Cathodic Protection Engineering
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Lecture – 03
Cathodic protection engineering: Electrochemical principles

Hello, welcome to the 2nd lecture on Cathodic Protection Engineering. As I mentioned in the 1st lecture cathodic protection engineering is concerned with protecting engineering structures buried in soil and offshore structures against corrosion. I hope from the previous lectures you had an insight into corrosion basics, various forms of corrosion and their control.

We also saw in the previous lecture, cathodic protection engineering is one of the most important ways of controlling corrosion. In this lecture we will be touching, discussing electrochemical principles as applicable to cathodic protection engineering.

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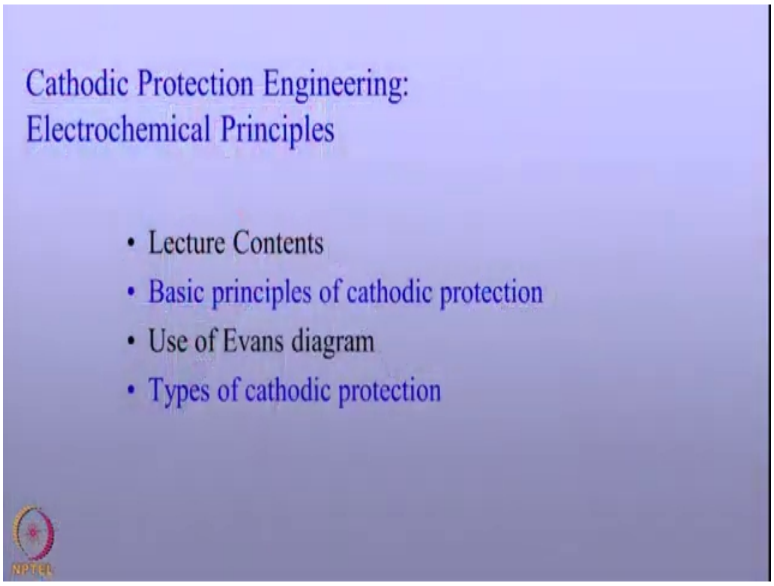

Cathodic Protection Engineering:
Electrochemical Principles

- Lecture Contents
- Basic principles of cathodic protection
- Use of Evans diagram
- Types of cathodic protection

We cover three important aspects of electrochemical principles; basic principles of cathodic protection, use of Evans diagrams and the type of cathodic protection that one may apply to engineering structures.

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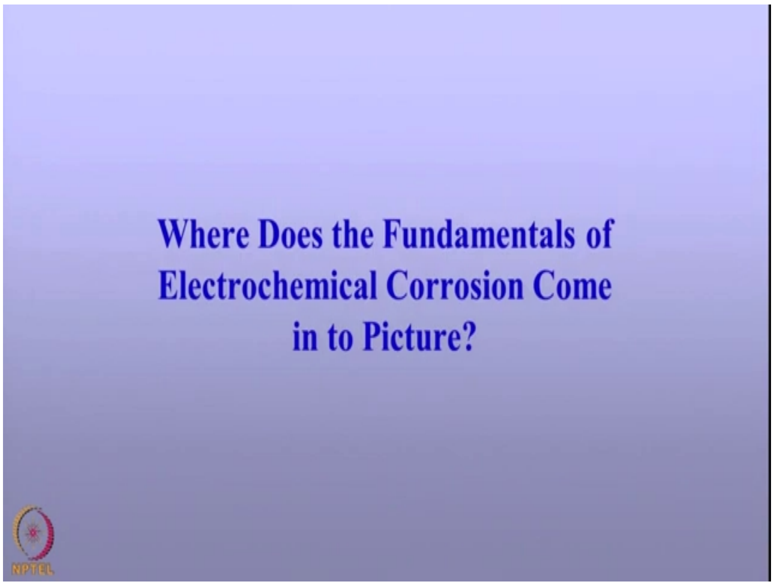

Where Does the Fundamentals of Electrochemical Corrosion Come in to Picture?

We shall now look at the important aspect of electrochemical corrosion; where does the fundamentals of electrochemical corrosion come into picture in cathodic protection engineering? In order to understand this I am going to replay one of the slides which we discussed in the previous lecture.

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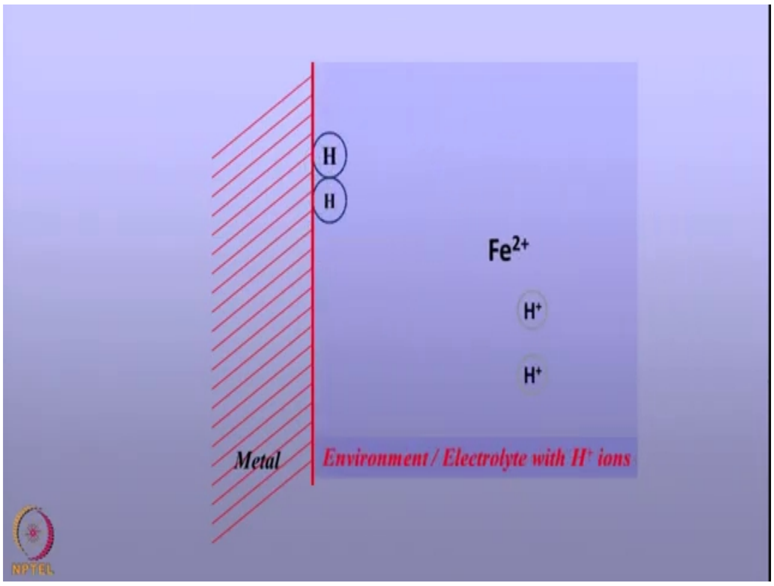

We talk about corrosion of iron in hydrochloric acid.

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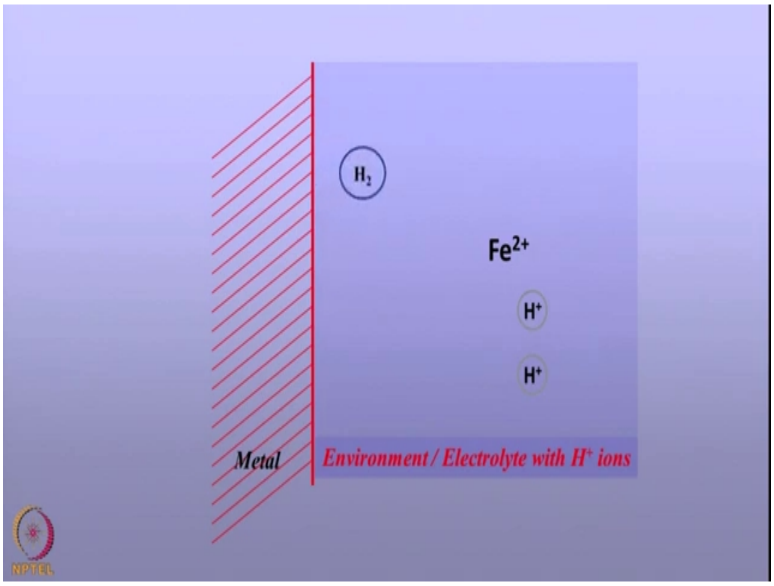

You see that iron gets oxidized and then the electrons so released are accepted by the hydrogen ions present in the solution.

