**Cathodic Protection Engineering**
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**Lecture – 09**
**Cathodic protection engineering: Anodes**

Welcome to the lectures on Cathodic Protection Engineering. In the lecture on anode ground bed; we discussed the relation between soil resistivity, anode dimension, and the relation to the ground bed resistance offered for cathodic protection of engineering structures. It is however important to understand; how the anodes perform in order to have better anodes for cathodic protection of structures. So, in this lecture we will discuss these aspects.

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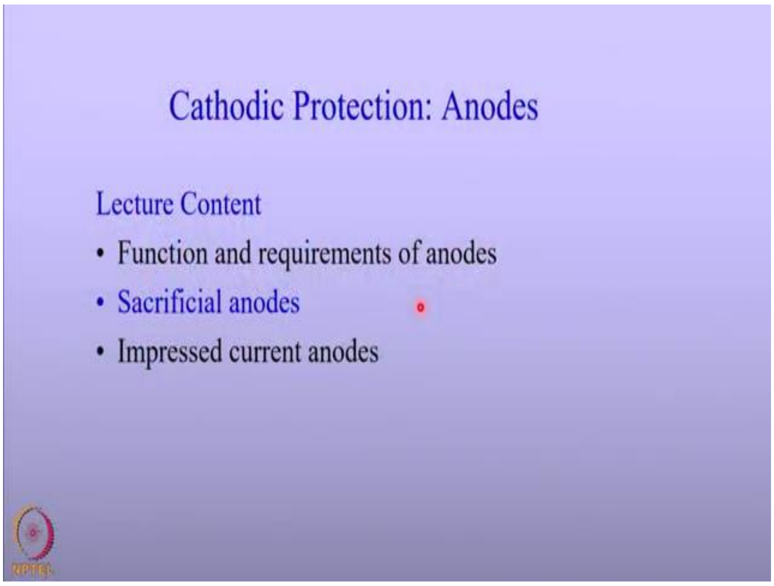


We will start with function and requirements of the anodes, then we will move on to understand how the sacrificial anodes are performing and then we will have a very brief discussion on the impressed current anodes.

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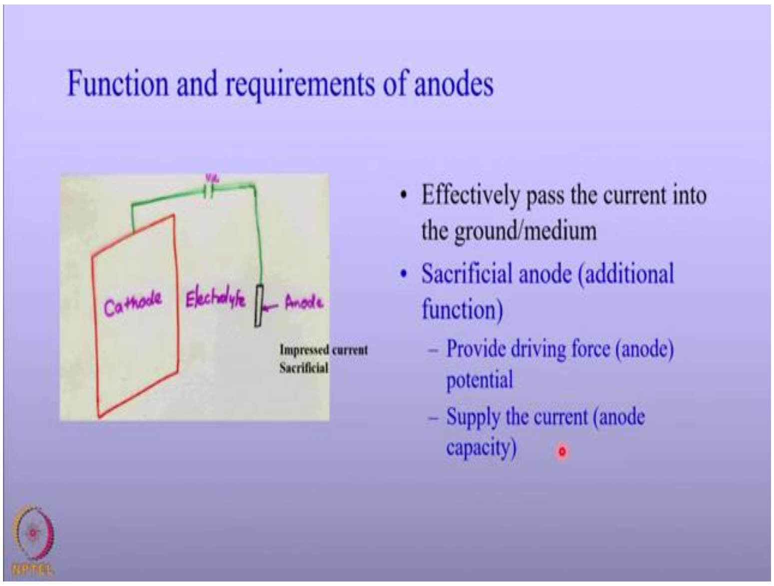


To start with the functions and the requirements of anodes, this is the diagram we saw in the last class itself; what you notice here is the anode in the cathodic protection system. The anode is very small and is buried in the soil and the current leaves the anode and goes through the electrolyte and then enters the cathode.

We have two types of anodes available for cathodic protection of engineering structures. They are the impressed current cathodic protection anodes and the sacrificial anodes. In both these anodes the main function is to effectively pass a current in the ground and the medium, that is the main function of this anode.

However, when you talk about the sacrificial anode, it has to do an additional function. One is it has to provide a driving force to pass the current between the anode and the cathode, that is given by the potential of the sacrificial anodes. And, then it also has to give the current that is given in terms of the anode capacity; whereas, in the case of impressed current cathodic protection system, the rectifier provides the driving force, the rectifier provides the current.

So, when you talk about sacrificial anodes we need to look at the two important characteristics. These characteristics are driving force available for the cathodic protection of the structures and how much is the current capacity these anodes would give so that we can design a particular life required for the structures.

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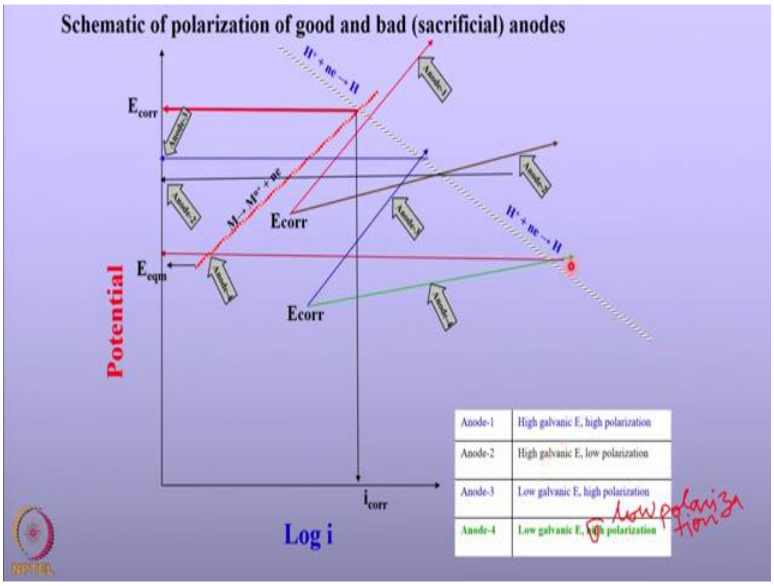


