Module -2.

CORROSION SCIENCE

Syllabus:

Definition and scope of corrosion, Dry and wet corrosion; Direct chemical corrosion, Electrochemical corrosion and its mechanisms; Types of electrochemical corrosion, (differential aeration, galvanic, concentration cell); Typical Electrochemical corrosion like Pitting, Inter-granular, Soil, Waterline; Factors affecting corrosion, Protection of corrosion.

Course Outcome: Utilize the knowledge of electrochemistry and corrosion science in preventing engineering equipments from corrosion.

Objectives:

- **To know about the basic nature of corrosion and its processes**
- **To identify types of corrosion**
- **To recognize the various factors affecting corrosion**
- **To understand about the various protective measures against corrosion**

1.0 Introduction

We use a wide collection of engineering materials such as plastic, rubbers, composites, ceramics, metals & alloys, etc. in many modern technologies for various applications like constructions, automobiles, aerospace, and bio-medicals in our day-to-day life. The choice of a particular material for an appropriate application under a specific condition is the sole responsibility of the design engineer. Whenever a design engineer choose a metal for any application, he/she consider the various properties of materials like mechanical, physical, chemical, etc. But, it is also true that a construction engineer gives importance to mechanical and physical properties of a metal and completely ignores the chemical properties, i.e., *effect of interaction of a metal with its environment.* For example, in construction we usually concentrate on the mechanical strength of metallic rods and normally ignore its chemical reactivity towards the environment. However, the interaction of metals & alloys with its environment plays an important role in selection and hence the performance of materials for any purposes. So, effective use of any constructional materials depends on mechanical, physical and chemical properties of materials.

For example, lead (Pb) pipes are not used for plumbo-solvent water (soft water) as concentration of Pb beyond 0.05 ppm is highly toxic and galvanized iron containers are not used for storing food stuff as zinc salts obtained via chemical interaction are toxic to human beings.

This lesson largely confined to interaction of metal with its environment, factors affecting such interaction and various way to control their interaction.

1.1 What is Corrosion?

Corrosion is "any process of loss of metallic materials from its surface through an undesirable chemical or electrochemical attack by its environment". It is a naturally occurring process, i.e., a thermodynamically feasible process for which $\Delta G < 0$. Corrosion always starts from its surface because it is active due to presence of unsatisfied valency forces known as active sites.

Examples of corrosion: (1) R*usting of iron:*

Fe (substrate) + O_2 (environment) + H_2O (electrolyte) $\rightarrow$ $Fe_2O_3 . xH_2O$ (rust)

Fig. 1. Rusting of iron pipe

(2) *Tarnishing of silver:*

$Ag + H_2S \rightarrow AgS$ (black layer on the Ag-surface) + H_2

Fig. Tarnished silver articles

(3) *Greenish layer on copper articles:*

$$2Cu + CO_2 + H_2O + O_2 \rightarrow \underbrace{CuCO_3 + Cu(OH)_2}_{\text{(Green layer; basic copper carbonate)}}$$

Fig. Green layer on the surface of a copper strip

1.2 Why corrosion occurs in metal?

We know that metals are extracted from their ores (i.e., combined form of metals) by the expense of huge amount of energy. It means that ores are energetically stable than pure metal. In other words, isolated pure metals are lies in excited state (a higher energy state) than their corresponding ores. For example, as pure Ca metal has a higher energy than its combined state, it prefers to lies in a lower energy & higher stability state, i.e., $CaCO_3$. So, when metals (possessing higher energy) are exposed to various environments (such as gases, moisture, liquids, etc.) during their uses, they interact with environment chemically or electrochemically cause loss of metal from its surface in the combined form (lower energy state). So in conclusion, the stability matter. If we people prefer to be in calm & cool lower energy state, then why not materials? We term such interaction as corrosion.

Fe (higher energy unstable state) + O_2 + H_2O → $Fe_2O_3 . xH_2O$ (lower energy stable state) + energy; ΔG is negative

In the above reaction, the rust ($Fe_2O_3 . xH_2O$) formed is thermodynamically more stable than the pure iron metal. In general, corrosion leads to loss in many useful properties like mechanical strength, luster, ductility, conductivity, etc. of the pure metal.

1.3 Consequences of corrosion

Corrosion is a big problem. It is a costly process in terms of costly to repair, costly in terms of contaminated product, in terms of environmental damage, and costly in terms of human safety. For example, the worldwide annual direct cost involved due to metallic corrosion is 2.2 trillion US dollar. This amount can be reduced by 25-30 % by employing suitable corrosion prevention methods. The various effects of corrosion are as follows:

A. *Production related consequences are*:

(i) Decrease in production rate
(ii) Increase in maintenance cost (repair/replace) resulting in an increase in the overall production cost
(iii) Loss in some important properties of metals

B. Health related consequences are:

(i) Contamination of foods
(ii) Leakage of toxic gases, liquids from the cylinder/pipes
(iii) Contamination of drinking water (water pollution)
(iv) Contamination of medicines
(v) Infection caused by rusted iron articles

C. Safety related consequences are:

(i) Sudden collapse of bridges, buildings results in loss of life/resources
(ii) Unpredicted failure of machineries/ machineries parts

So, by adopting suitable protection measures one can reduce this cost considerably. One can also check the rate of corrosion to a great extent by regular inspection and maintenance of equipments. For example, some equipment requires regular repainting and occasional inspection but equipment used in power plants, processing plants, aircraft, marine, etc. needed extensive maintenance schedules.

N.B.: Corrosion is not always unwanted. It is wanted in various processes like electroplating, surface finishing/smoothening, in research for sample preparation, etc.

Q.1 Mention some health related issues with corrosion.

Ans. Some of the health related issues due to corrosion are:

(i) Contamination of foods
(ii) Leakage of toxic gases, liquids from the cylinder/pipes
(iii) Contamination of drinking water (water pollution)
(iv) Contamination of medicines
(v) Infection caused by rusted iron articles

Q.2 **Mention some production related consequences with corrosion.**

Ans. *Production related consequences are*:

(i) Decrease in production rate
(ii) Increase in maintenance cost (repair/replace) resulting in an increase in the overall production cost
(iii) Loss in some important properties of metals

Q.3 **Mention some safety related outcomes with corrosion.**

Ans.

(i) Sudden collapse of bridges, buildings results in loss of life/resources
(ii) Unpredicted failure of machines/ machineries parts

Lecture-2

1.5 Chemical or Dry Corrosion:

Dry corrosion of metals occurs in non-aqueous solution and in non-humid (dry) atmosphere. It occurs due to direct chemical interaction between the surfaces of metal and corrosive environment like atmospheric gases (e.g., O_2, H_2S, Cl_2, etc.) or anhydrous liquid like HCl, H_2SO_4, etc.

Most common type of dry corrosion is **Oxidation Corrosion.**

Oxidation Corrosion: It occurs when a reactive metal is exposed to O_2 in absence of moisture. Upon oxidation a thin layer of oxide formed on the surface of metal

(i) $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
(ii) $Ca + 1/2O_2 \rightarrow CaO$
(iii) $Mg + 1/2O_2 \rightarrow MgO$

1.5.1 Nature of Oxide layer

A thin layer of oxide formed on the surface of metal can be non-porous, porous, unstable or volatile.

(i) ***Non-porous oxide layer*:** It is stable, impervious and tightly sticks on the surface. It acts as a protective coating and prevents further corrosion.
Example: Metals like Cu, Al, and Cr forms protective oxide layer such as CuO, Al_2O_3, Cr_2O_3, respectively.

(ii) ***Unstable oxide layer:*** Such layer is formed by gold (Au) and platinum (Pt). As oxide layer decomposes back to metal and oxygen, Au and Pt do not undergo oxidation corrosion.
Example: $4Au + 3O_2 \rightarrow 2Au_2O_3$

(iii) **Volatile oxide layer:** The moment it is formed it gets volatilized and the metal surface is again gets exposed for further attack leading to continuous and rapid corrosion.
Example: $2Mo + 3O_2 \rightarrow 2MoO_3$ Molybdenum oxide (volatile oxide layer)

$2V + 2.5O_2 \rightarrow V_2O_5$ Vanadium oxide (volatile oxide layer)

- ✓ *This is the reason why Molybdenum and Vanadium undergo rapid corrosion in oxygen atmosphere.*

(iv) ***Porous oxide layer*****:** Due to porous nature, oxygen attacks the metal through pores and corrosion continues till the entire metal is converted into metal oxide.

Metals like Fe, Ca, Mg, K, etc. form porous oxide layer.

Q.5 Define oxidation corrosion with a suitable example.

Ans. It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2. $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

Q.6. How many types of oxide layer can be formed on the surface of metal?

Ans. **Four type** (Porous, non-porous, unstable, Volatile)

Q.7. Which type of oxide results in rapid and continuous corrosion?

Ans. Volatile

Q.8 Name a metal which can form a volatile oxide layer (mention reaction).

Ans. Molybdenum (Mo); $2Mo + 3O_2 \rightarrow 2MoO_3$

Q.9 Name two metals which form porous oxide layer.

Ans. Na, K

Q.9 Name two metals which form non-porous oxide layer.

Ans. Al and Cr

Q.9 Name two metals which form unstable oxide layer.

Ans. Au and Pt

Q 10. Corrosion resistance of iron can be significantly improved by alloying with aluminum. Justify it.