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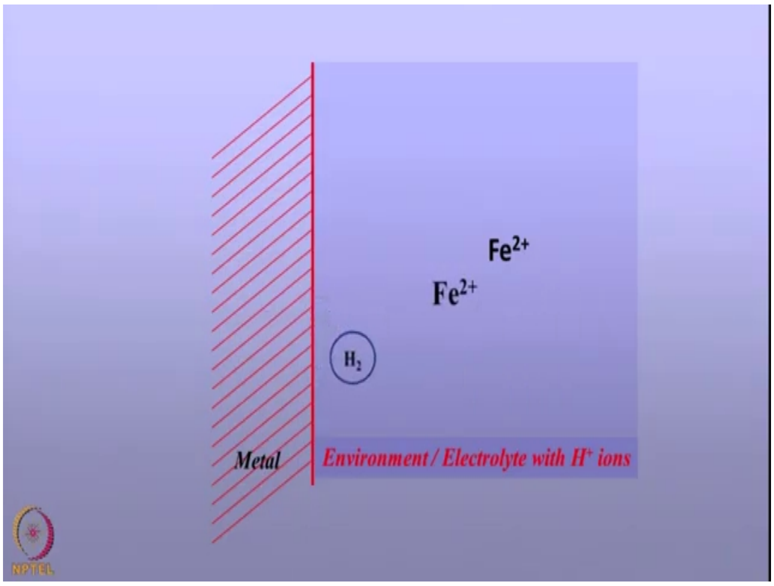

Now, in this process you see that the positive charges moves in one direction and the negative charges move in the counter direction. And, all this, a change of charges occur at the metal solution interface; that means, the reaction which is oxidation and the reduction they occur on the metal surface and they are involved in charges and they go in the counter direction and so there is net flow of current occurring on the metal surface. So, there is a flow of current occurring on the metal surface.

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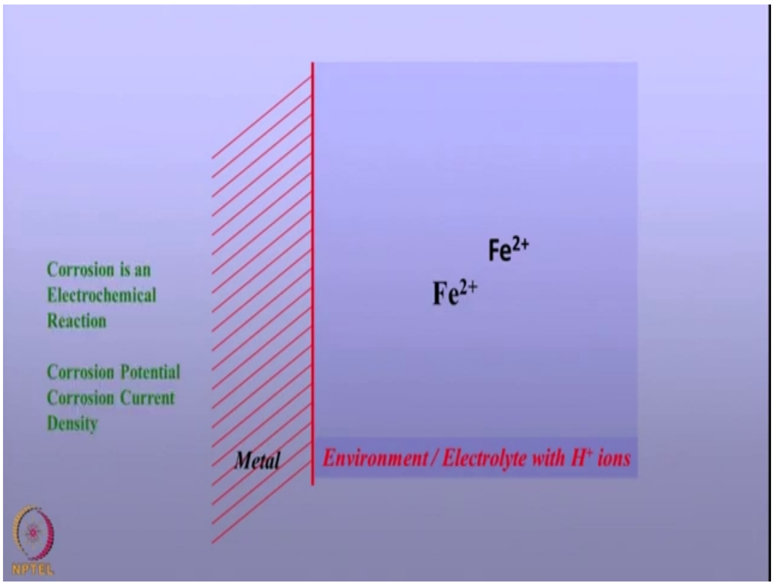

Corrosion is an
Electrochemical
Reaction

Corrosion Potential
Corrosion Current
Density

So, the current is flowing along with the reaction. So, the corrosion is electrochemical in natures. Because the charges are interacting at the interface, we can use potential to control the flow of charges in either directions. Interesting to ask is that suppose I immerse this metal surface in the acid and I use a reference electrode to measure the potentials, the metal will show a potential called as corrosion potential.

In the cathodic protection parlance we call them as natural potentials or it is also called as open circuit potentials. Because the current does not leave the metal surface, the oxidation reaction and the reduction reaction they occurred equally on the metal surface. There is a charge conservation taking place.

So, if you look at the metal oxidation and if you can use the Faradays law then you can calculate the corrosion rate. So, the charges flown per second is related now to corrosion current density in a sense that the aqueous corrosion is electrochemical in nature. Now, let us look at how do we really control the corrosion of this metal.

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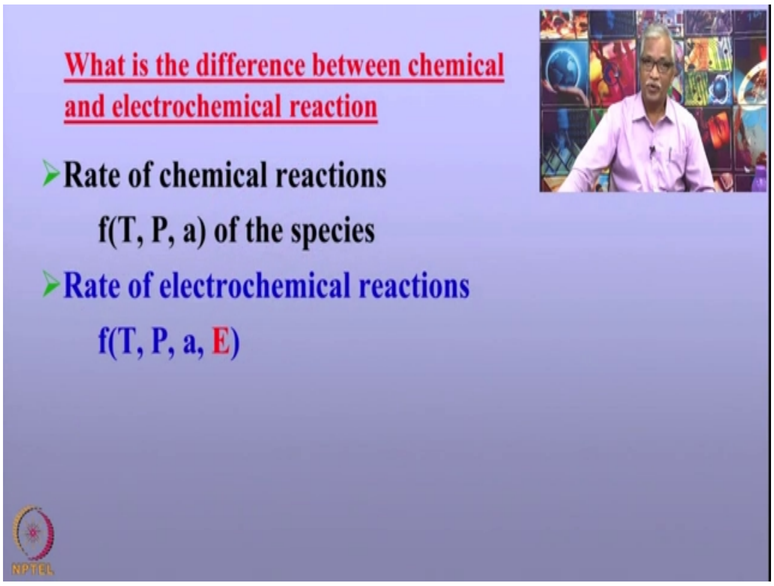

What is the difference between chemical and electrochemical reaction

- **Rate of chemical reactions**

  f(T, P, a) of the species

- **Rate of electrochemical reactions**

  f(T, P, a, E)

So, before we get into the cathodic protection I also want to bring out the difference between a chemical reaction and electrochemical reactions which you saw before. To summarize here, I can say that the rate of chemical reaction is a function of temperature, pressure and activity of the species. As opposed to that the electrochemical reaction is a function of again temperature, pressure, activity and in addition to that we have a potentials.

So, the potentials can be used to control the electrochemical reaction, in this case the corrosion process; you can either increase the rate of reaction or you can reduce the rate of reaction by applying the potential in appropriate manner.

