys, zirconium and titanium, tantalum.

As you notice that these alloys as you move from the top to bottom, their ability to resist corrosion is increasing because they have extended passivity and also lower passive current density.

As you have seen earlier in the polarization curve that the corrosion potential can lie in the active region, the passive region and the transpassive region depending upon the conditions of sulfuric acid, and so we define this sulfuric has reducing, mildly oxidizing and strongly oxidizing conditions. So, the nature of sulfuric acid indeed affects the corrosion rate of the metals. Some cases, it is advantages; some cases, it can lead to more corrosion.

sulfurit 97-	100 % H ₂ SO ₄ at 70-120°C
Alloys	Corrosion rate
	mm/y
Steel	>2.4
Cast Iron	0.12-4.2
Ductile Iron	0.25
Type 304L	0.03-0.5 (can be as high as 2500 mm in 60% sulfuric acid)
Type 316L	0.06 -3.44 (can be as high as 1200 mm in 60% sulfuric acid)
Alloy C-276	0.33 Mo containing alloys
Alloy B-2	2.3 Concentrations

(Refer Slide Time: 19:11)

Some examples of the range of corrosion rates the sulfuric acid causes is given here. It is let us say you talk about sulfuric acid in the concentration range of 97 to 100 percent in the temperature range of 70 to 120 degree Celsius. You can see that the corrosion rate of steel, it can be greater than 2.4. There are cases where the steel can corrode even as much as 2000 millimeter per year if the sulfuric acid goes to about 60 percent and 70 percent concentration.

And same is the case with the cast iron and the ductile irons. 304L is relatively better than steel, but it also can exhibit a range of corrosion rates depending upon the concentrations. As I told you earlier that the corrosion rate of 304L stainless steel can be as much as 2500 millimeter per year in 60 percent sulfuric acid. And 316 is slightly better as compared to 304L, but however, it can reach the corrosion range which is not practicable to use 316L for any of the sulfuric acid applications.

Now, when the acid concentration is such that it is become reducing conditions that is when the concentration of the acid is lower, it is mostly reducing conditions then the alloys having high moly content is used. Because in reducing conditions, you see that you need to reduce the critical current density and molybdenum reduces the critical density.

So, these alloys are applied in reducing conditions or low concentration sulfuric acid. So, the application of stainless steels for low acid concentration is very difficult, because the acid becomes highly corrosive.

(Refer Slide Time: 21:21)



The advantage of sulfuric acid is that the sulfuric acid is a good conductor of electricity. And therefore, it has very high throw power. If you install a cathode the current can reach at a distance as much as 4.5 to 6 meter length.

And so if you have a typical heat exchangers, if you keep an cathode on both the sides of the heat exchangers, you find that heat exchanger can be completely protected using anodic protection. So, because of high throwing power of current, the anodic protection can be used for complex structures on the shell sides of stainless steels.

The stainless steels again as I said that it depending upon the temperatures and the concentrations the anodic protection is really applied. Generally the anodic protection is applied to 93 percent sulfuric acid, and somewhere between 98 and 99 percent sulfuric acid in these temperature ranges because the corrosion rate can be reduced to 0.01 in the range of 0.01 to 0.1 millimeter per year as you seen they are really higher at this concentration of sulfuric acids.

(Refer Slide Time: 22:42)



The beneficial effects of anodic protection is seen here. The corrosion of steel structures in sulfuric acid leads to contamination of sulfuric acid to an extent of to 5 to 20 ppm per day ok. By installing anodic protection, the constant the quality of sulfuric acid can be significantly increased, that means, you are going to produce high purity acids or even during transportation of sulfuric acid the anodic protection helps to retain the purity of sulfuric acid.

And it can be applied over a range of components say heat exchangers, shell and tube type, spiral and plate-type. And, and so the anodic protection is integral part of sulfuric acid manufacturing and transportation processes. As I told earlier you can see that the corrosion rate can be significantly reduced from 5 millimeter per year to 0.025 millimeter per year for sulfuric acid in the range of 96 to 98 percent up to a temperature of 110 degree Celsius and at a very low cost.