Ans. The improved corrosion resistance of iron upon alloying with Al is that alloying element forms a protective layer of Al_2O_3 on the surface of host metal.

Q 10. Corrosion resistance of iron can be significantly improved by alloying with chromium. Justify it.

Ans. The improved corrosion resistance of iron upon alloying with Cr is that alloying element forms a protective layer of Cr_2O_3 on the surface of host metal.

Q 11. Stainless steel maintains its luster for a longer period of time. Give reason.

Ans. Stainless steel is an alloy of iron with alloying elements like Al, Cr, etc. These alloying elements upon exposure to oxygen form a protective layer of Al_2O_3/Cr_2O_3 on the surface of it to prevent formation of rust.

1.5.2 Piling-Bedworth Rule (PBR)

PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

According to this rule, smaller is the specific volume ratio; greater is the rate of oxidation corrosion, because oxide films will be porous.

[N.B: **Specific Volume Ratio SVR = (Volume of metal oxide formed/Volume of metal)]**

In general, If,

- SVR $\geq$ 1; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.)
- SVR >>>1; Oxide layer is non protective in nature (usually > 2), example, Fe_2O_3

Q. 12. What is PBR?

Ans. PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

According to this rule, smaller is the specific volume ratio; greater is the rate of oxidation corrosion, because oxide films will be porous.

Q 13. What is specific volume ratio (SVR). Mention its significance.

Ans. **Specific Volume Ratio SVR = (Volume of metal oxide formed/Volume of metal)]**

In general, If,

- SVR ≥ 1; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.)
- SVR >>>1; Oxide layer is non protective in nature (usually > 2), example, Fe_2O_3

1.5.3 Mechanism of Oxidation Corrosion

The various steeps involved are as follows:

Step-1 Metal gets oxidized to generate metal ions and electrons.

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

Step-2 Electrons so released by Mg is captured by atmospheric O_2 and forms oxide anion (O^{2-})

$$\tfrac{1}{2} O_2 + 2e \rightarrow O^{2-}$$

Step-3 The metal ions and O^{2-} are moved towards metal-atmosphere interface and form metal oxide (MgO) at the point of meeting.

$$Mg^{2+} + O^{2-} \rightarrow MgO \text{ (formed at the surface)}$$

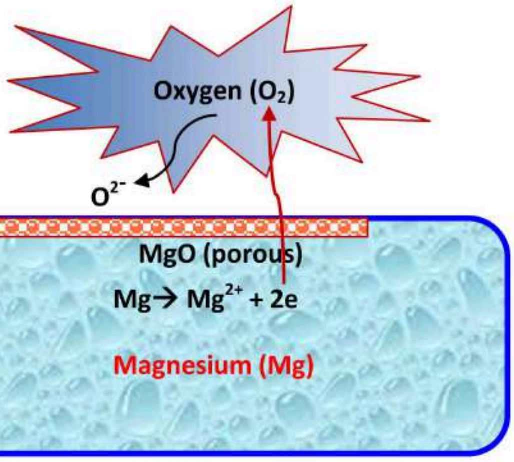


Fig. Mechanism of oxidation corrosion

Here, MgO is a porous layer, so further oxidation occurs till whole metal is converted into oxide.

But in case of Al, it forms a protective layer of Al_2O_3 and hence it resists further oxidation process.

Q. 14. Define oxidation corrosion. Discuss its mechanism.

Ans. It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2. $Mg + 1/2O_2 \rightarrow MgO$

For mechanism, refer section 1.5.3

Lecture-3

1.6 Electrochemical or Wet corrosion:

Wet corrosion of metals occurs in aqueous solution and in humid atmosphere through formation of a large number of minute electrochemical cells. The mechanism of corrosion can be explained by *electrochemical theory*. It involves anodic dissolution (oxidation) of metal and cathodic reduction of oxidants (e.g. oxygen) present in the solution/electrolyte.

1.6.1 Electrochemical theory of wet corrosion:

According to this theory, the various steps involved in wet corrosion are as follows:

Step 1: Formation of anodic and cathodic areas

Step 2: Oxidation at anodic areas results in liberation of electrons and generation of metallic ions, for example Fe^{2+} from metal Fe

Step 3: Generation of non-metallic anions like hydroxyl anion (OH^-) by absorption of electrons (e^-) by oxidants like O_2

Step 4: Formation of corrosion product near cathode

Depending on the nature of the corrosive environment, the reaction occurs at the cathode (cathodic reaction) proceeds with (i) absorption of oxygen or (ii) hydrogen evolution

1.6.2 Mechanism of wet corrosion

A. Oxygen absorption mechanism:

Rusting of iron (Fe) in *a neutral aqueous medium* of electrolyte (such as NaCl) with dissolved oxygen or oxygen in the atmosphere follows oxygen absorption mechanism.

Let us consider that an iron piece is exposed to a humid environment that is not acidic in nature. Also assume that a small piece of metal with lower oxidation potential (relative to Fe) is sat on its surface. Under this situation, pure iron with higher oxidation potential acts as anode and undergoes corrosion/rusting.

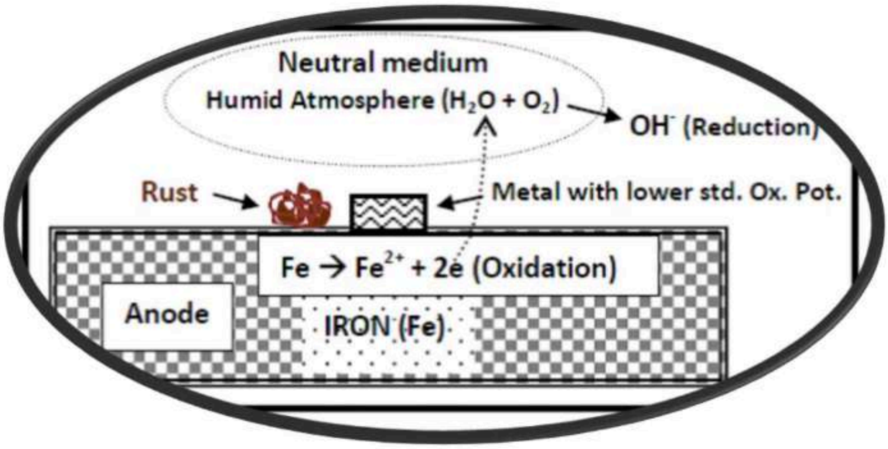


Fig. 2. Mechanism of wet corrosion by oxygen absorption.

The mechanism of rusting of iron piece in neutral medium involves the following steps:

(i) Oxidation of 'Fe' results in formation of metallic ion (Fe^{2+}) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ ------ (oxidation)

(ii) The liberated electrons are captured by the oxidants (O^{2}) at the cathode to form non-metallic ions (OH^-)

At Cathode: $1/2O_2$ (oxidant) + $H_2O + 2e^- \rightarrow 2OH^-$ ----- (reduction)

(O_2 absorption occurs)

(iii) The cations Fe^{2+} and anions OH^- liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide $Fe(OH)_2$. As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ($Fe_2O_3.xH_2O$) or ferric hydroxide $Fe(OH)_3$-a brownish product (called rust) and deposited near the cathode.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3$ or $Fe_2O_3.xH_2O$ (in pr. of excess O_2)

N.B.: In limited oxygen environment, ferrous hydroxide converted into a blackish oxide Fe_3O_4 (Ferrous ferric oxide, $FeO.Fe_2O_3$)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe_3O_4$ (limited supply of O_2)

Factors affecting the rate of rusting: The various factors are:

a. Amount of dissolved oxygen
b. Presence of acid and electrolytes
c. Deposition of rust on its surface
d. Potential difference between iron and the metal sat on its surface

B. Hydrogen evolution mechanism:

Rusting of iron (Fe) *in an acidic medium* (such as HCl) follows hydrogen evolution mechanism.

Let us consider that an iron piece is exposed to an acidic environment. Also assume that a small piece of metal with lower oxidation potential (relative to Fe) is sat on its surface. Under this situation, pure iron acts as anode and undergoes corrosion/rusting.

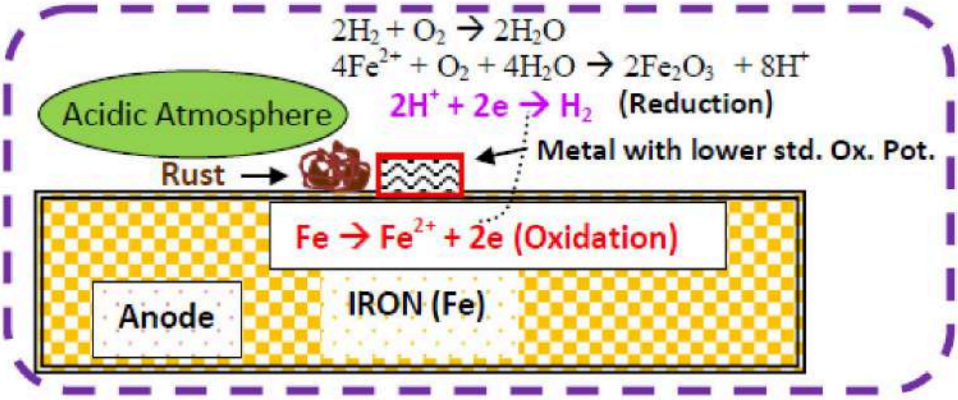


Fig. 3. Mechanism of wet corrosion by hydrogen evolution.

