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Don Bosco Institute of Technology, Mumbai

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Department of Basic Sciences & Humanities

Course Code: 25FE1BSC03

Engineering Chemistry

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It is intended to supplement the prescribed textbooks and classroom discussions, offering students an accessible and structured reference for better understanding of the subject.

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Module 2: Corrosion

2.1 Introduction to Corrosion: Definition and significance. Types of Corrosion: a) Dry (chemical) Corrosion-Concept of stability of oxide films, b) Wet (electrochemical) Corrosion-Mechanism of Electrochemical Corrosion

2.2 Factors affecting Corrosion Rate: Humidity, Position of metal in Galvanic series, pH, Temperature, Relative area of cathode to anode, Presence of Impurities. Factors contributing to corrosion in electronic devices.

2.3 Different forms of Corrosion: Galvanic corrosion, Differential Aeration corrosion, Intergranular Corrosion

2.4 Corrosion Prevention: Non-Metallic Coatings-Acrylic, Epoxy. Anti-Rust Lubricant-Definition of Lubricant and Acid Value of Oil and Its Significance, Numerical on Acid Value, Corrosion Inhibitors in Engine Oils. Metallic Protective Coatings: Differences Between Galvanization and Tinning. Surface Treatment- Anodizing,

2.5 Cathodic Protection: Principle and Application of Sacrificial anode and Impressed Current Systems

Self-Learning Topics: Introduction to Electrochemistry, Corrosion Control Techniques based on Design considerations, Material selection and modification

2.1- Introduction to Corrosion: Definition and significance. Types of Corrosion

Learning Outcomes

Upon completion of this topic, you will be able to,

- define and describe the concept of corrosion and its various types.
- explain the mechanisms of chemical and electrochemical corrosion

Introduction

What is Corrosion?

Destruction or deterioration or gradual eating away or disintegration of a metal by chemical or electrochemical reaction with its environment is called corrosion.

Corrosion is the disintegration of metal through an unintentional chemical or electrochemical action, starting at its surface. Hence when metals are put into use in various forms they are exposed to the environment as a result of which the exposed metal surfaces start decaying by converting into more stable metal compounds more or less rapidly. Thus it is a reverse process of extraction of metals.

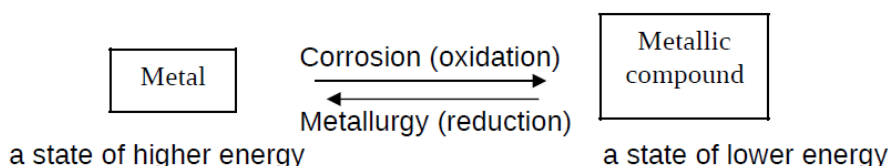


Figure2(a): Corrosion of metal

The environment could be of any type such as atmosphere, water, sea-water, acids, steam gases, soils, liquid metals etc.

The most familiar examples of corrosion are :

Rusting of iron when exposed to the atmospheric conditions. During this a layer of reddish - brown scale and powder of oxide (Fe_2O_3) is formed which makes iron weak.

Green film of basic carbonate [$\text{CuCO}_3 + \text{Cu}(\text{OH})_2$] formation on the surface of copper when exposed to moist air containing CO_2 .

The consequences of corrosion:

Corrosion is a slow process and occurs only at the surface of metals. The loss from corrosion cannot be measured by the cost of metal alone but also the high cost of its fabrication into machine tools, equipment, structures. The dangerous effect of corrosion is weakening of metallic structure such as bridges, boilers, buildings etc. It may also cause consequent defects in machinery resulting in casualties and injuries to workers. It also introduces metallic poisons into water and foodstuff.

Classification of Corrosion:

Corrosion occurring in an environment can be classified broadly with respect to the following factors.

Nature of the corrodent:-

Corrosion can be *dry or wet*. Dry corrosion occurs in absence of moisture & usually involves reaction of metal with dry gases at higher temperature. Wet corrosion occurs in presence of water or a conducting liquid.

Mechanism of corrosion: -

Corrosion can be direct chemical corrosion indirect electrochemical corrosion. In direct chemical attack metal corrodes in presence of reacting chemicals. In electrochemical attack one metal undergoes corrosion in presence of another metal when in contact with a conducting medium.