I am going to spend a couple of minutes, in discussing the role of the polarization diagrams in order as to understand, what is a good sacrificial anode and what is not an acceptable sacrificial anode. This is a famous Evans diagram we all know the potential versus Log i current, the lines given here are the tafel lines, the tafel relation between the anodic current and cathodic current in any electrochemical system.

Now, I would like to point out here, that this particular tafel line that is represented here which is;

$$M = M^{n+} + ne$$

M equals M n plus n electron is the anodic tafel line. How it varies with respect to the polarization? On the same metal of course, there is a reduction reaction occurring, that is probably here in H plus combining the electrons giving rise to n H 2 plus 2 actually ok and you can also have other cathodic reactions.

$$H^{+} + ne = H$$

The other cathodic reactions are like, the oxygen reduction reaction or reduction of water, that can occur when the metal corrodes. So, when you have a cathodic reaction represented by these kinetics and the anodic reaction represented by these kinetics, you have a corrosion potential established by the metal and then the corresponding corrosion current density.

Now, the metal that has to be protected cathodically the potential of this metal that is corrosion potential, it has to be suppressed towards a more negative direction here. How is it possible? It is possible by connecting this structure to a sacrificial anode. Now, let us look at the four different characteristics of the anodes ok.

Now, in these four different characteristics we have taking two different anodes of differing corrosion potentials. That is with these anodes are buried in the soil and buried in the electrolyte, they establish a potential called the corrosion potential you call $E_{corr}$ here. Now, the characteristics of the anodic dissolution of these anodes are given here.

What you notice here the anode 1. When you raise the potential it polarizes steeply; that means, the tafel slope is higher in this case. The same anode when you increase the potential, it polarizes at a much lower rate actually; that means, with increase in potential it delivers more current as compared to the anode 1 here.

You also can have another anode of lower corrosion potentials you can see here; wherein, you can establish a higher polarization as represented by the line here anodic 3 here or you can also have a lower polarization, that is seen here ok. So, depending upon how it polarizes the net potential is changing. Now, as you notice here that the anode 1, when galvanically coupled with this metal here it establishes a corrosion potential.

I mean galvanic potential somewhere here that is small drop in the corrosion potentials. And, as a consequence the reduction in corrosion rate is less significant, but for the same $E_{corr}$, if you take this anode 2 here the corresponding intersection point you notice by this line here leaves a galvanic potential of given over here for this galvanic potential the corrosion rate of the metal is given over here.

So, there is a significant drop in the corrosion rate of the structure the metal that we are talking about. But, take this case of the second anode the other anode for example, having same $E_{corr}$, but whose polarization is quite fast quite steep, but it establishes a galvanic potential slightly higher than the anode 2.

That means, it is able to protect the steel structure at a much lower capacity as compared to that Anode, it is having a low $E_{corr}$ itself. So, $E_{corr}$ is one factor, but what is more important is how the polarization really occurs. I mean the anodic polarization really occurs. Coming to this anode 4, it has got a lower potentials and it is less polarized and so, it gives you much lower galvanic potentials.

As a consequence, the metal is protected much better as compared to anode 1 2 and 3. So, in summary we can classify the sacrificial anode as the one having high galvanic potentials what is seen here and high polarization. You can also have high galvanic potentials, but lower polarization.

You can also have low galvanic potentials and high polarization and you can have low galvanic potentials and high polarizations. So, the efficacy of the anode depends upon both the galvanic potentials and as well as the polarizations.

So, if you have I am sorry this should be lower polarization, anode should be of lower polarization, I just want to make a correction here, this should be low polarization ok. So, ideally the anode the characteristics should be as follows; lower galvanic potentials are lower $E_{corr}$ potentials and lower polarization. Let me take this pointer again. It is to be noted; however there are some cases where low galvanic potentials or low corrosion potentials are not wanted.

Especially, when we are talking about use of high strength steels and in marine conditions you do not want the potential to come down the protection potential to come down to very low value. As you notice that when the metal is when the metal potential is brought down to lower values, the amount of hydrogen that is evolved on the surface is also increasing.

So, one has to also take care of the problems associated with over protections. So, which means you can have a combination of the potentials and the polarization. So, that you can also take care of the hydrogen evolution, you can reduce hydrogen evolution. In the case of high strength steels the hydrogen evolution of the metal surface can lead to absorption of hydrogen and then as a consequence the hydrogen embrittlement.

The other important property of the sacrificial anode is the current efficiency. The current efficiency is given in terms of the amount of current that is available for protection of the structures. So, when the metal dissolves the electrons are liberated and these electrons travel through the circuit to the structures and these electrons are used to bring down the potentials.

But, it is possible that a part of these electrons are used to liberate hydrogen or it is possible that a chunk of anode drops from the surface. As a consequence, there is a loss in current efficiency.

The current efficiency is given by this equation;

current efficiency = (actual current / theoretical current) × 100

the percentage current efficiency is equal to the actual current upon the theoretical current multiplied by 100.