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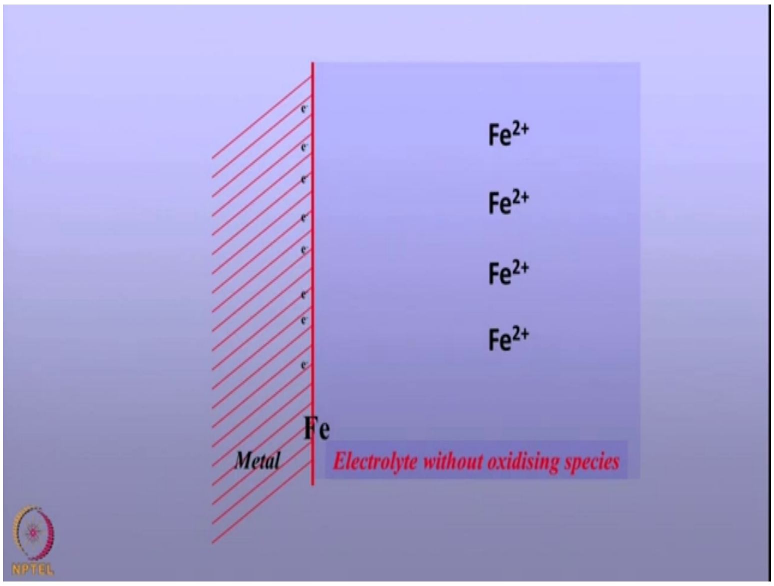

Now, when we come back to the corrosion; how do you control corrosion? Again I am going to replay this slide which we used in the previous lecture. Now, you see here that I have immersed the metal in electrolyte where the oxidizing species are not available. Assume for a moment that the metal has the tendency to get oxidized and if there are no species in the electrolyte to take away these electrons, then what happens? The oxidation of the metal does not continue.

That means as long as there is no oxidizing species in the environment, corrosion will not occur or if the metal surface is negatively charged using electrons, the corrosion will not occur. Then we go further in terms of how in practice we apply this science to prevent corrosion.

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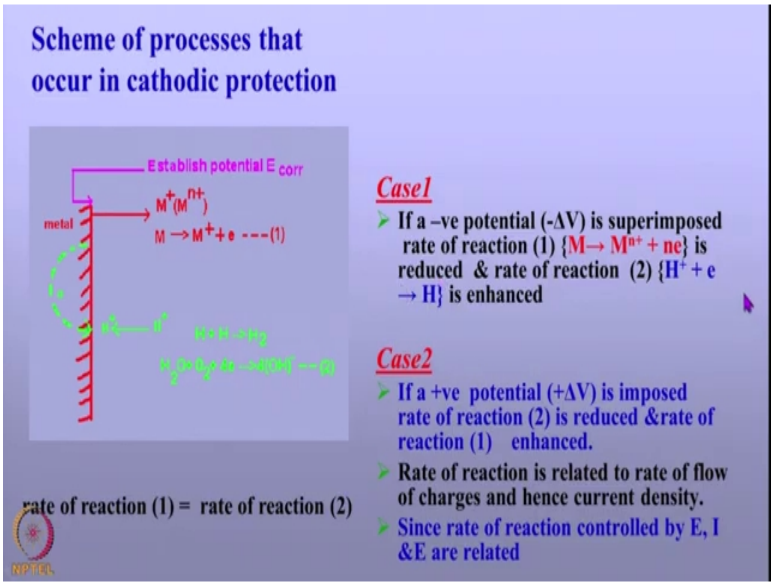

Scheme of processes that occur in cathodic protection

rate of reaction (1) = rate of reaction (2)

Case1

- If a –ve potential ($-\Delta V$) is superimposed rate of reaction (1) {$M \rightarrow M^{n+} + ne$} is reduced & rate of reaction (2) {$H^+ + e \rightarrow H$} is enhanced

Case2

- If a +ve potential ($+\Delta V$) is imposed rate of reaction (2) is reduced &rate of reaction (1) enhanced.
- Rate of reaction is related to rate of flow of charges and hence current density.
- Since rate of reaction controlled by E, I &E are related

This is a schematic of the corrosion processes occurring on the metal surface, there are two types of reactions; one on the top is given here is the metal is getting oxidized as metal ions here. And you can have either of these two cathodic reactions or you can have both of these reactions occurring together, wherein the electrons so release in this process they come over here to another location and the cathodic reactions accept these electrons and then reaction continues here.

As I told you earlier that the metal so established with these kind of reactions will have a potential called corrosion potentials. It is also to be noted that the rate of the reaction 1 and the rate of reaction 2 they must be equal in order that the metal will continue to corrode.

Now, let us look at what can happen if I change the potential on the metal surface? Let us take the case 1, if I am going to bias this metal surface with the negative potentials which means I am going to pump in electrons to the surface then what happens this reaction 1 is going to get reduced as per the least area principle right because you are going to increase the number of electrons on the surface, the reaction 1 will get reduced.

At the same time it is necessary to understand that the reaction 2 will increase, why does it increase, because in these case the electrons will combine with the H^+ and form hydrogen. So, the rate of the first reaction is getting reduced and the rate of second reaction is getting increased. So, this is one of the fundamental problems if you want to call it in the cathodic protection.

So, whenever you are going to reduce the corrosion by applying the potentials you will tend to increase the cathodic reaction we will see that some place at some place that it can cause some problems. So, this is something you should be understanding.

So, let us look at the second case for argument sake, now if I am going to increase the potential on this, if I am going to make this potential here little more positive by applying a relatively positive bias on the metal surface then what could happen? The reaction 1 will increase because you are going to take the electrons out, because you have bias the surface with the positive potentials.

So, this reaction increases and what would happen to the second reaction is very obvious that the second reaction rate will be decreased, because of the reason that the electrons are starved from the surface. So, the case 2; that means, if when you apply a positive potentials you see that the metal corrosion increases and the reduction reaction decreases.

So, this is the fundamental understanding of any electrochemical processes. To sum up so far what you have seen we can say that the reaction rate at the interface are controlled by the potentials and the potential in turn controls the current, the current in turn controls the rate of reaction. So, this is essence of the electrochemical reaction and the electrochemical corrosion processes and also applicable to cathodic protection engineering.

So, we have seen qualitatively what differences does it make when you apply a potential on the metal surface. Let us go little bit more quantitative in natures and see what kind of relationship exist between the potential and the current that is very important actually, because if I want to bring down the potentials I must know how much current do I have to apply in order to bring down the potentials so that the cathodic reaction is reduced.