Appearance of the corroded metal:-

Corrosion may be either uniform or localized. In uniform corrosion metals gets corroded over the entire surface at the same rate, while in localized corrosion only small and specific area of the metal get corroded.

2.1.1 Corrosion Type -DRY-Chemical Corrosion or Direct chemical corrosion)- Mechanism

This type of corrosion occurs mainly through the direct chemical action of atmospheric gases such as O_2 , CO_2 , H_2S , Halogens (Cl_2 , Br_2 , I_2 etc), SO_2 etc with metals or alloy surfaces. Some organic and anhydrous inorganic liquids as well as liquid metal may corrode solid metal as a result of direct chemical attack.

In all the cases extent of corrosion depends upon,

- a) the chemical affinity between metal and corrosive environment (gas or liquid)
- b) the ability of metal to form protective film.

The surface of metals is directly attacked by the atmospheric gases and gets coated with corresponding compounds like oxides, sulphides, carbonates etc. Such type of corrosion which is brought about by the atmospheric conditions is also called atmospheric corrosion.

This type of corrosion produces two important effects on the metal,

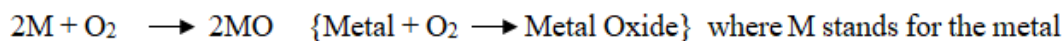
- a) the metal is consumed
- b) the properties of metal are changed.

The types of chemical corrosion include,

- a) Corrosion due to oxygen gas
- b) Corrosion due to other gases

a) Corrosion due to oxygen (oxidation corrosion) :

It has been found that oxygen present in the medium directly attacks the metal surface at low or high temperature usually in absence of moisture.



- At ordinary temperature, metals in general are slightly attacked.
- At low temperatures, alkali metals (Li, Na, K etc) and alkaline earth metals (Ca, Sr, Mg etc) are even rapidly oxidized.
- At high temperatures, almost all metals (except Ag, Au, and Pt) are oxidized.

(Normally more active metals get corroded faster than less active metals)

The extent of corrosion depends upon the type of oxide film formed by metals.

The oxide films formed are classified into three categories,

- 1) Stable
 - i) Porous oxide film (non protective),
 - ii) Non porous oxide film (protective).
- 2) Unstable
- 3) Volatile

1) Stable Oxide film:

A stable oxide film consists of fine grains in its structure and it can get adhered tightly to the metal surface. Hence such oxide film can be impervious in nature and decreases corrosion to great extent.

The sealing or shielding of the metal surface from any further contact with atmospheric oxygen depends on the type of stable oxide film formed.

The protective and non-protective nature of the oxide film depends mainly upon the “Pilling Bedworth Rule”.

Pilling Bedworth rule:

According to this rule, “an oxide layer is protective or non porous if the volume of oxide layer is at least as great as the volume of metal from which it is formed. On the other hand, if the volume of oxide layer is less than the volume of metal from which it is formed, then the

oxide layer is porous and hence non-protective because it cannot prevent the access of oxygen to the fresh metal surface below.”

- **Pilling Bedworth Rule:** it says that “smaller the specific volume ratio greater is the oxidation corrosion”

$$\text{Specific Volume Ratio (SVR)} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

- i. If $V_{MO} > V_M$, metal oxide layer is tight and non porous and protect to further oxidation.
- **Example:** Tungsten(W)- 3.6, Chromium(Cr)- 2.0, Nickel(Ni)-1.6. So rate of corrosion: Ni > Cr > W.
- ii. If $V_{MO} < V_M$, metal oxide layer is porous and non protective, corrosion continues till all the metal undergo oxidation corrosion.
- **Example:** Lithium(Li), Sodium(Na), Potassium(K).

This can be understand better by taking examples of alkali metals such as Li, Na, K or alkaline earth metal such as Ca , Mg etc. These metals react with oxygen, forming oxides such as Na_2O , K_2O , CaO , MgO etc. Here the volume of oxide formed is less than the volume of metal from which they are formed. Thus oxide layer is not able to cover the entire surface of metal block/piece and hence the oxide layer faces stress and strain. As a result, pores and cracks are developed on the oxide layer. These pores give free access to oxygen which attacks the underlying pure metal which causes unobstructed and serious corrosion.