If there is no anodic protection, then you may have to apply stainless steels or nickel base alloys which are very highly expensive. And it is indeed being applied to large storage tanks of like 20,000 tons using the anodic protection. And because of anodic protection, the maintenance cost comes down and there is no need to apply any coatings. However, for smaller tanks, anodic protection is not viable; people go for phenolic coatings which resist the corrosion of sulfuric acid.

(Refer Slide Time: 24:48)

	Information a anodic pro	about tectio	the n		
	Solution	Electrode	and the second second second		
	H2SO4	Calomel, Pt-PtO, Hg-HgSO+.			
	Kraft solutions, fertilizer	Ag-AgCI Ag-AgCI			
	solutions				
	Sodium carbonate solutions	Mo-CoO3 Bismuth			
	Fertilizer solutions, oleum	Type 316 L st	ainless steel		
	hydroxylamine sulfate	Hg-HgSO4			
	Cal Metals Platinum cladded bi	thodes (permanent) Environment Various	0	
	applications)				
	Steel		Kraft digester liquid		
2	Illium G , C-276		H ₂ SO ₄ (78-105%)		
(-)	Silicon cast iron, C-27	6	H ₂ SO ₄ (89-105%)		
1	Copper		Hydroxylamine sul	ate	

There is some information that you might be needing in order to understand the anodic protection of engineering structures. You need various types of reference electrodes. This has been listed here. There is no need for me to go in details, there are ranges of electrodes.

Generally, if you are going to use let us say sulfuric acid, try to avoid contamination with the chlorides. They try to use micros micro sulfate mercury micro sulfate electrodes can be much useful. And so depending upon the nature of the chemicals, you have a range of reference electrodes which are applied in practice.

There are different types of cathode available in fact as opposed to the cathodic protection where we use anodes which disintegrate over a time period. The cathodes by nature because we are applying a cathodic current they are very stable; the range of cathodes starting from platinum down to copper are being used for various applications.

(Refer Slide Time: 26:07)



Typical anodic protection system that consists of a potentiostat as you see in here which is connected to a cathode and a reference electrode and of course, it is an internal protection of the tanks.

(Refer Slide Time: 26:31)

Summary-Anodic Protection

- Passive systems (metallic/environment) are amenable to anodic protection, provided they exhibit steep passivity, at a fraction of current required for cathodic protection and avoid using expensive alloys and coatings
- Anything in the system that damages passivity can be detrimental to protection of metallic system
- Anodic protection is done through a potentiostat that can hold the potential intact

To summarize the anodic protection what you have seen so far, it is obvious that only passive systems and the passive system depends upon metallic in the environment are amenable to anodic protection, that too only when the passive current density is significantly lower than the corrosion current density of the metallic structures.

If it is amenable for anodic protection, you need significantly lower current as compared to what you apply in the case of cathodic protection engineering. And also you avoid expensive alloys and coatings in the case of anodic protections. You will see later that cathodic protection by default requires coatings. As opposed to cathodic protection anodic protection does not require coatings.

The another problem with the anodic protection is that anything in the system that damages passivity can be detrimental to protection of metallic systems. For example, if there are chloride contamination, you see that the passivity deteriorates, the pitting potential drops, and the rise in potential towards anodic direction can be very detrimental. It can lead to pitting; it can lead to crevice corrosion.

The other important thing about anodic protection is it requires a potentiostat that should hold the structure at a given potential intact. If there is a drift in potential towards a negative direction, the metal will start corroding at a higher rate. So, potentiostat is an important part of anodic protection.