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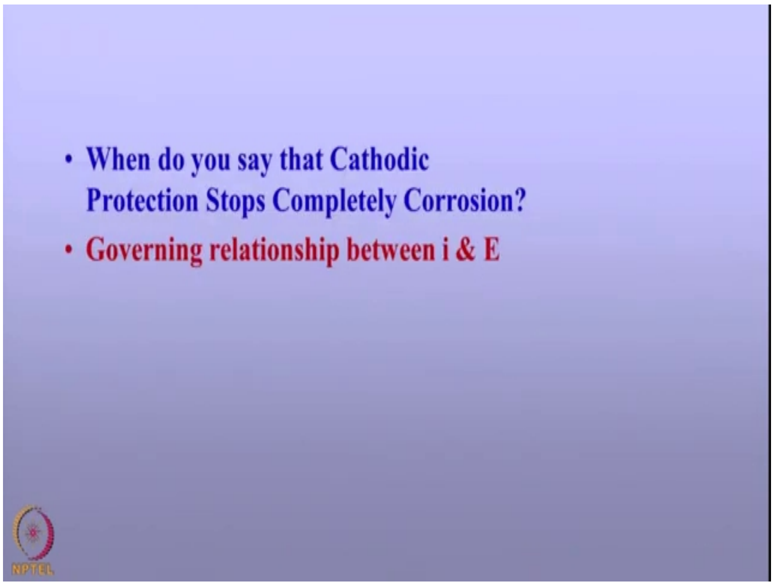

- When do you say that Cathodic Protection Stops Completely Corrosion?
- Governing relationship between i & E

Now, so that means, we need to know the relation between the current density or current and the potentials. In order to answer this question that, when does a cathodic protection completely stop the corrosion on the metal? Or we are going to in fact, see do we really need to completely stop corrosion at all will there be a problem at all.

So, these issues of course, we will talk about when you talk about the cathodic protection engineering. A cathodic protection engineering is more practical and the scientific principle that you apply you know sometime may lead to engineering problems. So, we will see that to what extent you can apply potentials so that you can have control corrosion of the metal structures.

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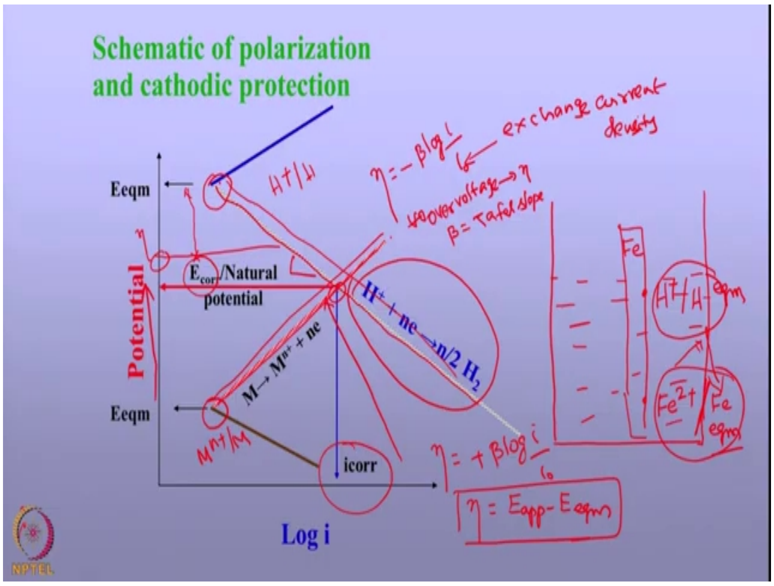

Schematic of polarization and cathodic protection

Let me now go to the important topic a bit more a difficult topic actually I will try to explain this particular diagram, this diagram is called as the Evans diagram. So, let us now look at the governing relation between the potential and current, this is very much important.

And that governing relationship is given by this diagram which is called as the Evans diagram. What you see in this diagram? There are two locations, one is representing the equilibrium potential for one type of reaction that is the equilibrium between let us say H^+ and H occurring on the metal surface.

There is also another equilibrium that occurs on the same metal surface between a metal and the metallic ions. I shall now illustrate the two equilibria that we have just now discussed in terms of the metal the environment interaction using a schematic diagram. Suppose I take a beaker and dip a metal strip into this beaker and the steel is immersed in an acid, suppose I immerse like this at the time equal to 0 just after immersion I would say assume that at two locations the two equilibria are established.

Let us say H^+ is establishing an equilibrium with hydrogen, in another case this being iron I will say establishes an equilibrium with iron and iron 2+ and these two locations would have different potentials which are called the equilibrium potentials of that. And these equilibrium potentials would depend upon the standard potentials for these two equilibria and the activity of these species present in the solutions.

So, without going much into details about the values of the equilibrium potentials, it is sufficient to say that these two equilibria would establish two different potentials on the same metal surfaces. And, because they have two different potentials the metal is conducting now and it is very difficult for these two locations to maintain these potentials, the resistance offered by this metal is going to be very small.

So, what would happen naturally is the potential of this equilibria will move towards the potential corresponding to this. Similarly, this equilibrium will start moving towards the H^+ and that is what is represented in this diagram here. In this Evans diagram, the equilibrium potentials of in this case the H^+ and H is given here and the equilibrium potential of metal ions and metal is given over here.

When the drift takes place, when the potential corresponding to the H^+-H is moving towards the oxidation of the metal and the oxidation of the metal move towards the reduction of other species, when the potential starts moving what is the relationship between the current is given here. So, as you start raising this potential and see the current starts increasing for the metal oxidations.

Similarly, the current for this also increasing as it is moving towards potential here. And so that is what is represented in this diagram; this is for the reduction reaction H^+ plus electron gives you hydrogen, in this case the metal is getting oxidized to M^{n+} plus n electrons here. Now these are governed by some equations; this is governed by a Tafel equations which is, $\eta = -\beta \log \frac{i}{i_o}$ where η corresponds to the over voltage and β corresponds to the Tafel slope. The slope can be obtained from this particular plot and i_o corresponds to the exchange current density.

Similar relationship exists for the metal oxidation as well you can also write a similar equation for that wherein in this case, $\eta = \beta \log \frac{i}{i_o}$. Now, you will ask me, what is η? The η is the deviation from the equilibrium potentials, any potential that you take and the difference between these values are called as η here.

So, to get to give it in the equation form, $\eta = E_{\text{applied}} - E_{\text{equilibrium}}$. So, there is a clear relationship between potential and the current in the electrochemical corrosion process of metals. And, these governing equations unfortunately we cannot discuss much in details it is out of the scope of this course, but those who are interested I would recommend for you to read further.

But let us come back to this the implication of this diagram right what are the implications of this. Let us take this oxidation of the metal that goes like this and reduction of the H^+ ions following this line here and you see somewhere at this particular point the rate of oxidation is equal to rate of reduction.