The mechanism of rusting of iron piece in an acidic environment involves the following steps:

(i) Oxidation of ‘Fe’ results in formation of metallic ion (Fe^{2+}) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) At the cathode, the liberated electrons are captured by the hydrogen ions (H^+-ions) to form H-atoms and later form H_2 molecules. The H_2 molecules combine with dissolved oxygen forms water.

At Cathode: $4H^+ + 4e^- \rightarrow 4H\ (2H_2\uparrow)$ (Reduction)

(H_2 evolution occurs)

$$2H_2 + O_2 \rightarrow 2H_2O$$

Therefore, the net cathodic reaction is: $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$

(iii) As the ferrous ions are unstable, they are oxidized by atmospheric oxygen to form rust as per the following reactions.

$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$

$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3.\ xH_2O$ (rust)

Long Questions

Q.1. Define wet corrosion. Discuss the mechanism of rusting of iron in a neutral or alkaline medium.

Ans. Wet corrosion of metals occurs in aqueous solution and humid atmosphere through formation of a large number of minute electrochemical cells.

Mechanism of rusting of iron: refer section 1.6.2 A

Q.2. Discuss the mechanism of rusting of iron in an acidic medium.

Ans. refer section 1.6.2 B

Short type answer

Q.1 Mention the factors affecting rusting of iron.

Ans. The various factors are:

1. Amount of dissolved oxygen
2. Presence of acid and electrolytes
3. Deposition of rust on its surface

4. Potential difference between iron and the metal sat on its surface

Q.2 Write the chemical reaction which occurs at cathode during rusting of iron in a neutral medium.

Ans. $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Medium type Answer

According to this theory, the various steps involved in wet corrosion are as follows:

Step 1: Formation of anodic and cathodic areas

Step 2: Oxidation at anodic areas results in liberation of electrons and generation of metallic ions, for example Fe^{2+} from metal Fe

Step 3: Generation of non-metallic anions like hydroxyl anion (OH^-) by absorption of electrons (e^-) by oxidants like O_2

Step 4: Formation of corrosion product near cathode

Depending on the nature of the corrosive environment, the reaction occurs at the cathode (cathodic reaction) proceeds with (i) absorption of oxygen or (ii) hydrogen evolution

Q.1 Discuss the electrochemical theory of wet corrosion.

Ans. Refer 1.6.1

Lecture-4 and 5

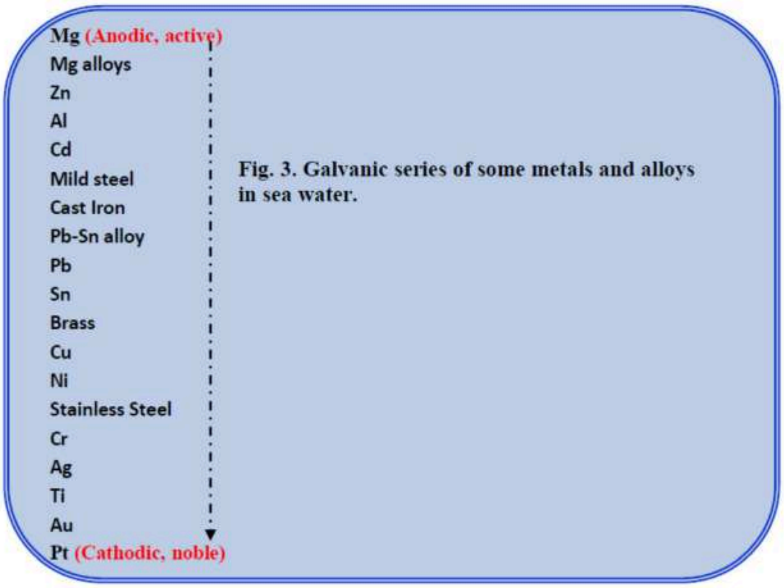
1.7 Electrochemical and Galvanic Series

Electrochemical or EMF series is obtained when metals are arranged as per their increasing standard reduction potential. The metals located at the top of the series are considered the most active, with the highest level of negative electrochemical potential. The metal that can be found at the bottom is the most noble and contains the highest amount of positive electrochemical potential.

It is observed that some metals like aluminum (Al) exhibits more noble (passive) behavior towards corrosion. But, this quality is going against what predicted by the electrochemical or EMF series. As per the EMF series, the standard oxidation potential of 'Al' is higher than that of 'Fe', but Fe suffers from corrosion whereas 'Al' resists it. So, scientist thought of another series which could provide real and useful information about the corrosion of metals and alloys in a particular environment. This series is known as "*Galvanic Series*".

Galvanic series is a list of metals and alloys which are arranged in a specific sequence as per their relative corrosion potential in a specific environment (usually sea water). In this series, there is no place for non-metals like chlorine, fluorine, etc.

Galvanic Series: (*Corrosion tendency decreases for Top to down*)



Mg (Anodic, active)
Mg alloys
Zn
Al
Cd
Mild steel
Cast Iron
Pb-Sn alloy
Pb
Sn
Brass
Cu
Ni
Stainless Steel
Cr
Ag
Ti
Au
Pt (Cathodic, noble)

Fig. 3. Galvanic series of some metals and alloys in sea water.

Q. What is Galvanic series? What is its use?

Ans. Galvanic series is a list of metals and alloys which are arranged in a specific sequence as per their relative corrosion potential in a specific environment (usually sea water). It is useful for studying the corrosion of metals and alloys.

1.7.1 *Differentiate between EMF series and Galvanic series* ***(medium type-3 marks)***

Sl. No.	*EMF series*	*Galvanic series*
1	It is a list of metals and non-metals which are arranged in a specific sequence as per their relative standard Ox. Potential/Red. Potential.	It is a list of metals and alloys which are arranged in a specific sequence as per their relative corrosion potential in a specific environment (usually sea water).
2	The position of metals and non-metals are fixed in the series.	The position of metals and alloys are not fixed in the series. Position may change by changing the environment.
3	No place for alloys	No place for non-metals
4	It predicts the relative displacement tendencies.	It is useful for studying the corrosion of metals and alloys.

1.8 Some typical electrochemical/wet corrosion

In general, wet corrosion is more common than the dry corrosion. Rusting of iron in a neutral/alkaline/acidic environment is belongs to this class of corrosion. Some of the typical wet corrosions are: *(1) Galvanic corrosion, (2) Waterline corrosion; (3) Pitting; (4) Caustic Embrittlement; (5) Soil corrosion, (6) Microbial corrosion, etc.*

1.8.1 Galvanic Corrosion/Differential Metal Corrosion/Bimetallic Corrosion

Galvanic corrosion occurs when two different metals or alloys are in contact are immersed in a conducting medium. Here, the metal with higher standard oxidation potential acts as anode and undergoes dissolution/corrosion. When two different metals are joined together, they form a Galvanic couple. Some examples of Galvanic couples are: Zn and Cu; Fe and Cu, Zn and Ag, etc. This corrosion is otherwise known as *differential/bimetallic corrosion* as two different metals are used.

In Zn and Cu Galvanic couple, Zn with higher standard oxidation potential (+ 0.76 V) than Cu (-0.34 V) acts as anode and here Cu acts as cathode.

In order to discuss on the mechanism of corrosion, let us consider that a Zn-Cu couple is exposed to a neutral humid environment.

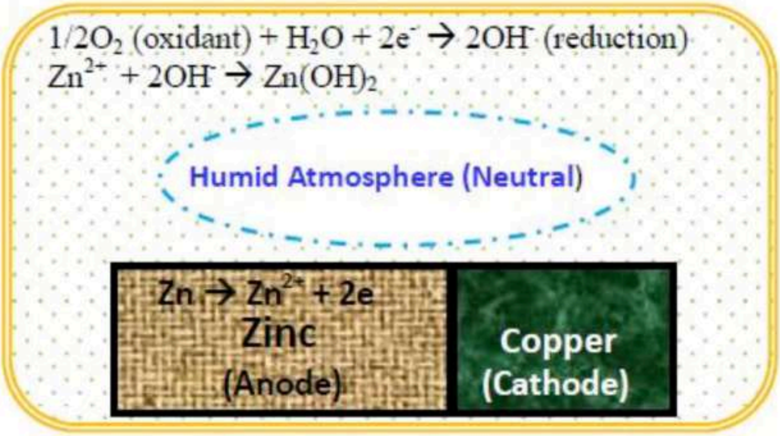


Fig. 4. Mechanism of Galvanic Corrosion.

Mechanism:

(i) Zn undergoes oxidation: $Zn \rightarrow Zn^{2+} + 2e$

(ii) Oxidant (O_2) in the atmosphere accepts these electrons to form anions

$1/2O_2$ (oxidant) + $H_2O + 2e^- \rightarrow 2OH^-$ (reduction)

(iii) Corrosion product forms by combination of cations and anions

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$

Factors affecting Galvanic Corrosion:

The various factors are enlisted as below:

1. Position of metals in the Galvanic series: The more apart the metals are from each other in the series, the greater is the corrosion.
2. Distance effect: Corrosion is highest at the junction and rate decreases progressively with distance from the interface.