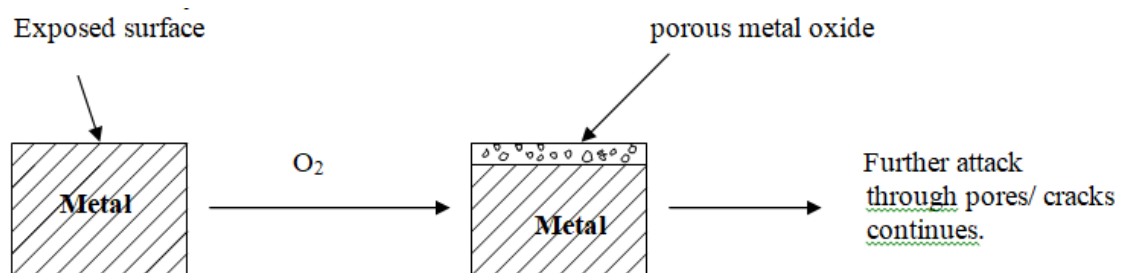


Figure-2(b-1): Stable porous metal oxide film

On the other hand if the oxide film formed is non-porous in nature, the rate of corrosion reduces considerably and in most of the cases corrosion of metal stops. Metals like Al, Cr etc. form oxides such as Al_2O_3 , Cr_2O_3 etc. Here volume oxide formed is greater than the volume of metals. Hence the oxide film formed covers the underlying metals completely not having any access for further attack of oxygen thereby stopping further oxidation. Thus metal develop a protective oxide layer and become passive until this layer is intact.

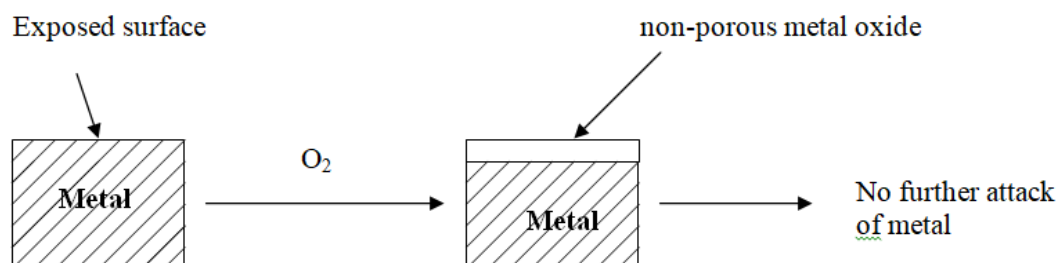


Figure-2(b)-2: Stable non-porous metal oxide film

2) Unstable Oxide film:

The oxide film formed on the surface of the metal is unstable and it decomposes back into metal and oxygen. For example oxides of metals like Gold, Silver, and Platinum etc. form unstable oxide film and hence do not get corroded.

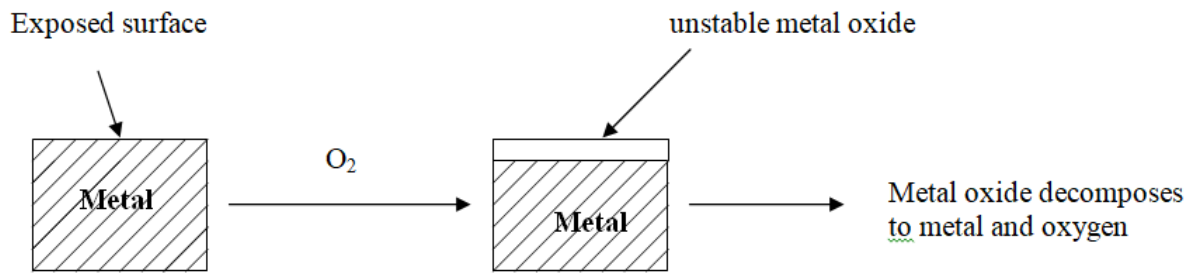


Figure-2(b)-3: Unstable metal oxide film

3) Volatile oxide film:

When the oxide film formed is volatile, it vaporizes as soon as it is formed and the underlying metal surface is exposed for further attack of oxygen. This will lead to continue and excessive corrosion. Molybdenum metal form MoO₃, which is volatile.