The metal will remain neutral at that particular potentials because the rate of the reaction 1 the reaction 2 are going to be the same and so the metal will remain neutral always. And this potential is called as corrosion potentials, this also called as natural potential in the parlance of cathodic protection engineering.

And because the metal is held in these particular potentials it dissolves at a rate given by the corrosion current density. So, this is in fact, an important diagram for cathodic protection engineering and those who practice cathodic protection engineering, I would request that you understand it more thoroughly so that you can apply it and you can model also cathodic protection using such diagrams.

So, now we have seen in this slide, how the corrosion potential occurs on the metal surface and what is the corresponding corrosion current density. And, when you know corrosion current density you can always determine the corrosion rate using Faraday’s laws right. It is possible to do that.

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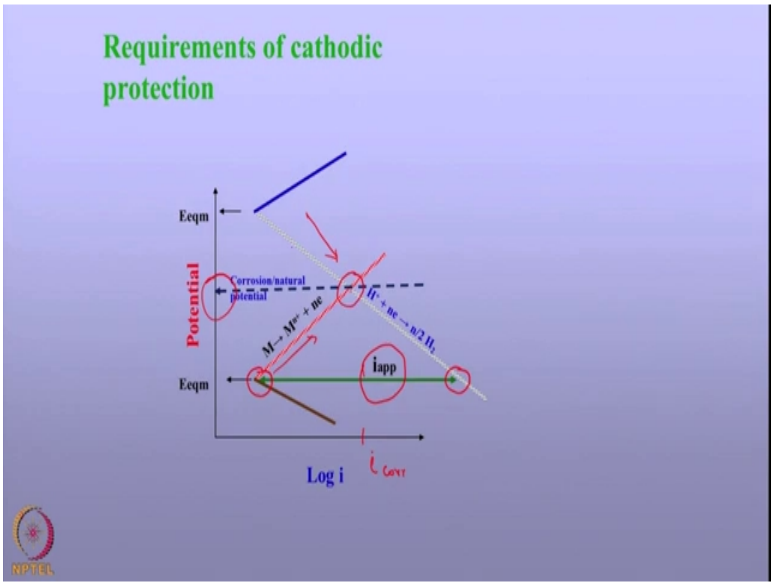

Requirements of cathodic protection

Having understood the relation between potential and the current and how the corrosion potential or so called natural potential has occurred in a metal that is immersed in the soil or maybe in a corrosion environment, you will also like to know how to prevent the corrosion, how to prevent this corrosion is given by the same Evans diagrams.

Let us look at this Evans diagram now a bit more closely. When a metal is immersed in a electrolyte or maybe a soil you may call it, it establishes a potential called corrosion potential which is given here, or natural potentials. Corresponding to that also there is a corrosion rate that happens here i_{corr} right.

Now, I need to bring down the corrosion current density to the equilibrium current density then the metal would show complete immunity to corrosion actually. So, that is what had to be done. So, how do you do this? That means, I need to bring this potential from this point to this point.

So, that is possible by applying an external voltage. By applying an external voltage I move from this particular potential to this particular potentials. If I do this the oxidation reaction decreases, but the reduction reaction increases you see this here now; that means, you need to apply more current in order to bring down the corrosion rate of the metal from the i_{corr} value to almost a nil value and this current is called as applied current.

So, the cathodic protection engineering requires current that is dictated by the anodic kinetics of the metal and the cathodic kinetics of the reduction reactions which means they are all following the Tafel lines.

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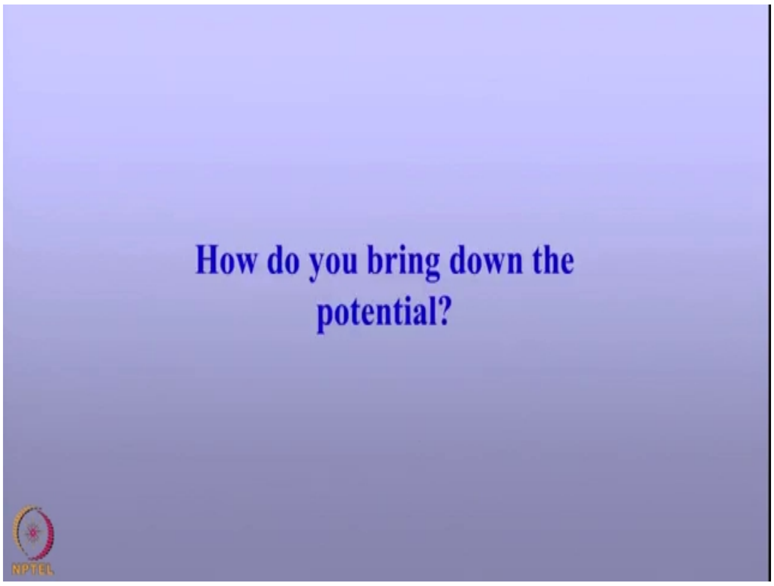

How do you bring down the potential?

So, the next question is, how do you bring down this potential? What are the ways to do that?

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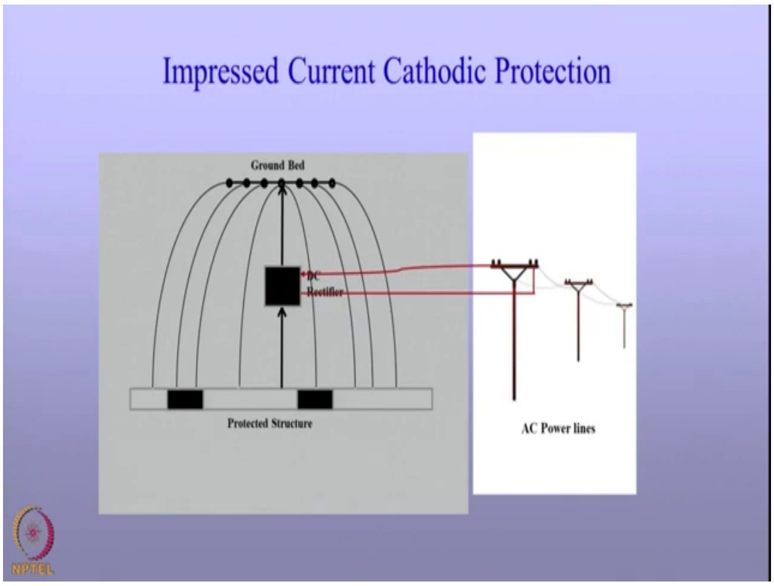

Impressed Current Cathodic Protection

There are two ways of doing it; first let us go into one method this is called as impressed current cathodic protection system. What is done in this system is that you have anodes which are buried in the soil or the electrolyte whatever be the case and you apply current to these structures through these anodes using a DC rectifier. And, the positive terminal of this rectifier is connected to the anode, the negative terminal or rectifier is connected to the pipeline.