So, this talks about how effectively the anode is used in protecting structures against cathodic protection. Let me move on to the next important requirements are the characteristics of sacrificial anodes that is; the anode current capacity.

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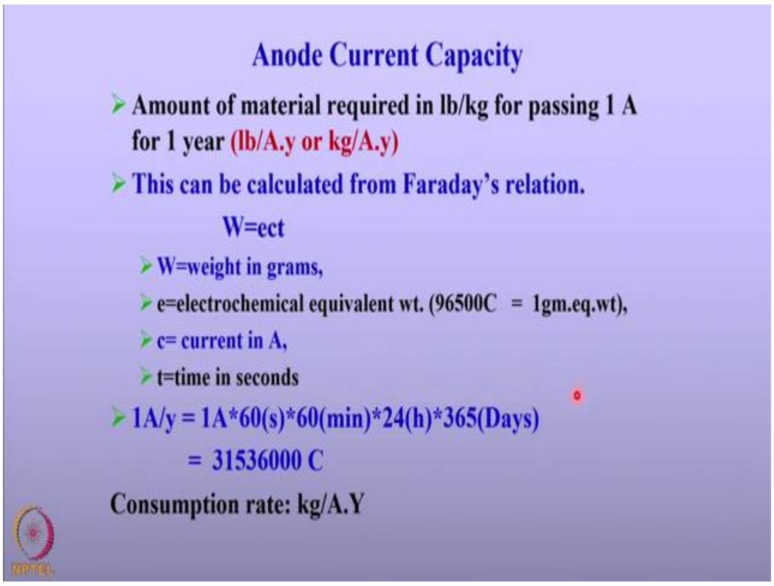


The amount of current let us say amperes given over a time period. That is the coulombs of current that a given weight of metal can offer to protect the structures. So, this is given by a term which is called as pound per ampere year or kilogram per ampere year. So, what does it will mean? It means how much weight of metal is required, if one has to pass 1 ampere of current for 1 year.

So, this is one of the parameters used to calculate life of the anodes. We will see that later how this can be used to calculate the selection of anodes for sacrificial cathodic protection system. Now, this parameter kg per ampere hour, ampere year can be calculated, if you just follow simply the Faradays relationship actually.

Now, I do not want to go in details about how to derive this ok. But, you can simply follow the relation that is the weight of the metal that is dissolved or deposited is equivalent to the electrochemical equivalent e multiplied by the current that passed in amperes and the time in seconds. So, it is possible for you to calculate using this equation, what is the consumption rate of a metal and so, that is can be calculated much easily.

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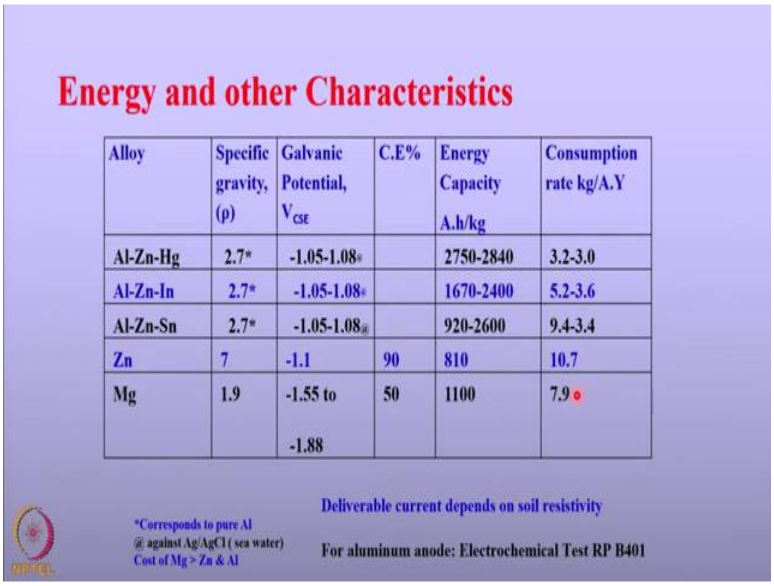
Energy and other Characteristics

| Alloy | Specific gravity, (ρ) | Galvanic Potential, $V_{CSE}$ | C.E% | Energy Capacity A.h/kg | Consumption rate kg/A.Y |
|---|---|---|---|---|---|
| Al-Zn-Hg | 2.7* | -1.05-1.08* | | 2750-2840 | 3.2-3.0 |
| Al-Zn-In | 2.7* | -1.05-1.08* | | 1670-2400 | 5.2-3.6 |
| Al-Zn-Sn | 2.7* | -1.05-1.08@ | | 920-2600 | 9.4-3.4 |
| Zn | 7 | -1.1 | 90 | 810 | 10.7 |
| Mg | 1.9 | -1.55 to -1.88 | 50 | 1100 | 7.9 |

*Corresponds to pure Al
@ against Ag/AgCl ( sea water)
Cost of Mg > Zn & Al

Deliverable current depends on soil resistivity

For aluminum anode: Electrochemical Test RP B401

So, what is summarized here is the various characteristics of the sacrificial anodes. We have seen before that there are three types of sacrificial anodes, based on the magnesium and the zinc ok. Then, we also have it is based on aluminum zinc tin, aluminum zinc indium, and aluminum zinc mercury. Now, aluminum is known to be a reactive material.

But however it passivates, in order to remove passivation there are activating elements and these are like tin, indium and mercury. So, they destroy the passive film formed on the aluminum surface so, that the current output is sufficient to protect the structures intended structures. As opposed to aluminum zinc and magnesium they do not passivate so, they dissolve actively so, the alloying elements are not added for deep passivation of aluminum and magnesium.