(Refer Slide Time: 28:50)



Before I end this course, let me give a brief overview of what we have seen so far. We all know that corrosion of engineering metals are spontaneous. No external force or energy is required to cause corrosion of engineering metals whether exposed to chemical environment. The other important point that we should keep in mind is aqueous corrosion follows electrochemical kinetics. Broadly it follows Butler-Volmer relationship comprehensively over a range of potentials. It follows Tafel relationship in a narrow range of potentials. In fact, the range of potentials we talk about in the cathodic protection, the aqueous corrosion follows the Tafel relationship ok.

Buried pipelines and storage tanks suffer different types of corrosion on both their sides. When they are exposed to soil, it undergoes different types of corrosion like differential aeration corrosion, microbial corrosions, even stress corrosion cracking and the like. And within the tank, if the corrosion is depends upon the nature of the process fluid that is being stored. So, as a case in the case of pipeline, the nature of the process fluid or the fluid that is being transported decide the corrosion of these structures internally.

The soil, when it comes to soil, as you noticed before it causes different forms of corrosion on the buried structures. Because the structures are so large like the pipelines or the storage tanks, and because they suffer different types of corrosion, cathodic protection is one of the most predominant means of controlling corrosion as opposed to the various methods available to control corrosion in a typical plant structures.

(Refer Slide Time: 31:31)

Cathodic protection criteria are used to establish cathodic protection system. Instant off-potential (-0.85 V CSE) and 100 mV (true polarized potential) Surveys: soil resistivity, structure to soil potential, line-current, drain-current, DCVG/ACVG to monitor the effectiveness of corrosion Establishing anode ground bed is one the most important aspect of cathodic protection engineering Anode resistivity (various governing equations) Anode potential and capacity (sacrificial anodes)

The important thing that one should understand and one should remember when you talk about cathodic protection is the cathodic protection criteria. The instant off-potential which we called as - 0.85 volt with respect to copper saturated copper sulfate electrode, and the 100 millivolt criteria which talks about the true polarized potentials.

The instant off-potential discounts any possible IR drop between the reference electrode and the structure whose potential is being measured with respect to the soil. So, these two criteria are very important. The first criteria that is its instant off-potential is reasonably easier as compared to the measuring the true polarized potentials.

When it comes to cathodic protection, the surveys are very very relevant and important. They involve soil resistivity, structures, structure to soil potential, line-current, draincurrent, DCVG that is Differential Current Voltage Gradient and ACVG that is Alternating Current Voltage Gradient to monitor the effectiveness of the corrosion. The DCVG and ACVG are mainly employed to look at the coating damages in the buried structures without being excavating the soil.

One of the most important thing in the cathodic protection is the anode ground bed. The anode as you know is something like an heart for the cathodic protection. It pumps the current into the soil, and the current then travels through the soil and then enters the pipeline. The current so entered in the pipeline brings down the potential to required levels. Establishing the anode ground bed involves understanding or calculating the anode resistivity with various governing equations we have seen actually.

And in the case of sacrificial anode, we have two more parameters the anode potentials and this anode capacity. The anode potential indicates the ability of the anode to drive the required current on to the structures, and the capacities of anode talks about the longevity of the anodes to protect the structures.

(Refer Slide Time: 34:21)



Let us look at the governing equations. The two kind of equations I would like to recall, one that is related to the current flowing within the soil and the current flowing in the metallic structures. And these two are governed by simple Ohm's law, but the relation between the pipe to soil potential and the current are of different kind and this relationship is related to either Butler-Volmer or the Tafel relationship which is logarithmic in natures.

What does it mean? Even a small variation in the potential can cause an exponential shift in the in the current density and vice versa. So, that means, even a small shift in the potential that applied on the metal surface can either increase the cathodic protection; or if you are not able to shift the potential towards cathodically, it might undermine the cathodic protection of the structures.

The other important aspect of stray current and AC interference corrosion is the other important aspect of cathodic protection is the stray current and the AC interference. The, these two factors affect the corrosion of the structures very significantly. In fact, for stray current, it can cause as much as few centimeters loss in thickness per year.