So, current enters the soil through this anode and then from the soil the current enters the pipeline, in that way you can bring down the potential of the pipeline to the required values and this is called as impressed current cathodic protection system. Obviously, for this you need to have the AC power lines, that is one of the requirement without which it is not easy to have impressed current cathodic protection application.

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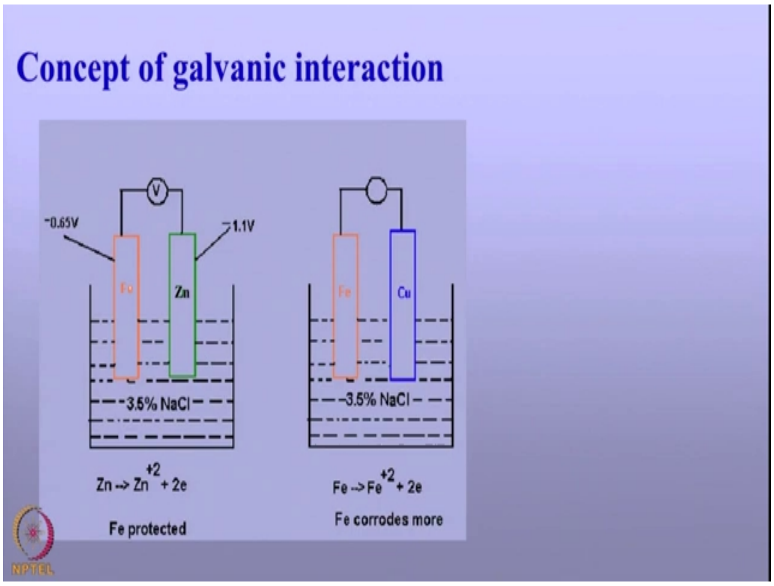

Concept of galvanic interaction

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

Fe protected

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

Fe corrodes more

There is one more concept that can be used in the cathodic protection of engineering structures, this is based on the galvanic interactions. I hope you remember that we talked about the galvanic corrosion, what is the galvanic corrosion? When you have two different metals let us say in this case iron and copper, the metal having a relatively positive potential will be cathode and the metal which is having relatively negative potential will be the anode.

And, the anode will get sacrificed to prevent any corrosion of the so called cathode here. So, this is called as a galvanic corrosion. In this case you do not want the corrosion of iron to occur because it is going to destroy the structure. Let us look at a different scenario now, suppose we have iron, a steel to that you are going to have a galvanic coupling with the zinc metal here.

Now, zinc metal you know, it has a potentially about -1.1 with respect to copper saturated copper sulfate reference electrode. And, the steel would have a potential somewhere in the range of -0.65 volt, if you do so then what happens is the zinc corrodes in this particular manner and the iron is getting protected. And, this is called as sacrificial action. This is another type of cathodic protection applied to prevent corrosion of metals.

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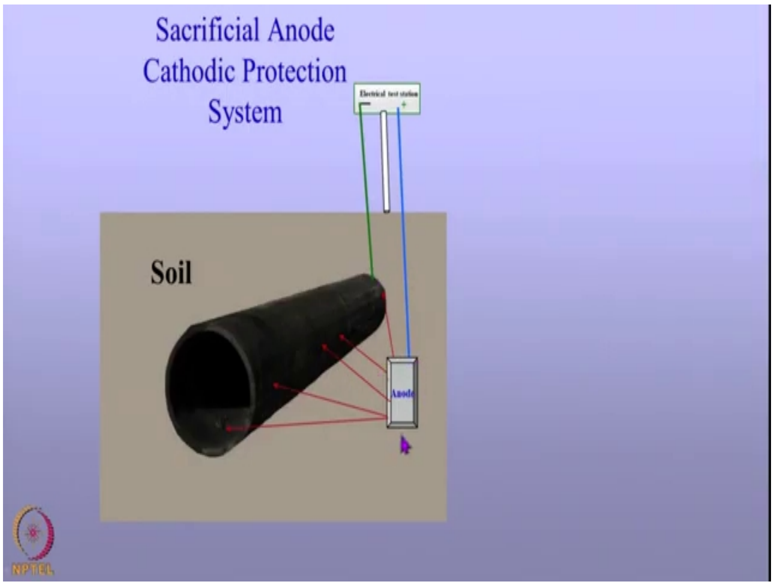

Sacrificial Anode
Cathodic Protection
System

The same is given in a schematic manner in this diagram here and you can see this is a pipeline buried in the soil, you have an anode and in this case of course, you have a test station. The anode is connected to the positive terminal of the test station and then the pipeline is connected to the negative terminal of the test station and the currents flows from the anode and then you know the pipeline is getting prevented from corrosion actually.

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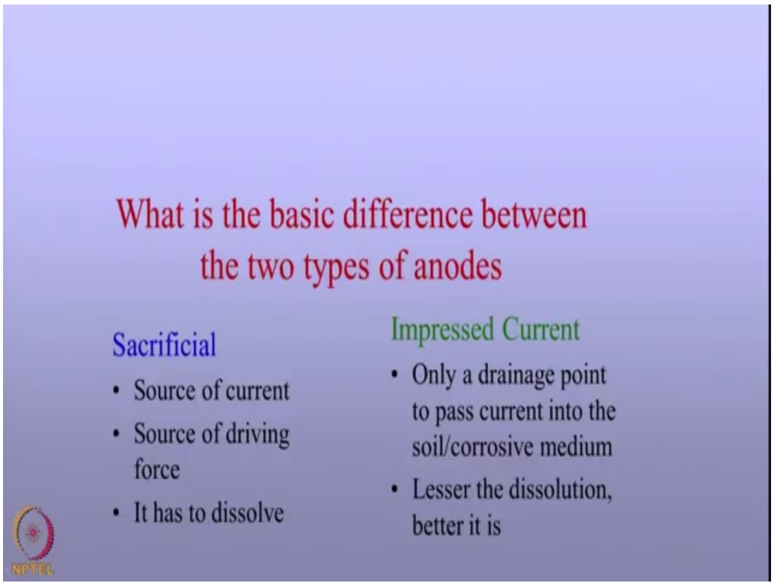

What is the basic difference between the two types of anodes

Sacrificial

- Source of current
- Source of driving force
- It has to dissolve

Impressed Current

- Only a drainage point to pass current into the soil/corrosive medium
- Lesser the dissolution, better it is

Now, we have seen two types of cathodic protection systems, in both cases we use anodes. What is the basic difference between the two types of anodes? It is very interesting and important to understand the differences actually because that decides the selection of the sacrificial anodes. In the case of sacrificial anode, the anode acts as a current source, it also drives a current. So, it undergoes the dissolution process.