The other important properties required for the sacrificial anode is the density. And, this density is required when you are going to use these anodes for marine applications especially ship hull, because higher the density it adds more weight more drag to the transporting vehicles ok.

So, the density is another important factor whenever the structures are mobile. The other pattern we saw just now is the galvanic potentials you may call as a corrosion potentials, you can see that zinc and aluminum the potentials are very much similar.

But; however, magnesium has a very high negative potentials. So, the driving force offered by the magnesium is significantly higher as compared to the driving force offered by zinc and as well as aluminum alloys. The other important factor in sacrificial anodes and especially with respect to aluminum alloy sacrificial anodes is that, that aluminum alloys sacrificial anodes can be used only for sea water applications.

And, in other environments they start passivating and so, it does not provide the sacrificial action at all. The current efficiency of these aluminum alloys and magnesium alloys are given here. I am sorry is what is not given here the aluminum zinc alloys have a current efficiency closed about 90 95, and indium could be in the range of about 80 85 and aluminum zinc tin is having lower current efficiency.

That is very much reflected in the energy capacity that is given in terms of ampere hour per kg; here the current capacity, the energy capacity is given is inverse of the consumption rate, that is how many amperes hour 1 kg of this particular sacrificial anode can provide to protect the structures. The energy capacity and consumption rate are inversely related to each other ok.

Now, one more point that one likes to note is that, the how much current these anodes can give. That is how many milliamperes of the current per unit area of this of the anodes is available to protect the cathodic structures depends on the soil resistivity. In highly resistant soils the anodes dissolution tendencies is reduced and so, the deliverable current is reduced as the soil resistance is increasing.

And, there are various methods to evaluate the performance of these anodes, for aluminum are given here the electrochemical test RP B401 is a test method employed to qualify aluminum anodes. The other factor that also comes into picture is in terms of the cost of these alloys, the magnesium is the most expensive that comes then the zinc and then aluminum is the least expensive among all these.

But, notably even though aluminum is less expensive the energy capacity of aluminum is much higher compared to magnesium and zinc. So, that is why an aluminum is a most more preferred sacrificial anode for marine applications.

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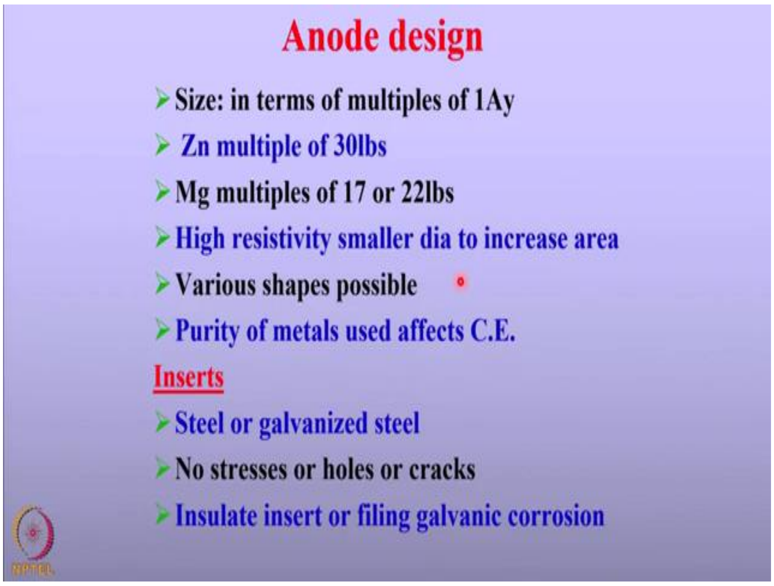


So, we talked about the characteristics of these anodes in actual applications, these anodes are designed in terms of multiples of ampere here actually you know. So, that means, the weight of these anodes would depend upon the density of these anodes. Zinc is in terms of multiples of 30 pounds magnesium is in terms of 17 or 22 pounds because these are all made easy to calculate the life of these anodes.

And, these anodes are also available in different shapes so that you know it can be fixed to the structures it can be flush mounted it can be bracelet kind of anodes and it can be done. The other important factor that you will see later is the purity of the metal affects the current efficiency.

These anodes the inserts are like steel or galvanized steels are used as inserts so which makes the electrical contact between the cable and the sacrificial Anode. And, when doing so, one should ensure that no stresses, holes and cracks are formed in these inserts. It can be insulated these inserts can be insulated.

Actually, in fact, even if you do not insert actually even if you do not insulate, these inserts are going to be, these inserts are going to be protected from corrosion by the galvanic action of the sacrificial anodes.

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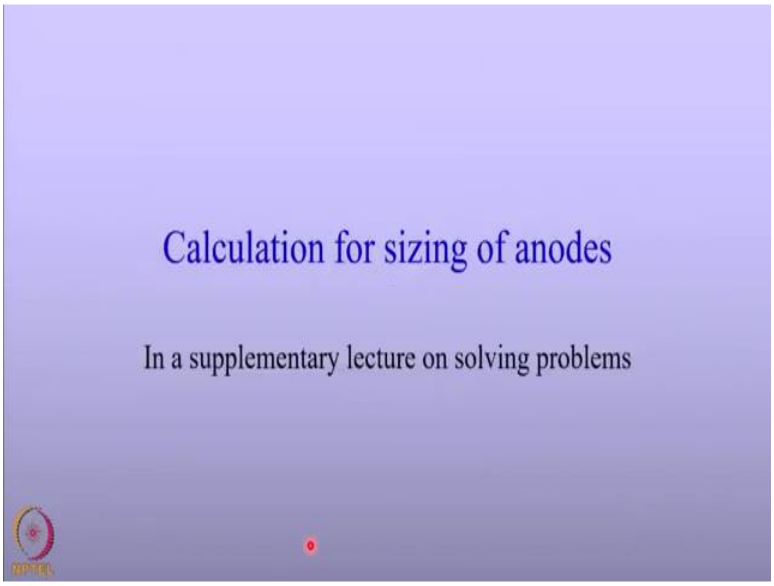


The important point with respect to sacrificial anodes is the calculation of sizing of anodes for given applications; what should be the dimensions of the anodes, how many number of anodes should be chosen, and how long these anodes will serve in protecting the structures and require some calculations.