As far as AC current is concerned, it does not significantly affect corrosion as much as a dc current does. However, beyond certain level of AC current a part of the AC current is converted to DC current by a phenomena called Faradaic rectification and that can induce corrosion of the structures.

How do you determine whether the structure is suffering stray current corrosion? The surveys that we have talked about like current flowing in the pipeline, pipe to soil potentials can be used to determine if a structure is suffering from stray current corrosion.

There are various methods to avoid, to minimize the stray current corrosion, that involves increasing the resistance for the current flow in the soil, or you can relocate the anode bed, try to redistribute the current by having many number of anodes or the worst case use metallic bonds that is avoid the electrolytic conduction mechanism which induces the corrosion of structures.

(Refer Slide Time: 37:29)



We have also seen the role of coatings in the cathodic protection of the engineering structures. Mainly it lowers the current requirement for cathodic protection. It also causes lower attenuation which means making the cathodic protection very efficient over a long distance. When it comes to coating, the following properties are very important; their resistivity, adhesion, cathodic disbondment are the major properties that one should look at in selecting the coatings.

Rectifier is the source of current for the ICCP system. And the selection of rectifier depends upon the anode ground bed resistance and the current required to protect the structures. The purpose of rectifier is to provide current, regulate them so that the required pipe to soil, or structured soil potential is maintained.

(Refer Slide Time: 38:52)



There are two topics which are not so closely relevant to the cathodic protection we covered, one of that is the internal corrosion of oil and gas pipeline. But if you look at the internal corrosion, that also affect the structural integrity of the pipeline or even the storage tanks.

While the cathodic protection minimize the corrosion of engineering structures that are buried in the in the electrolyte buried in the soil or immersed in the any electrolyte, the internal corrosion is of different kind. If the cathodic protection does not affect the internal corrosion of any storage tanks or the pipelines, it depends on the kind of chemicals that are being handled.

In the case of crude, we all know that crude and even the natural gas, there are noncorrosive, but the impurities like but the impurities like water, hydrogen sulfide, carbon dioxide, chlorides, they are responsible for corrosion. Notably and those pipelines used in the oil and gas, their metallurgy does not significantly affect corrosion excepting the stress corrosion cracking.

So, the only way of controlling internal corrosion is application of inhibitors, coatings or even lowering the impurities such as water, hydrogen sulfide, carbon dioxide chloride and so on. And of course, similar relationship can be found in storage tanks, depending upon the process fluid the corrosion rate can change. The last part of the lectures we covered anodic protection. As I told you earlier, the anodic protection has least resemblance to cathodic protection excepting the fact that the anodic protection and cathodic protection are the techniques which employ electro chemical principles to prevent the corrosion of structures.

In the anodic protection as opposed to cathodic protection, we use a relatively positive potentials so that the structure is held in the passive region. The other important aspect of anodic protection that one needs to consider is that only passive systems one can apply anodic protection. When I say passive systems, it refers to both the metallic as well as the environment. The combination of metal and environment would only decide whether a given system will passivate or not.

One of the most important aspect of the anodic protection is that it requires very low current density as compared to those required for cathodic protection. One more difference if you want to say that between anodic protection and the cathodic protection is cathodic protection always involves an additional coating of structures, whereas in anodic protections no coatings are really applied.

So, I have given you a overview of the course that we have seen so far. And I do hope that you get a perspective of this course. It is not giving you the finite details about how to implement the cathodic protection, but this course is expected to give you perspective the basic understanding of cathodic protection, basic understanding of corrosion processes, the basic understanding of anodic protection, the internal corrosion of the pipelines and the gas pipelines.

And I do hope that this helps you to understand better the cathodic protection of any structures. And if you have any doubts and questions, you are free to contact me at this email that given here. And I wish you all the success in engaging yourself in Cathodic Protection Engineering.

Thank you for attending these lectures.