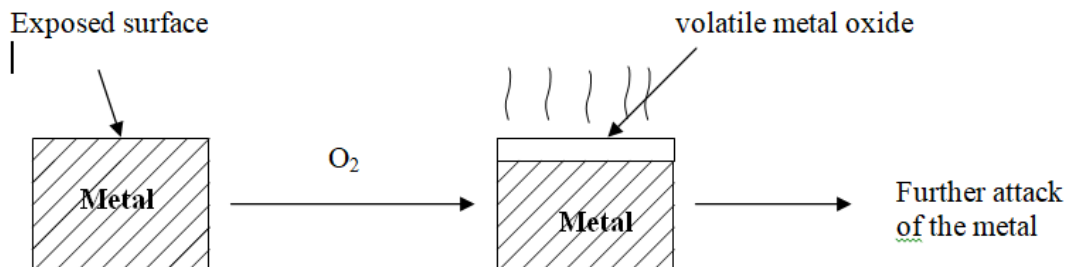


Figure-2(d): Volatile metal oxide film

b) Corrosion due to other gases:

Among the other dry gases which cause corrosion on metals are F₂, Cl₂, H₂S, SO₂ etc. The extent of corrosion depends upon the chemical affinity between the metal and the gas involved. The rate of further corrosion depends upon the volume of the corrosion film and the volume of the metal.

Example: Corrosion due to chlorine



Here the film of silver chloride is protective (non-porous), hence the rate of further corrosion is reduced while that of stannic chloride is volatile, hence rate of corrosion is enhanced.

2.1.2 -TYPE -WET-Electrochemical Corrosion (Wet or Indirect corrosion)

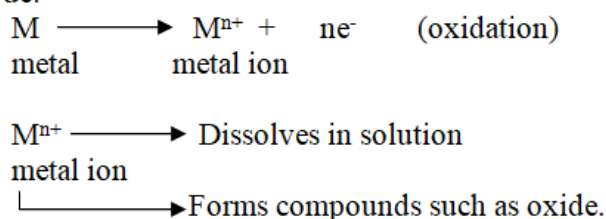
This type of corrosion occurs

- when a metal is in contact with a conducting medium or
- when two dissimilar metals or alloys are either immersed or dipped partially in aqueous solutions/conducting medium and when in contact

Electrochemical corrosion is brought about through ionic reaction in presence of moisture or solution as a conducting medium. This corrosion occurs due to the existence of separate anodic and cathodic areas between which current flows through the conducting solution.

At anodic area, oxidation reaction (i.e. liberation of free electrons) takes place, so anodic metal is destroyed by either dissolving or assuming combined state (such as oxide). Hence corrosion always occurs at anodic areas.

At anode:



On the other hand at cathodic area, reduction reaction (i.e. gain of electrons) takes place. Usually cathode reaction does not affect the cathode. Since most metal cannot be further reduced. So at cathodic part, dissolved constituent in the conducting medium accepts the electrons to form H_2 , OH^- , O^{2-} .

The metallic ions (at anodic part) and non metallic ions (formed at cathodic part) diffuse towards each other through conducting medium to form a corrosion product somewhere between the anode and the cathode. The electrons set free at the anode flow through the metal and are finally consumed in the cathode reaction.

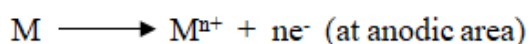
In electrochemical corrosion the three essentials are:

- **Formation of anodic and cathodic area, anode corrodes by forming ions and the cathode is protected.**
- **Electrical contact between anode and cathode for the conduction of electrons**
- **Electrolyte usually provided by the presence of moisture**

It should be noted that higher the metal in the electrochemical series, (that is metals with higher oxidation potential) the more easily it is corroded. (Exception: Aluminium, although it is placed near the top of the series, it resists atmospheric corrosion very effectively because of the formation of an oxide film on its surface which prevents further corrosion.)