And, there will be supplementary lectures and we will be looking at that in details. It is to be seen that the sacrificial anodes cannot be applied everywhere, it depends upon the resistance of the soil, as you notice that the magnesium has very high galvanic potentials.

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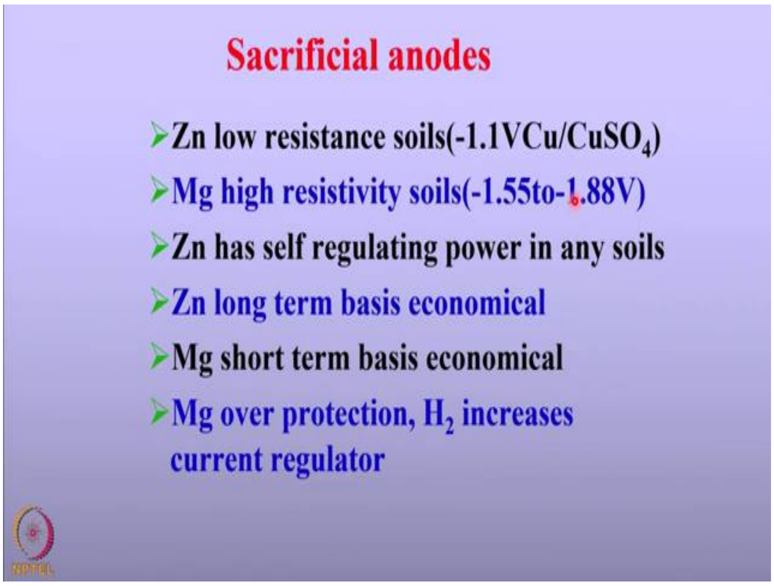


Hence, when the resistance of the soil becomes very high only the magnesium anodes can be used, and zinc cannot be used at all in a high resistance soils. And, other important factor is that zinc has self regulating effect, which means when the current demand is more, when the soil becomes wet for example, in seasonal conditions the zinc can deliver more current.

When the soil becomes dry, when the current requirements becomes lesser, the current output from zinc becomes less. So, it has a self regulating effect and so, structures are not over protected when zinc is used. On the other hand magnesium whenever you use magnesium one has to take care of over protections, should the current is more is required to apply some resistance to bring down the current output.

Let us spend a few minutes on the impressed current anodes. The impressed current anodes are of two types; one is a consumable anode, other one is a permanent anode. The consumable anodes generally used are like steel scraps, it does not cost much actually ok.

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But, when you say consumable anodes, it does not mean that the dissolution of the anodes or the steel scraps. The main function is not to provide current. There will be still a rectifier still the current is being passed and the dissolution of these anodes are unwarranted and is not a requirement at all ok. But, however, because of higher voltage applied these anodes they dissolve actually. And, these are generally used in pure water and sea water conditions these anodes are used.

The as compared to the consumable anodes, the permanent anodes are used predominantly. When you talk about permanent anodes, it does not really mean we see later, that these anodes are stable, free from corrosion and disintegration. There is certain amount of disintegration of these anodes with respect to time.

And, so, the permanent anodes here refers to a much longer life and it is contrasted with the steel scraps, the consumable anodes which have really very finite life, it is supposed to be replaced very frequently.

In the permanent anodes there are different types I have listed here, I do not need to go through all of them in detail here. And, you know it is of importance that predominantly say graphite, high silicon anode and platinum and platinum alloys or platinized niobium for example is used metal oxides that is titanium insoluble oxides and, lead oxide anodes are used and carbon fiber anodes are used and these are the permanent anodes.

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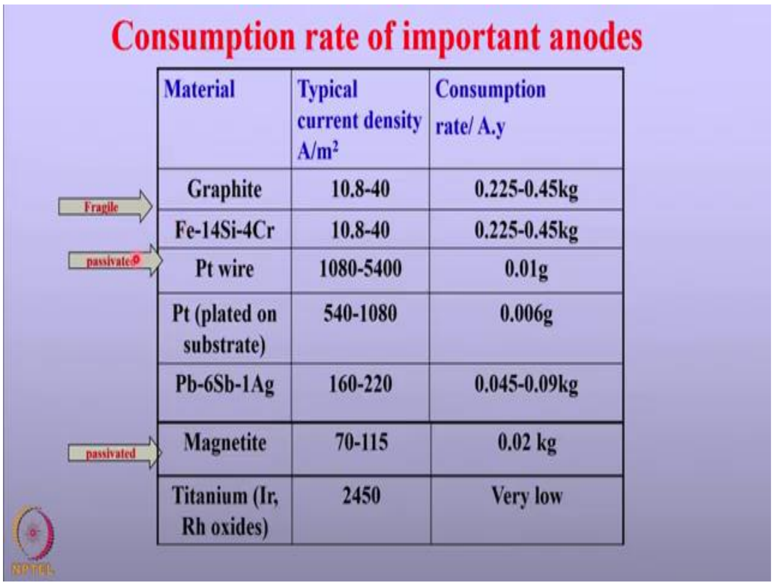