3. Area effect: If anodic area will be much smaller than cathodic area then rapid corrosion will be occur.

Control of Galvanic corrosion: It can be minimized by:

a. By avoiding direct contact
b. By choosing two metals close to one other in the Galvanic series
c. By proper designing (By keeping anodic area much larger than cathode)
d. By putting an insulating layer between two metals

✓ **Some examples of Galvanic corrosion**

1. Steel screws in Brass marine hardware (steel-anode)
2. Lead-antimony solder around copper wire (tin-anode)
3. A steel propeller shaft in Bronze bearings (steel-anode)
4. Steel or iron pipe connected to copper plumbing (steel-anode)

Q. Iron corrodes faster than Aluminium even though Fe is placed below Al in the EMF series. Give reason

Ans. It is because Al forms a protective oxide of Al_2O_3 on its where as Fe forms a porous Fe_2O_3 layer.

Q. What is Galvanic corrosion? How to control it? *Short answer*

Ans. Galvanic corrosion occurs when two different metals or alloys are in contact are immersed in a conducting medium. Here, the metal with higher standard oxidation potential acts as anode and undergoes dissolution/corrosion.

Control of Galvanic corrosion: It can be minimized by:

a. By avoiding direct contact
b. By choosing two metals close to one other in the Galvanic series
c. By proper designing (By keeping anodic area much larger than cathode)
d. By putting an insulating layer between two metals

Q. Mention factors affecting the rate of Galvanic corrosion. *Short answer*

Ans. The various factors are enlisted as below:

1. Position of metals in the Galvanic series: The more apart the metals are from each other in the series, the greater is the corrosion.
2. Distance effect: Corrosion is highest at the junction and rate decreases progressively with distance from the interface.
3. Area effect: If anodic area will be much smaller than cathodic area then rapid corrosion will be occur.

Long type

Q. Discuss the mechanism of Galvanic corrosion with a specific example. Mention the factors affecting its rate.

Ans. See section 1.8.1

Q. Impure metal corrodes faster than pure metal under identical conditions. Give reason.

Ans. Impurities in metal results in heterogeneity. Hence, it causes formation of a large number of small electrochemical cells and corrosion occurs at anodic part.

Q. A steel or iron screw in a brass marine hardware corrodes. Give reason.

Ans. This is due to Galvanic corrosion. Here, steel or iron screw acts as anode due to their higher standard oxidation potential.

Q. Where the wet corrosion takes place?

Ans. It always takes place at anode. At, anode loss of electron takes place.

Q. A piece of impure and pure zinc are placed in a salt solution. Which will corrode faster?

Ans. Impure one. As impurities leads to formation of Galvanic cells.

Q. Small anodic area results in intense corrosion. Give reason.

Ans. This is due to area effect. If anodic area will be very small than cathodic area then the huge demand of electrons by cathode can only be fulfilled by small anode by undergoing rapid dissolution. Rapid dissolution means rapid corrosion.

Here (Cathodic area/Anodic area) >>1.

Q. A copper equipment should not possess a small steel bolt. Give reason.

Ans. Here bolt will act as anode and (Cathodic area/Anodic area) >>1. So, rapid dissolution or rapid corrosion of bolt (anode) will occur.

Q. Why does a steel pipe in a large copper tank is undergoes rapid corrosion?

Ans. Steel is anodic to copper, i.e., steel pipe will act as anode. Again the steel pipe is much smaller than the tank. That is here (Cathodic area/Anodic area) >>1. So, rapid corrosion will occur in steel pipe.

Q. In a structure, two dissimilar metals should not allow to come in contact with each other. Give reason.

Ans. If they will contact, Galvanic corrosion will occur at metal with higher standard oxidation potential.

Q. Rusting of iron is quicker in saline water than in ordinary water. Give reason.

Ans. The presence of NaCl in saline water leads to increased conductivity of water layer in contact with the iron surface, thereby corrosion current increases and rusting is speeded up.

Numerical

How much rust ($Fe_2O_3.3H_2O$) will be formed when 10 kg of iron (Fe) have completely rusted away? (At. mass: Fe = 56, H =1, O =16)

Ans. Mol. Mass of rust ($Fe_2O_3.3H_2O$) = 214 g

Here, rust contains 2 Fe-atoms.

So, 214g of rust contains 2 x 56 = 112 g Fe

Or, 112 g Fe produces 214 g rust

Then, 10 kg = 10,000g of Fe will form = (214/112) x 10,000 = 19107 g = 19.1 kg.

1.8.2 Differential aeration corrosion

It is an electrochemical corrosion which occurs when a portion of metal is exposed to different air or oxygen concentration than the rest part. This difference in air or O_2 concentration causes a difference in standard oxidation potential between the two areas. Here, the poorly aerated/oxygenated part acts as anode and undergoes corrosion.

In order to study the mechanism of corrosion, let us consider that a metal (say Iron) is partially immersed in a dilute solution of NaCl (electrolyte). The metallic part which is not immersed in the electrolyte is strongly aerated whereas the part inside the electrolyte is poorly aerated. So, a difference in potential thus developed causes the flow of electron from anode to cathode. The poorly aerated part will acts as anode and suffers from metallic dissolution.

Mechanism:

(i) $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) $1/2O_2$ (oxidant) $+ H_2O + 2e^- \rightarrow 2OH^-$ (reduction)

(iii) $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow \underbrace{Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O}_{\text{(rust)}}$ (In pr. of excess O_2)

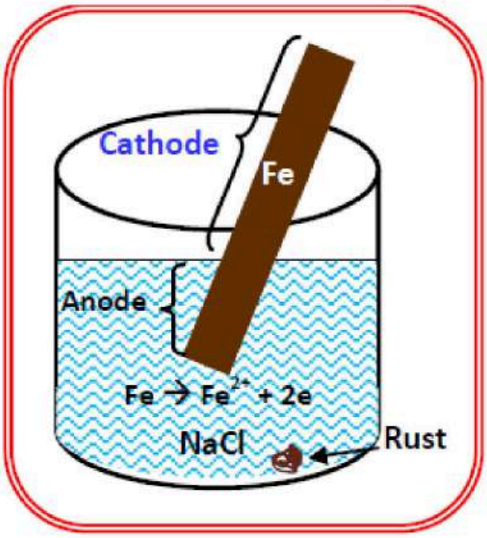


Fig. 5. Mechanism of differential aeration corrosion.

The two most common differential aeration corrosion is:

A. *Water-line corrosion*

B. *Pitting*

Q. What is the chemical formula of rust?

Ans. $Fe(OH)_3$ or $Fe_2O_3.xH_2O$

Q. What is differential aeration corrosion? Give an example.

Ans. It is an electrochemical corrosion which occurs when a portion of metal is exposed to different air or oxygen concentration than the rest part. Here, the poorly aerated/oxygenated part acts as anode and undergoes corrosion.

The two most common differential aeration corrosion is:

A. *Water-line corrosion*
B. *Pitting*

Q. A pure metal rod half-immersed vertically in water starts corroding at the bottom. Give reason.

Ans. This is due to differential aeration corrosion. The rod above the waterline is more strongly aerated and acts as cathode. On the other hand the lower part of the rod immersed in water is less-aerated and acts as anode and suffers from corrosion.

Q. Why does part of an iron nail inside the wooden structure undergoes corrosion easily?

Ans. The part of the nail inside the wood is not exposed to the atmosphere. So, it is very poorly oxygenated part as compared to the remainder part. So, nail inside the wood acts as anode and suffers from corrosion. It is differential aeration corrosion.

Water-line corrosion

It is a *differential aeration corrosion or oxygen concentration cell corrosion* wherein corrosion occurs just below the waterline when a steel tank is half-filled with water. Here, as the part just below the water-line is poorly aerated/oxygenated acts as anode and undergoes oxidation to form metallic ions. The part above the water-line has more access to air or oxygen acts as cathode.

Mechanism:

(i) $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) $1/2O_2$ (oxidant) $+ H_2O + 2e^- \rightarrow 2OH^-$ (reduction)

(iii) $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow \underbrace{Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O}_{\text{(rust)}}$ (In pr. of excess O_2)

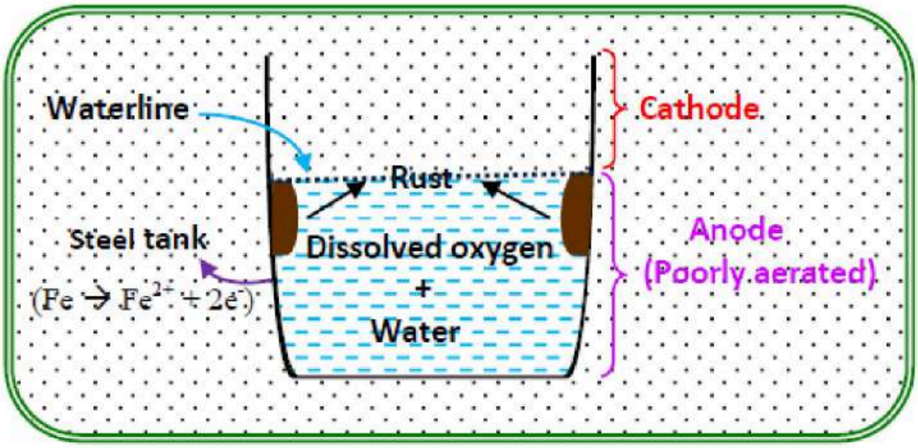


Fig. 6. Mechanism of water-line corrosion.

N.B.: ***Oxygen concentration cell corrosion:*** It is an electrochemical corrosion occurs when the metal surface is exposed varying concentration of air or oxygen. Here, metallic part exposed to less oxygen acts as anode and undergoes dissolution.