Mechanism of electrochemical corrosion

Corrosion of metal in aqueous solution is an electrochemical phenomenon, involving flow of electrons (electric current) between the anodic & cathodic areas. The anodic reaction involves dissolution of metal as corresponding metallic ions with the liberation of free electrons.



On the other hand, the cathodic reaction consumes electrons with either

a) evolution of hydrogen or
b) absorption of oxygen,
depending on the nature of corrosive environment.

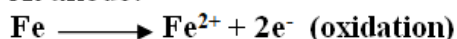
a) Evolution of Hydrogen : (acidic medium)

This type of corrosion occurs usually in acidic environment like industrial waste

Example: A steel tank containing acidic industrial waste with small piece of copper scrap in contact with the steel. The portion of the steel tank in contact with copper is corroded the most with the evolution of hydrogen gas at the copper piece.

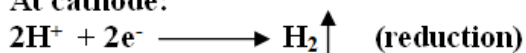
The reactions are:

At anode:

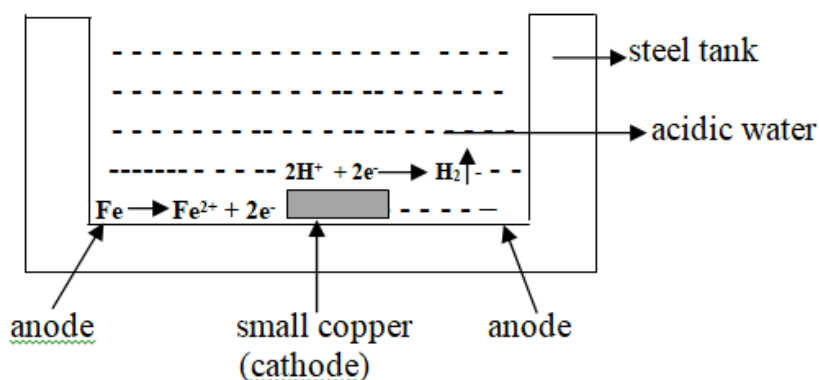


These electrons flow from anode to cathode through the metal.

At cathode:



Hydrogen Evolution Mechanism



Thus overall reaction is, $\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2$

Figure-2(e)-1: Hydrogen Evolution Mechanism-Wet Corrosion

This type of corrosion is, therefore nothing but displacement of hydrogen ion from the acidic solution by the metal ions. In general all metals above hydrogen in the electrochemical series have a tendency of dissolving in acidic solution with the simultaneous liberation of hydrogen.

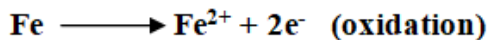
b) Absorption of Oxygen : (neutral or basic medium)

This type of corrosion is seen where there is rusting of iron in neutral aqueous solution of electrolytes such as NaCl in presence of atmospheric oxygen.

Example: Let us consider an iron metal exposed to the atmosphere. The surface of iron metal is generally coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface while iron oxide protected(steel/metal) acts as a cathode and moisture in the atmosphere acts as an electrolyte.

The reactions are as follows,

At the anode:



These free electrons flow from anode to cathode through iron metal where the electrons are intercepted by oxygen atoms present in the atmosphere in presence of moisture form hydroxyl (OH^-) ions.

At cathode:



Oxygen Absorption Mechanism

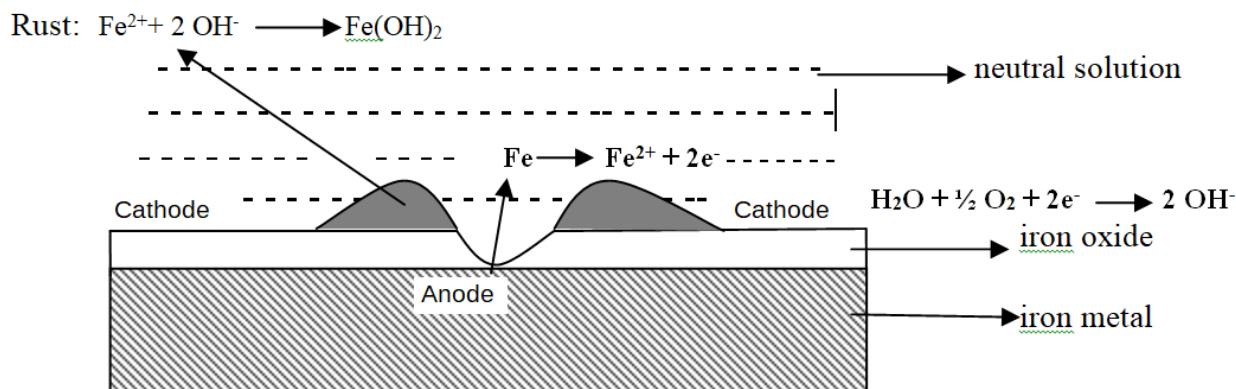
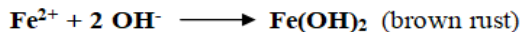