| Material | Typical current density $A/m^2$ | Consumption rate/ A.y |
|---|---|---|
| Graphite | 10.8-40 | 0.225-0.45kg |
| Fe-14Si-4Cr | 10.8-40 | 0.225-0.45kg |
| Pt wire | 1080-5400 | 0.01g |
| Pt (plated on substrate) | 540-1080 | 0.006g |
| Pb-6Sb-1Ag | 160-220 | 0.045-0.09kg |
| Magnetite | 70-115 | 0.02 kg |
| Titanium (Ir, Rh oxides) | 2450 | Very low |

The table here gives two important parameters, which are required for selection of the impressed current cathodic protection anodes. One is the current density, how much of current density these anodes can provide? You can use a rectifier, you can increase the voltage and as a consequence the anodes can get polarized and more current can be delivered.

However, by rising the voltage the anodes are not going to give a corresponding increase in current, because they disintegrate sometimes they start passivating. What is given here is; the range of current densities, these anodes can provide. Of interest to us is that the platinum and you know platinized substrate they provide the highest amount of current density. And, so, the area the surface area of the anode required for cathodic protection is less in this case.

Of course, platinum is very expensive you also have the graphite anode it is very highly conductive compared to many of these anodes, but the graphite is more fragile you can talk about. And, the titanium insoluble anodes, this actually is called metal mixed metal oxide anodes, iridium ruthenium oxides are coated by thermal decomposition technique. And, it gives very high current density it is somewhere like a platinum wire I would say I think here. The cost is significantly lower as compared to the platinum metal.

The consumption is a very important one we can look at here ok. And, as you notice that the graphite consumption is quite significant as compared to the platinum ok, the platinum is expensive. And, so, titanium insoluble anodes is an alternative to the platinum wire or and platinum plated substrate like niobium.

So, some of the disadvantages of these anodes are; the graphite is fragile we know that and I think this will go here, I think iron silicon chromium can be passivated actually. So, you can reduce the current now happen. And, when the graphite is fragile and you will see that the drain current from the anodes will reduced. You will recollect that drain current measurements is important survey to identify if the cathodic protection system is working very well.

And, such anodes like graphite even when you bury you know it can get damaged and so, the anodes may not function adequately. So, as your iron silicon chromium anodes, they are I mean they are really passivating and they are reasonably stable. But, however, if they are passivating too much then the current output will be reduced. Similarly, this will go here ok and lead anodes can also passivate and can bring down the current output of these anodes.

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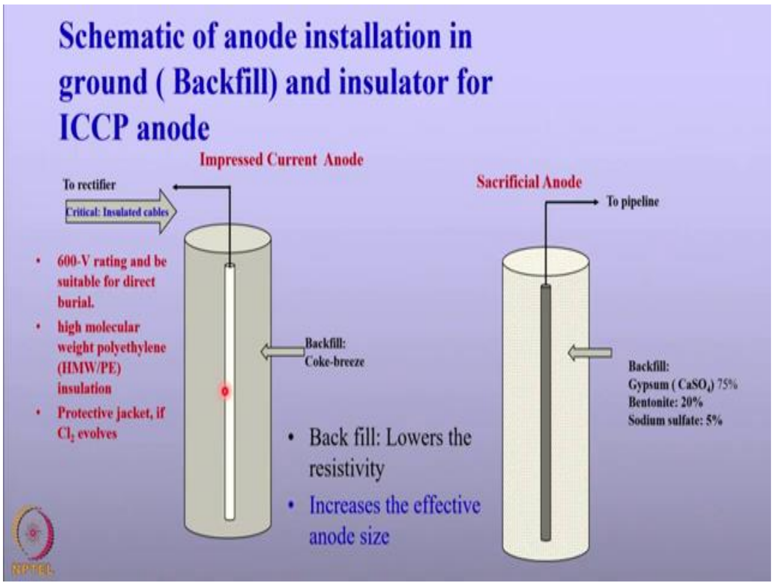


In all these cases, whether it is an impressed current cathodic protection anode or a sacrificial anode. In both the cases we have also seen in the last class itself that backfill is an important component. The backfill is very much required because it lowers the resistivity of the anode to the soil actually.

In fact, it also increases the effective anode size, when you are calculating the resistance offered by an anode at a ground bed for example, and you take the dimension of the backfill you do not take the dimension of the anode. So, backfill is a very important aspect of the these sacrificial and impressed current anodes.

The backfill of course, is not a requirement when you talk about sea water applications, where the sea water is very highly conducting. We talk about backfill only in the case of soils and where these structures are buried in the earth. The difference between the sacrificial anode and the impressed current anode also stems from one fact that, the cables, that connects the anode on the pipeline they behave differently.

In the case of sacrificial anode the potential between the pipeline or between the earth on this cable is always negative; whereas, in the case of impressed current anode cathodic protection system, this cable the potential between this cable on the earth is always positive. And, so, it is tend to corrode, in fact, the current density if you look at here is significantly higher on these cables and so, it has to be electrically insulated.

And, if it is not insulated then the it is quite fast that these cables get snapped and the current is not going to be flowing through these anodes. And so, there are various requirements people use, one of the requirement is 600 volt rating suitable for this one that is there should be no electrical breakdown in the insulation of that, this the insulating cable also should be resistance towards corrosion and degradation actually right and these cables are buried in the soil.