Pitting Corrosion

It is a highly localized differential aeration corrosion which proceeds at a rapid rate to form "pits" or cavities on the surface of the metal. Under the following situations pits are formed on the metallic surface:

1. When impurities like sand, dust, scale, etc. sat on the surface
2. When there is any breakage of protective oxide film at a localized area

Let us consider that a dust particle is sitting on the surface of an iron metal and the metal is exposed to a neutral humid atmosphere. The rusting of iron will occur as per the following steps:

(i) **At Anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) **At Cathode:** $1/2O_2$ (oxidant) $+ H_2O + 2e^- \rightarrow 2OH^-$ (reduction)
(O_2 absorption occurs)

(iii) **Rust formation:** The cations Fe^{2+} and anions OH^- liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide $Fe(OH)_2$. As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ($Fe_2O_3.xH_2O$) or ferric hydroxide $Fe(OH)_3$-a brownish product (called rust) and deposited near the cathode.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O \text{ (in pr. of excess } O_2)$$

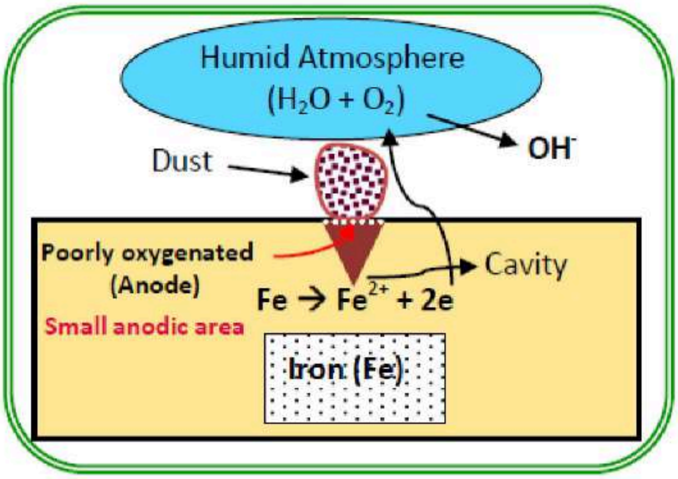


Fig. 7. Mechanism of pitting corrosion.

Lecture-6

Pitting Corrosion

It is a highly localized differential aeration corrosion which proceeds at a rapid rate to form "pits" or cavities on the surface of the metal. Under the following situations pits are formed on the metallic surface:

1. When impurities like sand, dust, scale, etc. sat on the surface
2. When there is any breakage of protective oxide film at a localized area

Let us consider that a dust particle is sitting on the surface of an iron metal and the metal is exposed to a neutral humid atmosphere. The rusting of iron will occur as per the following steps:

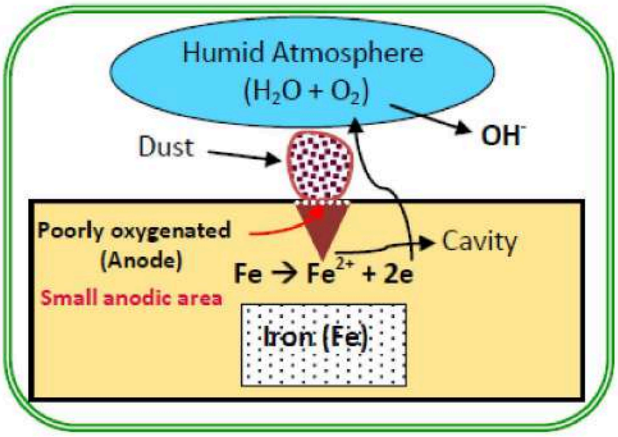
(i) **At Anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) **At Cathode:** $1/2O_2$ (oxidant) $+ H_2O + 2e^- \rightarrow 2OH^-$ (reduction)

(O_2 absorption occurs)

(iii) **Rust formation:** The cations Fe^{2+} and anions OH^- liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide $Fe(OH)_2$. As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ($Fe_2O_3.xH_2O$) or ferric hydroxide $Fe(OH)_3$-a brownish product (called rust) and deposited near the cathode.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O \text{ (in pr. of excess } O_2\text{)}$$



Q. Iron corrodes faster under drops of salt solution. Give reason.

Ans. This is due to differential aeration corrosion. As part of iron covered by drop is poorly oxygenated part, it acts as anode and undergoes rapid corrosion.

Q. Corrosion of water filled steel tanks occurs below water line. Give reason.

Ans. This is due to differential aeration corrosion. Here, as the part just below the water-line is poorly aerated/oxygenated acts as anode and undergoes oxidation to form metallic ions. The part above the water-line has more access to air or oxygen acts as cathode.

Q. Why wire mesh is corrodes faster at joints?

Ans. The joints of wire mesh are stressed due to welding, so becomes anode and undergoes corrosion.

Q. Why deposition of extraneous matter like dirt, sand, dust, etc. on the surface of metal for a long period is unwanted?

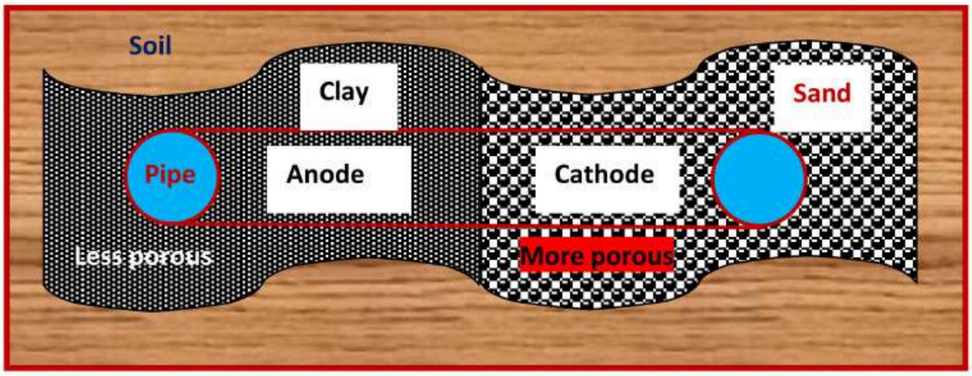
Ans. This causes differential aeration corrosion. Deposition of matter on the surfaces restricts the access of O_2 below it; thereby it becomes anode and undergoes localized corrosion.

Q. Why should nickel plated iron articles be free from pores and pin holes?

Ans. Here, Iron acts as anode and Nickel acts as cathode. Presence of pores in Ni-plated articles exposes the anodic Fe-metal to the atmosphere at these points. So, galvanic cell is form and intense localized corrosion occurs.

Soil Corrosion:

Soil corrosion is a concentration cell corrosion which occurs due to differential oxygen concentration. Buried pipelines are suffered from this. For example, let us consider that iron (Fe) pipelines are passing through clay-based soil and then through sand-based soil. Since clay is less aerated than sand, iron pipe passing through clay-based soil will act as anode and suffers from corrosion.



Mechanism: At Anode: Fe → $Fe^{2+} + 2e^-$------- (oxidation)

At Cathode: $1/2O_2$ (oxidant) + $H_2O + 2e^-$ → $2OH^-$ ---- (reduction)

Net reaction: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3$ or $Fe_2O_3.xH_2O$

Inter-granular Corrosion

It is an electrochemical corrosion in which corrosion occurs at the grain boundaries. In a particular corroding medium, the grain boundaries contain material with higher oxidation potential than the grains. So, grain boundaries acts as anode and suffers from corrosion. It is otherwise known as *inter-crystalline* corrosion.

Inter-granular corrosion usually occurs in alloys in specific environments. For example, in stainless steel SS (an alloy of Fe, Cr, Al, etc.) deposition of chromium carbide at grain boundaries results in depletion of Cr adjacent to it. Chromium carbides can be precipitated if the stainless steel is worked at the temperature range 550–850°C, for example during heat treatment or welding. If the temperature lies in the critical range for too long, chromium carbides will start to form in the grain boundaries, which then become susceptible to inter-granular corrosion. The area adjacent to the grain boundaries becomes depleted in chromium (the chromium reacts with carbon and forms carbides) and this zone, therefore, becomes less resistant to inter-granular corrosion. The depleted in Cr region acts as anode and results in corrosion along the grain boundaries. Inter-granular corrosion results in sudden failure of material.

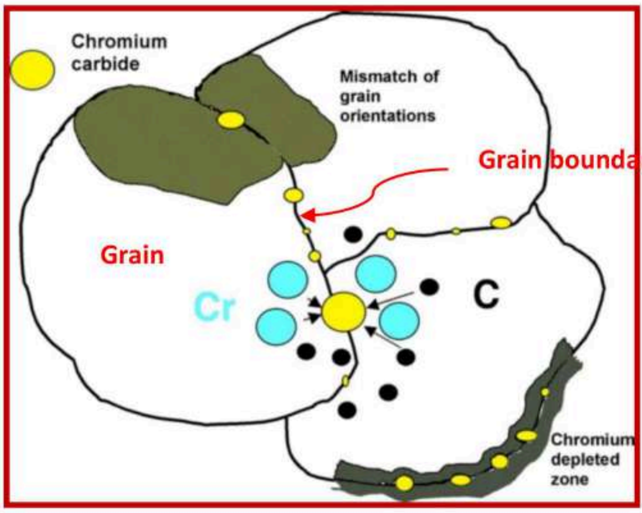


Fig. Inter-granular corrosion in SS-steel

Control methods:

Materials with good resistance to inter-granular corrosion are steel grades with low carbon content (0.03 % C) and Ti/Nb-stabilized steels.