Figure-2(e)-2: - Oxygen Absorption Mechanism -Wet Corrosion

The Fe^{2+} ions at anode & OH^- ions at cathode diffuse and combine to form ferrous hydroxide



If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide



If supply of oxygen is limited the corrosion product is black anhydrous magnetite (Fe_3O_4).

2.2 Factors affecting Corrosion:

Learning Outcomes

Upon completion of this topic, you will be able to,

- identify and explain factors influencing corrosion rates
- analyze the impact of environmental and material-related factors on corrosion behavior

2.2.1 Factors affecting Corrosion Rate

The rate and extent of corrosion depend upon the following:

- a) Nature of the metal
- b) Nature of the environment.

a) Nature of metal:

1) Position of metal in Galvanic series (oxidation potential):



Table No-1-ref: <https://www.icorr.org/>

- The extent of corrosion depends upon the position of metal in the electrochemical series or Galvanic series. The galvanic series ranks metals and alloys by their corrosion potential in an electrolyte, predicting which will corrode easily
- When two dissimilar metals or alloys are in electrical contact in presence of an electrolyte, the metal or alloy higher up in the Galvanic series (or having high oxidation potential) becomes anode and undergoes corrosion.
Example: when zinc and copper are in contact, zinc becomes anode and suffers corrosion while copper remains protected.
- Further, when two metals in the Galvanic series have greater difference in their oxidation potential, the greater will be the corrosion of anodic metal.

2) Purity of metal (impurities):

- Presence of impurities in the metal greatly affects the rate of corrosion.
- If the metal contains impurity metals then, tiny Galvanic cell can be set up easily and hence increases the rate of corrosion.

3) Relative areas of cathode and anode.

The corrosion of the anodic section is directly proportional to the ratio of the cathodic part area and anodic part area. Example: Small steel screws fitted to a large copper tank will undergo corrosion at a faster rate.

- When two dissimilar metals are in contact, the corrosion of anodic part is directly proportional to the ratio of areas of cathodic part and anodic part.
- Consequently, corrosion is more rapid and localized if the anodic area is small. This is because when the cathodic area is larger, the demand for electrons is more (increases) which can only be met by the anodic area by undergoing faster corrosion.

- Thus smaller area of the anode faster is the rate of corrosion.

Mathematically,

$$\text{Rate of corrosion} \propto \frac{\text{area of cathode}}{\text{area of anode}}$$

Eg: If steel plates (anodes) were joined with copper rivets (cathodes), slow corrosion of steel would occur, since the galvanic corrosive effect is spread out over a large area of steel

b) Nature of the environment:

1) Temperature and Corrosion:

- Corrosion rate increases with temperature because higher temperature speeds up chemical reactions and ion movement. The rate of chemical reaction increases with temperature. Increase in temperature increases ionization and mobility of reacting ions, molecules, diffusion rate **Hence increased temperature generally enhances corrosion rate.** But gases like oxygen dissolve less at high temperatures, which can reduce corrosion in some cases.

Example: Dissolved O_2 is absent in boiling H_2SO_4 . Stainless Steel corrodes more in boiling H_2SO_4 , because it needs oxygen to stay passive (protected).

2) Moisture and Corrosion:

- The rate of corrosion increases with the moisture around the metal.
- This is mostly due to the fact that moisture acts as the solvent for oxygen and other gases providing the electrolyte essential for setting up an electrochemical corrosion cell.

Example: Iron corrodes slowly in dry air but quickly in moist air.