And, so, these polymers mostly used they are they permeate the chlorides and water and so, they will start disintegrating. So, there should be more resistance against the corrosion damages. And, in fact, when you have deep well ground bed anodes where the potential is quite large and you have chances of chlorine evolution taking place on the anodes.

You know that chlorine is highly oxidizing and so, there has to be jacket to isolate the cables from exposure to the chlorine gas without which the cables can get damaged. And, lose the function of transporting current to the anodes.

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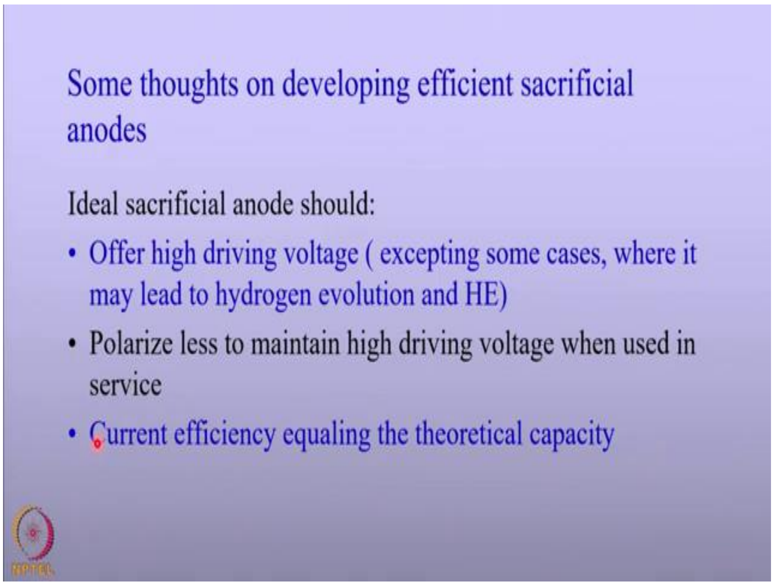


I thought I will spend a couple of minutes about the sacrificial anodes. What we should do for developing efficient sacrificial anodes? It is not from the engineering point of view, it is from the development of sacrificial anodes, maybe from material science or metallurgical point of view.

Now, if you look at a sacrificial anode you have seen already there are two kinds of requirement; you should offer high driving voltage. And of course, we also indicated that in some cases high driving voltage can be a problem, because it can lead to hydrogen evolution and hydrogen embrittlement. Barring this we would like to have high driving voltage. So, that the structures receive enough current from the anode.

The second is it should not the anodic curve of the sacrificial anode should be less polarized and it is a very important requirement. In this case zinc performs even far better, the zinc it does not anodically polarize. In fact, if you look at the marine structures especially the ship hulls, zinc is used as a reference electrode, because zinc least polarizes anodically.

That means, when you are going to measure the potential of the hull with respect to zinc electrode, zinc a zinc electrode and which is relatively having a negative potentials, the potential of zinc electrode does not change during the measurement, basically, because it polarizes much less as compared to the other sacrificial anodes. The other important parameter in deciding selection of a sacrificial anode is the current efficiency. You like to see that the current efficiency equals is theoretical current efficiency.

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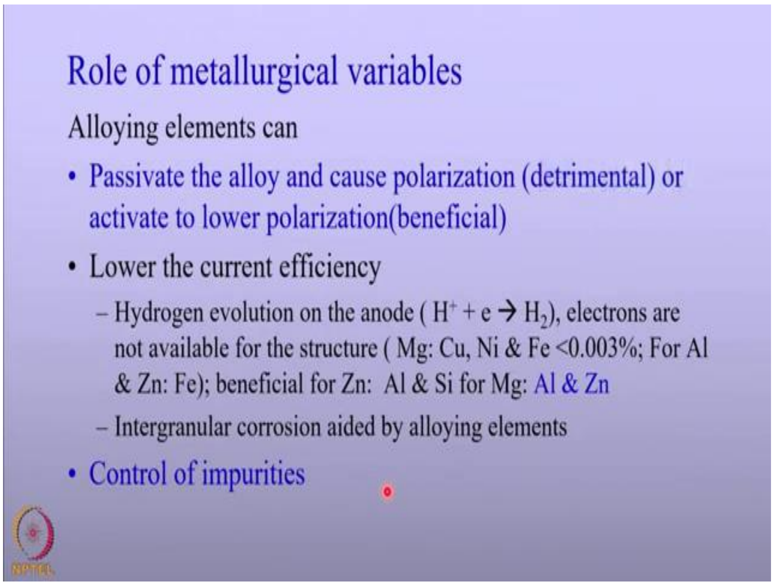


So, how do you achieve this? This is achieved by various alloying elements. And, one of the important aspect is the passivation of these anodes we do not allow the passivation of these anodes; passivation increases the polarization. So, those elements which encourage passivation with encourages less dissolution of the anodic reaction should be avoided from alloying.

The other factor is there are certain elements, which are added to this alloy they become source for hydrogen evolution. The metal when dissolves the electrons are released and these electrons travel to the structures and it reduces the potential of the structure. However, the electrons so, released on the metal surface can get consumed if another cathodic reaction can occur.

This reaction can be H plus ions present in the water can combine with this and it can form hydrogen here. So, when you add some alloying elements, it can forms the noble phases and these noble phases are the preferential sides for hydrogen evolution reaction to bring down the current efficiency of these anodes.