Q. What is inter-granular corrosion? Discuss it with a suitable example.

Q. Soil corrosion is differential aeration corrosion. Justify it.

Lecture-7

1.9 Factors affecting rate and extent of corrosion

As we know that corrosion occurs due to interaction between metal and its surrounding environment. So, any factor that has the ability to change either the nature of the metal or the nature of the environment or both is definitely going to alter the rate & extent of corrosion.

So, let us list first how the rate of corrosion depends on the nature of metal.

- ***Nature of the metal:***

(i) ***Particle size (grain size) of metal:*** Smaller is the particle size; larger is the rate of anodic dissolution. If particle size of the metal will be smaller then, the rate of anodic dissolution will be faster.

(ii) ***Residual stress in the metal:*** Stressed part acts as anode and undergoes corrosion in a corrosive environment. So, between a bent iron wire and a straight wire, the rate of corrosion will be faster in case of bent wire with stressed part (anode).

(iii) ***Purity of metal:*** Lesser is the % purity; greater is the rate of corrosion. For example, between a 99 % pure Zn and 60 % pure Zn, rate of corrosion will be more in case of later.

(iv) ***Nature of the oxide film:*** The smaller is the specific volume ratio (i.e., the ratio of volume of metal oxide to the volume of metal); greater is the oxidation/dry corrosion. Porous and volatile oxide layer causes rapid dry corrosion.

(v) ***Position of the metals and alloys in the EMF or Galvanic series*:** Grater is the difference in their position, faster is the rate of Galvanic corrosion.

(vi) ***Size of the anode*:** Smaller is the size of the anode; greater is the rate of corrosion. If cathodic area will be large, then it will demand more electrons from the small anode for reduction reaction to happen. So, in order to fulfill the huge demand of electrons by the cathode, anode will undergo rapid dissolution (i.e., loss of electrons) process. Hence, this causes rapid corrosion at anodic part.

(vii) ***Passive nature of metal*****:** Some metals like Al, Cr, Ni, Co, etc. resist corrosion as they form protective oxide layer on their surface. The exhibition of improved corrosion resistance than expected from their position in the Galvanic series owing to the formation of protective oxide layer is known as *Passivity*.

(viii) ***Solubility of corrosion products*****:** Larger is the solubility of the product in the medium; greater is the rate of corrosion. For example, Pb undergoes corrosion at smaller rate in H_2SO_4 medium. The reason is that when Pb reacts with $H_2SO_{4,}$ it forms a product $PbSO_4$ that is insoluble in the medium itself. This product gets coated over the metal and resists further dissolution process.

(ix) ***Volatility of corrosion products*****:** Volatile corrosion products result in rapid and continuous corrosion. Molybdenum (Mo) metal suffers from rapid oxidation corrosion as the product MoO_3 is volatile in nature and it volatizes leaving the underlying metal surface for further oxidation corrosion.

➢ ***Nature of the environment***

(i) ***Temperature:*** The rate of corrosion increases with rise in temperature (T) due to the following reasons (i) Decrease in concentration of dissolved oxygen with rise in T; (ii) Increase in rate of anodic dissolution; and (iii) Increase in rate of evolution of H_2 gas at cathode.

(ii) ***% Humidity:*** In general, greater is the % humidity in the atmosphere, the larger is the rate of corrosion. The reason is that moisture dissolves many gases like O_2, H_2S, SO_2, etc. and salt like NaCl to supply the electrolyte needed for setting up of electrochemical cell.

(iii) ***pH of the medium:*** Rate of corrosion is more in acidic media than in *alkaline or neutral medium. For example, rate of corrosion of Fe is faster* in a medium with pH = 4 and slower when pH = 11.

(iv) ***Conductance of the medium:*** Greater is the conductivity of the electrolytic medium; larger is the rate of corrosion. For example, the rate of corrosion of buried iron pipe is greater in clayey and mineralized soil than that of dry sandy soil. The reason is that clayey and mineralized soil is more conducing due to presence of ions than that of dry sandy soil.

(v) ***Formation of O_2 concentration cell:*** O_2 concentration cell is developed when a metal is exposed to differential aeration. The poorly oxygenated part acts as anode and undergoes corrosion.

For example, part of an iron nail inside a wooden structure suffers from this class of corrosion. As the part inside the wood has less access to oxygen, acts as anode and undertake corrosion.

(vi) ***Presence of impurities in the atmosphere:*** Rate of corrosion is more in industrial areas and coastal belt. The reason for is that presence of gases like H_2S, SO_2, CO_2 and fumes of acids like H_2SO_4 and HCl in industrial areas makes the environment more conducting near the surface of the metal. Similarly, in sea areas presence of NaCl in the atmosphere makes the environment a good electrolyte and hence, a more conducting medium.

(vii) ***Presence of suspended particles in the atmosphere:*** Presence of suspended particles like NaCl, $(NH_4)_2SO_4$, activated charcoal, etc. in the atmosphere has the ability to absorb moisture and providing a good conducting medium near the surface of metal.

2.0 Control of corrosion

As corrosion occurs in various forms and affected by numerous factors, the science behind control or prevention corrosion is highly complex. According to the requirements, different corrosion control methods are adopted by various industries to tackle unsafe effects and negative result of corrosion. Corrosion leads to water pollution. For example corroded pipelines, containers, etc. contaminates the drinking water and poses problem not only to the environment but also to the mankind. So, efficient preventive measures should be employed to check the detrimental effect of corrosion.

As corrosion is occurs due to interaction between metal and environment, one can check the rate of corrosion either by modifying the properties of metal or by modifying the environment. Accordingly, control methods are classified into two parts:

A. ***Corrosion control by modification of the environment:*** In this type, metals are protected by two ways: (1) by the removal of corrosion causing substances; and (2) by the use of substances (known as *inhibitors*) which can reduce the rate of cathodic/anodic reaction.

B. ***Corrosion control by modification of the properties of metal:*** The various methods applied to modify the properties of metal are:

1. Use of Protective coatings
2. Electrochemical or cathodic protection
3. By selection of suitable metal and proper designing of structures
4. By alloying

Corrosion Inhibitors

Corrosion inhibitors are chemical substances which are added in small amount (0.1 %) to the corrosion medium to prevent or slow down the oxidation or reduction reactions on the surface of the metal. Inhibitors do their job by providing a protective layer on the metal surfaces.

Inhibitors are of two types; (1) Inorganic, and (2) Organic

Inorganic Inhibitors: It includes chromates, phosphates, molybdates, zinc, polyphosphates, etc. They are mainly used in boilers, fractional distillation plant, cooling towers, etc.

Inorganic inhibitors are classified as (a) Anodic, and (b) Cathodic

Anodic Inhibitors: Chemical substances which inhibits the anodic (oxidation) reaction. Example includes molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), chromates ($Cr_2O_7^{2-}$), silicates (SiO_3^{2-}), etc. These anions react with metallic ions to produce insoluble precipitates. Insoluble substances so obtained are then get adsorbed on the surface of metal and hence slow down the rate of anodic reaction.

$$Cr_2O_7^{2-} + Fe^{2+} + H_2O \rightarrow Cr_2O_3 + Fe_2O_3 + 2OH^-$$

Cathodic Inhibitors: Chemical substances which inhibits the cathodic (reduction) reaction. Example includes $ZnSO_4$, $MgSO_4$, Na_2SO_3 and $Ca(HCO_3)_2$. $ZnSO_4$, $MgSO_4$, and $Ca(HCO_3)_2$ slow down the anodic reaction by forming a layer of $Zn(OH)_2$, $Mg(OH)_2$, $CaCO_3$ on the metallic surface. Na_2SO_3 inhibits by removing dissolved oxygen ($Na_2SO_3 + 1/2O_2 \rightarrow Na_2SO_4$).

Organic Inhibitors: It includes amines (RNH_2), mercaptans (R-SH), substituted urea, and thioureas, amides ($R\text{-}CONH_2$), Imidazoline, etc. These substances adsorbed on the surface of metal and acts as protective coating. They attach to the surface by chemisorptions and physical adsorption.

Q & A on Factors affecting corrosion

Q. Aluminium is not attacked by conc. HNO_3 but Iron gets rapidly corroded even by dil. HNO_3. Justify this statement.

Ans. In Conc. HNO_3, Al gets oxidized and forms a protective layer of Al_2O_3 on its surface.

Q. Give reason that Stainless steel (SS) exhibits high corrosion resistance in HNO_3 solution over a wide range of concentrations.

Ans. Because Cr present in SS forms a protective layer of Cr_2O_3 on its surface upon oxidation by HNO_3.

Q. What is meant by the term Passivity?

Ans. Passivity or passivation is a phenomenon by which a metal or alloy exhibit high corrosion resistance due to formation of a highly protective film on its surface.

Q. A 55 % purity Zn suffers from rapid corrosion as compared to 99.9 % Zn. Give reason.

Ans. Greater is the % impurity of a metal, faster is the rate of corrosion due to formation a large number of electrochemical cells.

Q. Corrosion of Zn can be minimized by increasing the ph to 11. Give reason.

Ans. At pH =11, Zn forms $Zn(OH)_2$ ppt. and gets adsorbed on the surface of Zn to resist further dissolution.

Q. Corrosion of metals occurs at a faster rate in clayey and mineralized soil. Give reason.

Ans. Conductivity of clayey and mineralized soil is more than sandy soil.