- Rainwater can also wash away protective layers, exposing fresh metal.

3) Effect of pH on Corrosion:

- Acidic media (low pH) usually cause more corrosion than neutral or alkaline (high pH) ones.
- Amphoteric metals like Al, Zn, Pb corrode in both acid and strong alkali due to complex ion formation.

Examples:

Iron: Corrodes more at pH below 5, especially with oxygen. Rust forms through a reaction involving Fe^{2+} and OH^- .

Zinc: Corrodes even in mild acids like carbonic acid. Best protected at pH 11.

4) Presence of impurities :

The presence of impurities in the environment—especially in industrial or polluted areas—can lead to the formation of corrosive chemicals that accelerate the degradation of metals and electronic components.

Examples:

Sulfur compounds like hydrogen sulfide and sulfur dioxide react with metal surfaces, forming corrosive layers such as sulfides and oxides.

Chlorine can create acidic conditions in presence of moisture that break down protective coatings and attack solder joints

2.2.2 Corrosion In Electronics

Corrosion of electronics due to ambient air pollution has been a long-standing issue, especially in heavy industrial environments such as paper mills, petrochemical refineries, and wastewater treatment plants. These facilities often produce sulfur-containing gases like hydrogen sulfide, sulfur dioxide, and mercaptans, which are corrosive to electronic components. Electronic corrosion refers to the deterioration of electronic circuits and components due to corrosion-related factors.

Understanding Key Components:

- Integrated Circuits (ICs): Made from materials like silicon, gold, silver, copper, zinc, and aluminum, ICs connect various active elements on silicon wafers.
- Printed Circuit Boards (PCBs): These macro-electronic structures integrate multiple electronic parts, including ICs, on fiberglass epoxy polymer with interconnecting lines. Corrosion can manifest as oxidation, moisture-related damage, or chemical degradation

Types of Components which get affected:

Certain electronic components are particularly susceptible to corrosion due to environmental factors, which can lead to inadequate performance or system failure. These components include:

- Integrated Circuits (ICs), Printed Circuit Boards (PCBs), Transistors, Capacitors, relays, switches, connectors, Magnetic recording media (e.g., hard drives), Packaging and shielding parts