I have just listed here some examples, in the case of magnesium, copper, nickel and iron should be kept all should be lower than 0.003 weight percent, for aluminum and zinc the most detrimental element is iron that should be reduced. There are also some elements, which are beneficial which are listed here for zinc it is aluminum and silicon.

And, of course, aluminum and silicon to be added together or aluminum can be added you know, alone they have same effect. And, in the case of magnesium, aluminum and zinc are also beneficial.

The other factor which we have seen in our own laboratory is that when the sacrificial anode dissolves the attack occurs along the grain boundaries the grains fall and so, there is loss in metal. As a consequence the current efficiency decreases. This is called as inter granular corrosion it could happen in zinc alloys and it can happen in magnesium, it can also happens in aluminum.

So, there are certain impurities, which go to the grain boundaries and then promote this reaction so, it should be suppressed in order to reduce the loss in current efficiency; so, the control of impurities in the alloys or the key to reduce the current loss to increase the current efficiency.

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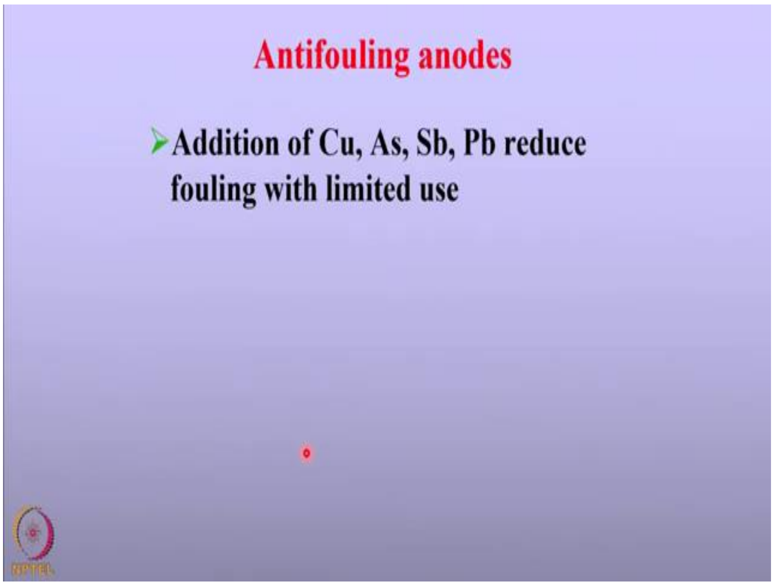


There are also anodes required wherein it resists the fouling; especially, in sea water applications that can be fouling there can be organic matters; you know the living organisms, can get deposited on the surfaces. So, the elements like, copper, arsenic, antimony and lead when they are added to this the sacrificial anodes may be the zinc or aluminum. For example, they bring down the fouling on the anodes.

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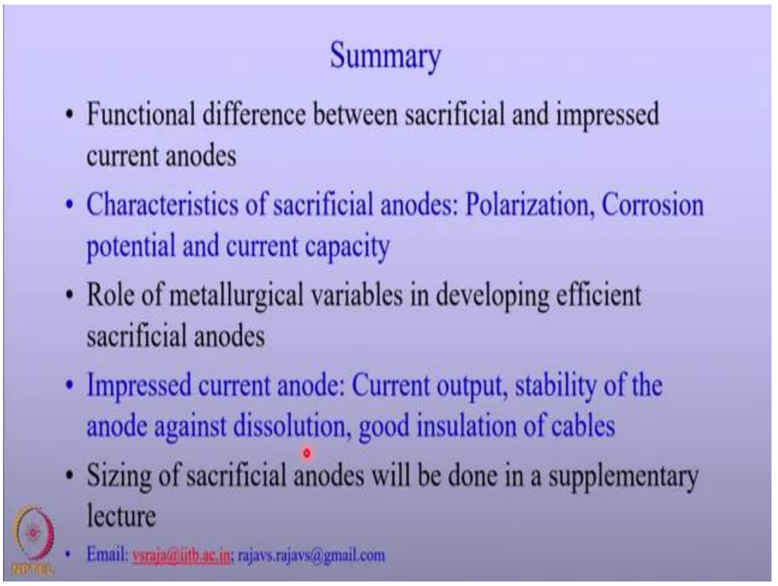


So, before we end the lecture, we can summarize what we have discussed so far. We have to remember that, there is a difference between sacrificial anode and impressed current anode in terms of their functions. The sacrificial anodes it is function is to provide the current to also provide the driving force; whereas, the impressed current anodes they act as only electrical conductor.

The potential the driving potential and the current they are derived from the rectifiers. When I come to a sacrificial Anode, the following are important the characteristics you should worry about polarization. The anodic polarization of the sacrificial anode should be lower, the corrosion potential should be as negative as possible and it should offer high current capacity so that the life of this anode per unit weight is quite higher.

We also seen how the metallurgical variables you know control the above properties of corrosion potential polarization and current capacity. When you come to impressed current anode system, the current output which means how much current per unit area the electrode delivers is an important parameter. The other parameter is that the stability of these anodes against dissolution ok, lower the dissolution the longer the life of these anodes.

And, because these anodes exhibit a positive potential with respect to the soil and they required to be insulated well, without which these cables would it get corroded and so the current will not be passing through these anodes. When you come to the sacrificial

Anode, life estimation of the sacrificial anode is important factor, we called sizing of the sacrificial anodes.

We will discuss this in a supplementary lecture, wherein we will use that lecture to clarify the concept of polarization, the concept of resistivity measurements of anodes and also sizing of sacrificial anodes. And with this I would like to end my lecture and.

Thank you very much.