On the other hand, in the impressed current cathodic protection system, the anodes mainly function to as a connector to pass a current into the soil and so, we do not want the metal to dissolve we do not want this anode to dissolve. So, we expect this to be of lesser dissolution. So, the function of these two anodes are different from sacrificial to the impressed current systems.

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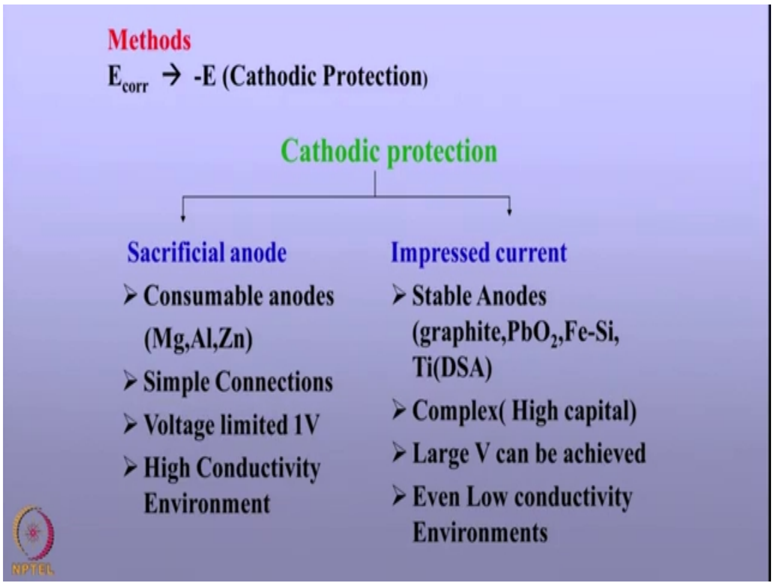

Methods

$E_{corr} \rightarrow -E$ (Cathodic Protection)

Cathodic protection

Sacrificial anode

- Consumable anodes (Mg,Al,Zn)
- Simple Connections
- Voltage limited 1V
- High Conductivity Environment

Impressed current

- Stable Anodes (graphite,PbO_2,Fe-Si, Ti(DSA)
- Complex(High capital)
- Large V can be achieved
- Even Low conductivity Environments

We also like to see what is the major difference between the two types of cathodic protection systems. I have given a few of them here, you can have more but these are the major differences between the sacrificial anode cathodic protection system and the impressed current cathodic protection system.

In the sacrificial anodes cathodic protection systems, as we discussed earlier, we use consumable anodes like magnesium aluminum and zinc; not only they are consumable, their potential has to be significantly negative enough to drive the current onto the buried structures; the potentials are equally important.

In the case of impressed current cathodic protection systems, the anodes are expected to be stable. Of course, there are also consumable anodes, but generally we prefer stable anodes. These are like graphite, lead dioxide, iron silicon anode, titanium insoluble anodes, for example. So, these are the predominantly used impressed current anodes, as you seen in the previous diagram, the circuitry involved in the sacrificial anode cathodic protection system is quite simple.

But, in the case of impressed current system, the circuitry the control systems are quite complex and it involves high capital as well. Because, the sacrificial anodes have a definite potentials it cannot operate in environment of low conductivity or high resistivity; you can apply only in high conductivity environment, as opposed to that the impressed current systems are driven by the a rectifier.

So, you can use even in highly resistive environment there should be no problem. So, these are some of the major differences, but there are few more differences that you will discover as you start working on cathodic protection of structures.

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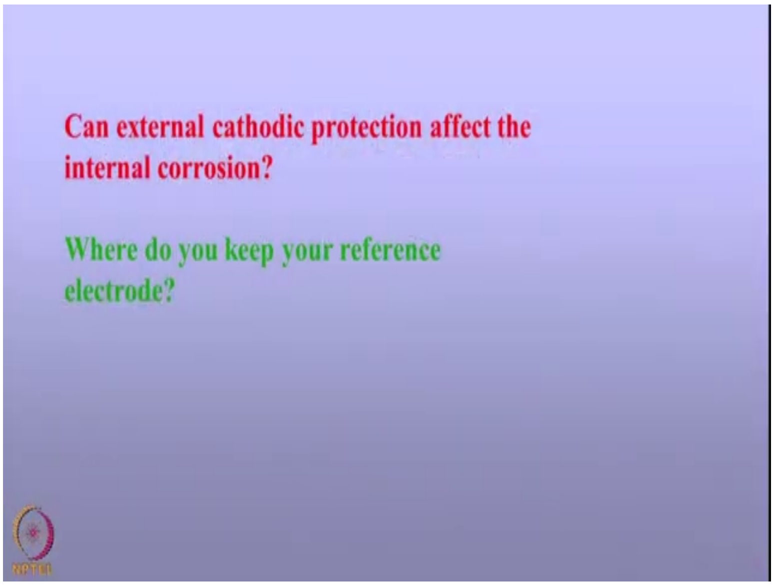

Can external cathodic protection affect the internal corrosion?

Where do you keep your reference electrode?

The question that people ask often is suppose we carry out the cathodic protection for the external surface, can it really affect the internal corrosion at all? It is necessary to understand that the external cathodic protection does not affect the internal corrosion because the current flows between the anode on the external surface and it does not enter into the internal surface of the metal. As to the second point where do you keep your reference electrode, we will come back to this later we will discuss later on this.

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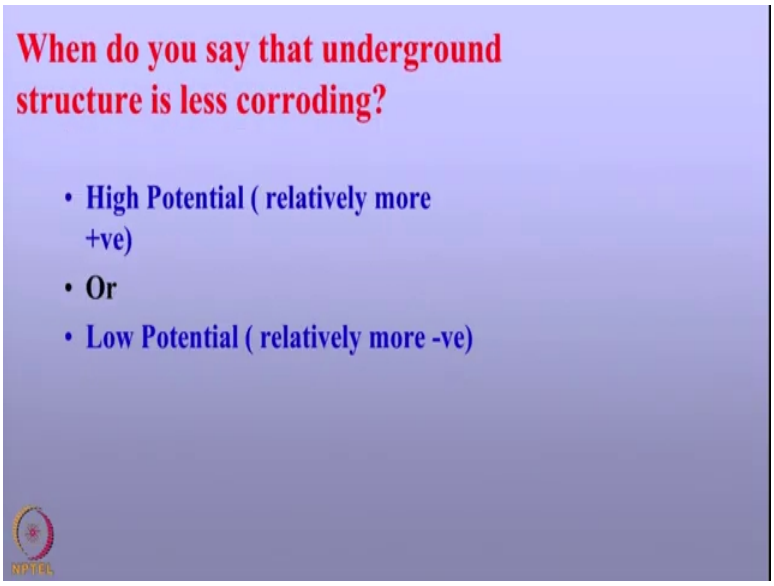

When do you say that underground structure is less corroding?