Q. Which gases in the atmosphere are likely to accelerate the rusting of iron?

Ans. CO_2, SO_2, SO_3, NO_2, etc.

Q. Rate of metallic corrosion increases with increase in temperature. Give reason.

Ans. Corrosion rate increases with temperature due to increase in the rate of diffusion of ions.

Q. What are the factors which affects the rate of corrosion? (5 marks)

Ans. Refer above (section 1.9)

Lecture-9

2.0 Control of corrosion

As corrosion occurs in various forms and affected by numerous factors, the science behind control or prevention corrosion is highly complex. According to the requirements, different corrosion control methods are adopted by various industries to tackle unsafe effects and negative result of corrosion. Corrosion leads to water pollution. For example corroded pipelines, containers, etc. contaminates the drinking water and poses problem not only to the environment but also to the mankind. So, efficient preventive measures should be employed to check the detrimental effect of corrosion.

As corrosion is occurs due to interaction between metal and environment, one can check the rate of corrosion either by modifying the properties of metal or by modifying the environment. Accordingly, control methods are classified into two parts:

A. ***Corrosion control by modification of the environment:*** In this type, metals are protected by two ways: (1) by the removal of corrosion causing substances / corrosion stimulants; and (2) by the use of substances (known as *inhibitors*) which can reduce the rate of cathodic/anodic reaction.

B. ***Corrosion control by modification of the properties of metal:*** The various methods applied to modify the properties of metal are:

1. Use of Protective coatings
2. Electrochemical or cathodic protection
3. By selection of suitable metal and proper designing of structures
4. By alloying

A. Corrosion control by modification of the environment

1. Removal of corrosion causing substances / corrosion stimulants

- Corrosion due to DO can be prevented by its removal by addition of reducing substance like hydrazine
- To prevent corrosion due to acids, they are neutralized with lime

- To prevent corrosion due to alkalis, they are neutralized with acids
- To prevent corrosion due to salts, they are removed by ion-exchange methods.
- To prevent corrosion due to moisture, they are removed by dehumidification using silica gel.

2. Using Corrosion Inhibitors

Corrosion inhibitors are chemical substances which are added in small amount (0.1 %) to the corrosion medium to prevent or slow down the oxidation or reduction reactions on the surface of the metal. Inhibitors do their job by providing a protective layer on the metal surfaces.

Inhibitors are of two types; (1) Inorganic, and (2) Organic

Inorganic Inhibitors: It includes chromates, phosphates, molybdates, zinc, polyphosphates, etc. They are mainly used in boilers, fractional distillation plant, cooling towers, etc.

Inorganic inhibitors are classified as (a) Anodic, and (b) Cathodic

Anodic Inhibitors: Chemical substances which inhibit the anodic (oxidation) reaction are called *Anodic Inhibitors.* Example includes molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), chromates ($Cr_2O_7^{2-}$), silicates (SiO_3^{2-}), etc. These anions react with metallic ions to produce insoluble precipitates. Insoluble substances so obtained are then get adsorbed on the surface of metal and hence slow down the rate of anodic reaction.

Cathodic Inhibitors: Chemical substances which inhibit the cathodic (reduction) reaction are called *Cathodic Inhibitors*. Example includes $ZnSO_4$, $MgSO_4$, Na_2SO_3 and $Ca(HCO_3)_2$. $ZnSO_4$, $MgSO_4$, and $Ca(HCO_3)_2$ slow down the anodic reaction by forming a layer of $Zn(OH)_2$, $Mg(OH)_2$, $CaCO_3$ on the metallic surface. Na_2SO_3 inhibits by removing dissolved oxygen ($Na_2SO_3 + 1/2O_2 \rightarrow Na_2SO_4$).

Organic Inhibitors: It includes amines (RNH_2), mercaptans (R-SH), substituted urea, and thioureas, amides ($R\text{-}CONH_2$), Imidazoline, etc. These substances adsorbed on the surface of metal and acts as protective coating. They attach to the surface by *chemisorptions* and *physical adsorption*.

Q. How to control rate of corrosion removing corrosion stimulants from the environment? (5 marks)

Ans. Some of the methods of removal of corrosion stimulants are as follows:

- Corrosion due to DO can be prevented by its removal by addition of reducing substance like hydrazine
- To prevent corrosion due to acids, they are neutralized with lime
- To prevent corrosion due to alkalis, they are neutralized with acids
- To prevent corrosion due to salts, they are removed by ion-exchange methods.
- To prevent corrosion due to moisture, they are removed by dehumidification using silica gel.

Q. What is an inhibitor?

Ans. It is a chemical substance which when added to the environment slows down the corrosion reaction. Example- molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), $ZnSO_4$

Q. Define anodic inhibitor with an example.

Ans. Those Chemical substances which inhibit the anodic (oxidation) reaction are called as anodic inhibitor. For example molybdates (MoO_4^{2-})

Q. Define cathodic inhibitor with an example.

Ans. Those Chemical substances which inhibit the anodic (oxidation) reaction are called as anodic inhibitor.

Q. What is an organic inhibitor?

Ans. It is an organic substance which decreases the rate of corrosion. For example: Thiourea

B. *Corrosion control by modification of the properties of metal*

1. Alloying: Corrosion resistance of most metals is increased by alloying them with suitable elements like Al, Cr, etc. Chromium is the best alloying metal for iron.

2. Protective Coatings

In this route a thin layer of material (e.g.; metal, non-metal, polymer, etc.) is applied on the surface of another material which is to be protected from corrosion by various techniques such as spraying, hot dipping, electroplating, etc. In general there are two types of protective/surface coating:

1. Metallic coating (includes coating of Zn, Sn, etc. on iron)
2. Non-metallic coating: It is again classified as organic (e.g. paints, polymer, etc.) and inorganic coating (e.g. phosphate, chromate, cement coating, etc.)

A good coating material should have the following characteristics:

a. Coating should be non-porous, non-volatile, and continuous
b. Coating should be hard
c. Coating should be able to withstand direct attack of environment

Metallic Coatings

The materials in construction (iron and steel) are suffers from corrosion in acidic and alkaline environment. Construction materials should have high mechanical strength, high corrosion resistance and low cost. In order to make materials resistant against corrosion, their surfaces are coated with metals like, zinc, tin, copper, chromium, etc.

Depending on the nature of coating material, metallic coating is classified into two categories:

A. Anodic or Sacrificial Coatings, and
B. Cathodic or Barrier Coatings

Anodic or Sacrificial Coatings: In this method, an active or more anodic metal is coated over the base metal which is to be protected from corrosion. For example, iron (Fe) is protected from corrosion by applying a coat of Al, Cd, or Zn. Here, active metal (Al, Cd, or Zn) protect the base Fe-metal sacrificially.

Galvanization: The process of coating of Zn-metal over the iron is known as Galvanization. It is an anodic coating. It can be done by spraying or hot dipping. Zn is active and acts as anode as its standard oxidation potential (0.76 V) is higher than that of Fe (0.44 V). Galvanization protects the iron by the following two ways:

(i) By providing a non-porous, non-volatile continuous oxide layer (ZnO) on the surface of iron, and

(ii) By sacrificially (i.e, Zn acts as anode and undergoes dissolution)

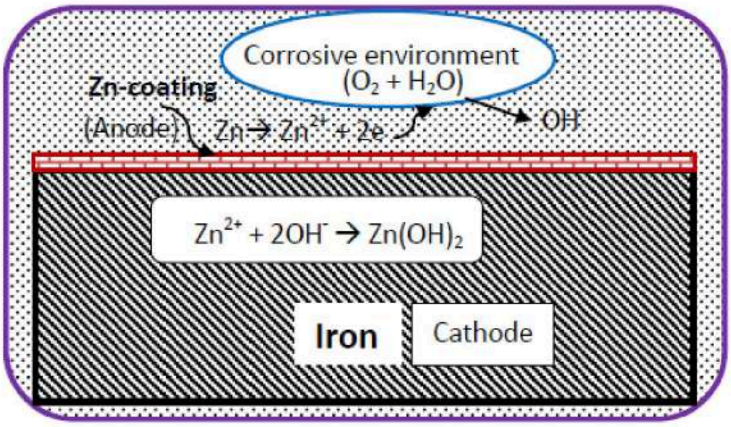


Fig. 10. Anodic coating (Galvanization of Iron)

So, *Galvanization* is a double protection route. As Zn is more anodic, it protects the underlying metal sacrificially when the protective oxide layer breaks at some point of time by the environment.

Cathodic or Barrier coating: In this method, a passive or less anodic metal is coated over the base metal which is to be protected from corrosion. For example, iron (Fe) the base metal is protected from corrosion by applying a coat of passive metals like Sn, Pb, or Ni. Here, less active or passive metal (Sn, Pb, or Ni) protect the more active base Fe-metal only by developing a protective oxide layer.

*** Remember that any breakage in the coating layer results in rapid corrosion. This happens because metal exposed at the breakage point acts as anode which has relatively very small area. When anodic area is much smaller than the cathodic area, rapid corrosion like pitting occurs on the surface.

Tinning: The process of coating of tin (Sn)-metal over the iron is known as Tinning. Sn is less active and acts as cathode as its standard oxidation potential (0.14 V) is lower than that of Fe (0.44 V). So, here base metal is more active than the coating metal. The coat metal protects the underlying metal Fe only by forming an impervious oxide layer of tin oxide (SnO_2). Any damage on this layer results in pitting or formation of cavity on the surface of iron. So, a lot of care should be taken to tin plated iron can otherwise leads to rapid corrosion. Tinning is a single protection method.

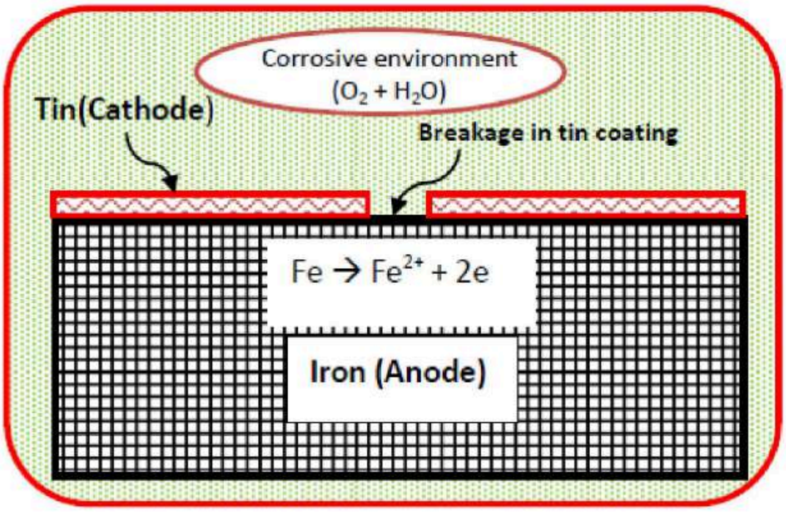


Fig. 11. Cathodic coating (Tinning of Iron)

Distinguish between Galvanization and Tinning

Sl. No.	Galvanization	Tinning
1	A process of covering the surface of iron by a layer of zinc (Zn)	A process of covering the surface of iron by a layer of tin (Sn)
2	Zinc protects the iron by both sacrificially and formation of protective oxide layer	Tin protects the iron only by formation of protective oxide layer
3	Double protection route	Single protection route
4	Galvanized iron (GI) containers are not safe to store foodstuffs as food acids reacts with Zn to form toxic masses. Always there is a chance of food poising.	Tin coated container is safe to store foodstuffs. No food poisoning occurs.

Q. Why are Galvanized utensils not used?

Ans. Zn of Galvanized utensils gets dissolved in dilute food acids and forms highly toxic compounds may lead to food poisoning.

Q. Why are tinned utensils used for storing foodstuffs?

Ans. Tin is non-toxic in nature and not dissolved in dilute food acids.

Q. Zn-coated iron article is protected from rusting even when the coating is scratched. Explain it.

Ans. Zn is anodic to Fe, so when the ZnO film is scratched, Zn is preferentially attacked by the corrosive environment to form $Zn(OH)_2$ corrosion product and Fe is protected.

Q. Name two metals used for anodic coating.

Ans. Zn, Al

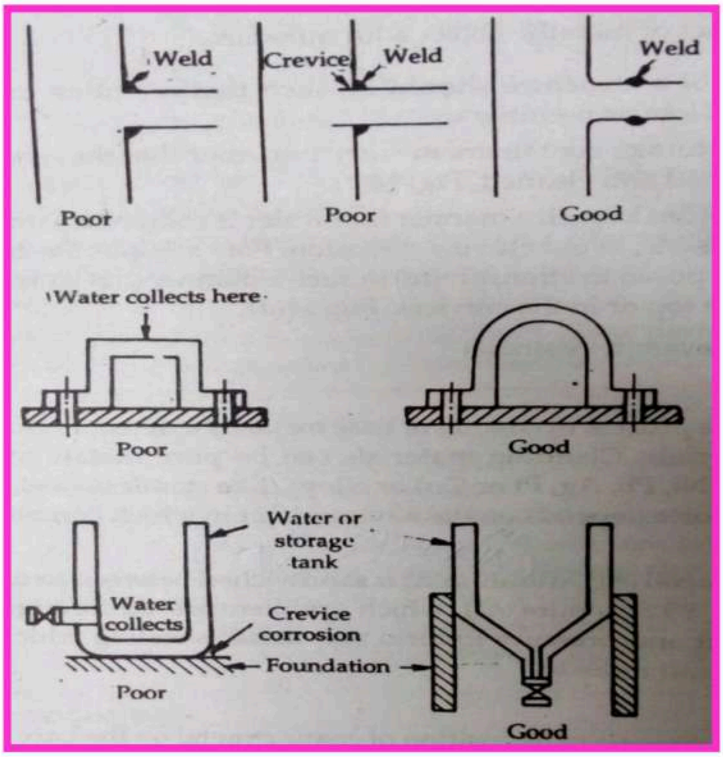
Q. Name two metals used for cathodic coating.

Ans. Sn, Pb

3. Proper designing

Some of design principles are as follows:

A. Avoid contact of dissimilar metals in presence of a corrosive environment
B. Keep the anodic area much larger than cathodic area
C. Anodic metal should not be painted or coated
D. Sharp corners, edges, etc. should be avoided (i.e., avoid L, T, V shaped profiles in constructions)



4. Cathodic or Eletrochemical Protection

It is a technique applied to reduce corrosion of underground metallic structures by forcing it to behave like a cathode. There are two types of cathodic protection:

A. Sacrificial Protection
B. Impressed current method

Sacrificial Protection

We know that wet/electrochemical corrosion occurs via formation of separate anode and cathode. The existence of potential difference between anode and cathode causes loss of electron (oxidation) at anode. So, without cathodic protection, active metal suffers from corrosion. If a more active metal is connected via an insulated Cu-wire to a metallic structure which is undergoing corrosion then corrosion occurs at more active metal and the metallic structure can be protected. As the more active metal is sacrificed in the process of protecting the metallic structure, it is known as *sacrificial anode*. Examples of sacrificial anode are Zn, Mg, Al, and their alloys.

Sacrificial cathodic protection methods are widely used for the protection of relatively small structures like underground pipelines, storage tanks, etc.

Fig. Sacrificial protection of buried water pipe.

Impressed current cathodic protection

In this protection method, current from an external source such as battery is applied to the metallic structure to neutralize the corrosion current. This is done to forcing the metallic structure (anode) to behave as cathode and hence protected. **(Actually during corrosion, current passes from anode to cathode, so to nullify it, current is applied in the opposite direction) In this process materials such as graphite, high silica iron, stainless steel, etc. are acts as anode. The anode is surrounded by a conducting medium (back fill) to have an electrical contact between itself and the surrounding soil. This method is applied in various relatively bigger structures like ship, transmission line towers, tanks, etc.

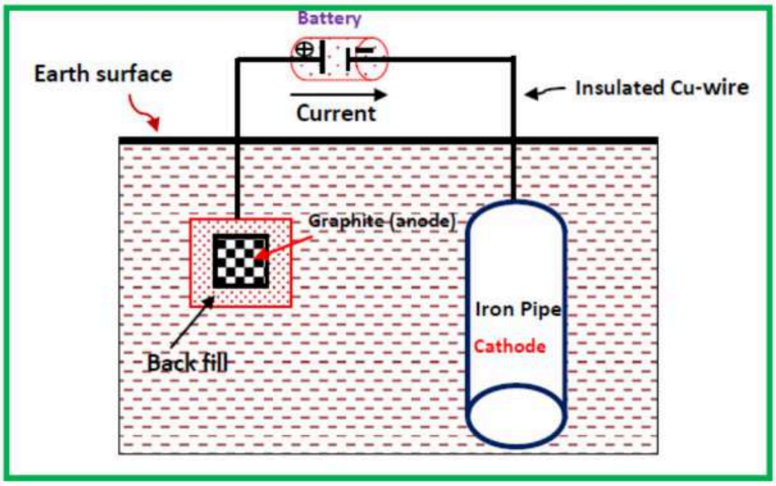


Fig. Impressed current cathodic protection

Q. Give reason that Zinc is used as sacrificial anode for protection of iron from rusting.

Ans. As std. oxidation potential of Zn is more than Fe, corrosion will be takes place at Zn and iron will be protected.

Q. Sharp corners should be avoided in any structural design. Give reason.

Ans. As sharp corners region are poorly oxygenated part acts as anode and undergoes differential aeration corrosion.

Q. What is cathodic protection? Give an example.

Ans. It is a corrosion control technique applied to reduce corrosion of underground metallic structures by forcing it to behave like a cathode. Example: sacrificial cathodic protection.

Q. What is impressed current cathodic protection?

Ans. It is a corrosion control method in which a battery is connected to the metallic structure in order to cancel out the corrosion current.

Q. What is sacrificial anode? Give an example.

Ans. It is a metal with higher standard oxidation potential than the metal which is to be protected from corrosion. For example for iron, Zn is acts as sacrificial anode.

Q. How is cathodic protection of iron is different from Galvanization?

Ans. In cathodic [protection, the iron structure is made cathode by connecting it with a metal with higher std. Ox. Pot. Like Zn, Mg, etc. On the other hand, Galvanization is coating of Zn-metal on the surface of Iron.

Q. Ship hull is connected to Zn-rod. Give reason.

Ans. Here Zn acts as sacrificial anode and protects the ship from corrosion.

Long Questions

1. **What is cathodic protection? Discuss the sacrificial cathodic protection with a suitable example.**
2. **Discuss Galvanization and tinning process with a suitable example.**
3. **What is cathodic protection? Discuss the impressed current cathodic protection with a suitable example.**