- High Potential (relatively more +ve)
- Or
- Low Potential (relatively more -ve)

There are other questions people ask and sometimes they get confused; when you measure the natural potentials or the corrosion potentials it gives an indication about the corrosion tendency of the metal.

Now, you have a number right, you have a number measured with respect to copper saturated copper sulfate electrode or maybe silver chloride electrode or reference electrodes for example, by measuring the potential in fact, you will see later potential are one of the indicators of the corrosion tendency of buried structures.

One would sometimes get confused should we have relatively positive potential to say that the metal is less corroding or should it be relatively more negative potentials to call the structure is less corroding.

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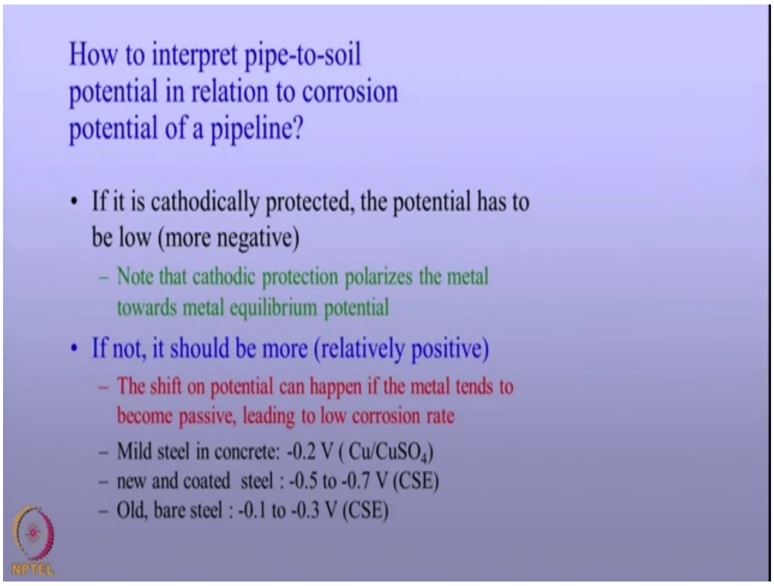

How to interpret pipe-to-soil potential in relation to corrosion potential of a pipeline?

- If it is cathodically protected, the potential has to be low (more negative)
  - Note that cathodic protection polarizes the metal towards metal equilibrium potential
- If not, it should be more (relatively positive)
  - The shift on potential can happen if the metal tends to become passive, leading to low corrosion rate
  - Mild steel in concrete: -0.2 V ($Cu/CuSO_4$)
  - new and coated steel : -0.5 to -0.7 V (CSE)
  - Old, bare steel : -0.1 to -0.3 V (CSE)

Now this is a important one I would like to summarize this without going much into details. There are two criteria, you should look at, one is whether the structure is cathodically protected or not. If the structure is cathodically protected more negative is a potential and less is the corrosion tendency of the metal.

If it is not protected cathodically, if it is freely corroding metal then the issue is somewhat different, the issue is that if the metal shows relatively more negative potentials it will corrode more. If it shows relatively less negative potentials it will corrode less because these potentials arising out of the cathodic polarization and anodic polarization of the metal.

If the metal is strongly passivating, the corrosion potential moves upward it becomes relatively more noble I would say. And so, if the metal is not cathodically protected less negative value of the potential means it is less prone to corrosion.

You can also see this in real life situations that the bare metals or new metals you know which are exposed to the soil would have relatively more negative potentials, they suffered more corrosion as compared to the old metal where the surface is covered with an oxide film which is a passive films.

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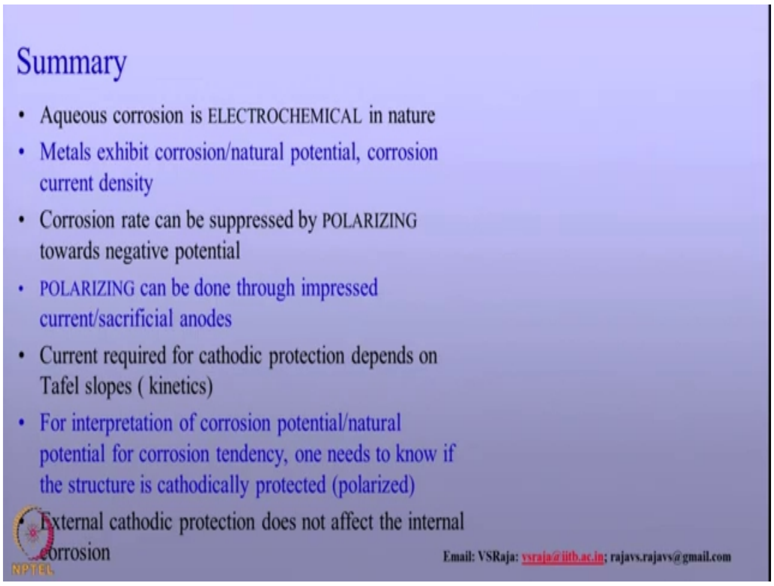

Summary

- Aqueous corrosion is ELECTROCHEMICAL in nature
- Metals exhibit corrosion/natural potential, corrosion current density
- Corrosion rate can be suppressed by POLARIZING towards negative potential
- POLARIZING can be done through impressed current/sacrificial anodes
- Current required for cathodic protection depends on Tafel slopes (kinetics)
- For interpretation of corrosion potential/natural potential for corrosion tendency, one needs to know if the structure is cathodically protected (polarized)
- External cathodic protection does not affect the internal corrosion

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So, I am going to summarize what we have discussed so far. We are now clear that aqueous corrosion is electrochemical in natures. Metals when they are exposed to the corrosive environment they show a potential we call them as corrosion potential or in the cathodic protection engineering terminology we call them as natural potentials.

At these potentials, the metal exhibits rate corrosion which is given by corrosion current density. The corrosion rate can be surprised by polarizing towards negative potentials. So, the polarization is an important concept in cathodic protection engineering. You bring down the potential from the open circuit potentials or from the natural potentials towards equilibrium potentials actually the corrosion rate is getting reduced.

Polarization can be done through two methods: impressed current cathodic protection system and sacrificial anode systems. Current required for cathodic protection it depends upon the Tafel slopes or Tafel kinetics actually. In fact, those who are interested in modeling cathodic protection of metals these concepts are very very important.

For interpretation of corrosion potential, also called natural potential in relation to the tendency of the metal to corrode, one needs to know if the structure is cathodically protected which is polarized or if the metal is not protected cathodically; that is a very important thing you should know before we interpret the pipe to soil potential and to corrosion of the metals. We also saw that the external cathodic protection does not affect the internal corrosion of metals. And, with this we shall end today’s lecture.

Thank you very much.