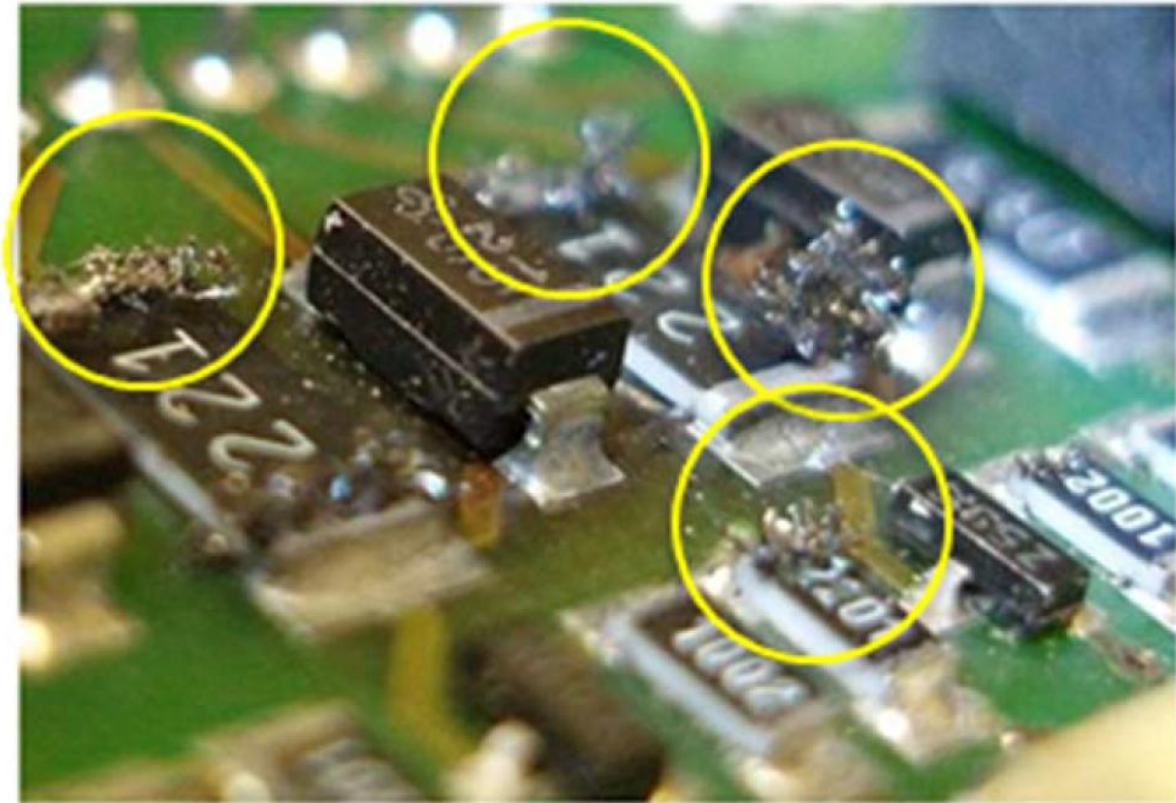


Figure 2(f)-i Silver whisker growth on circuit boards is a clear indicator of sulfur contamination

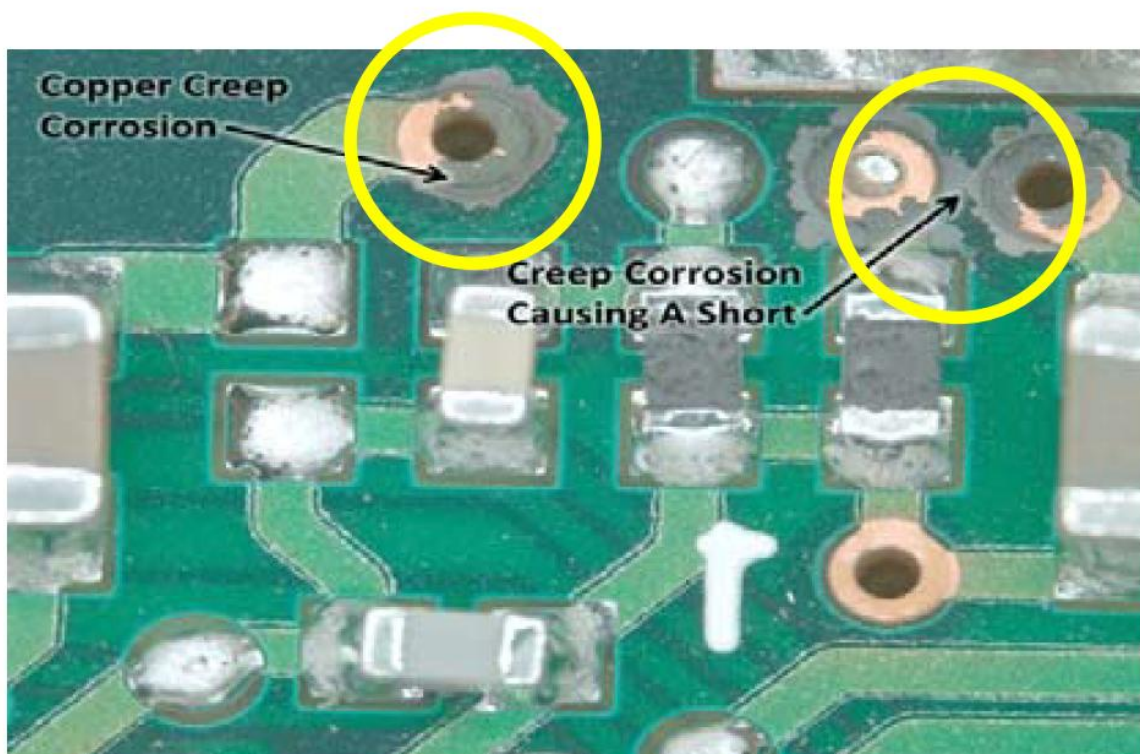


Figure 2(f)-ii--- Creep Corrosion-ref- <https://mas-innovations.com>

Two common forms of electronic corrosion are:

- **Whisker Growth:** Metallic filaments, such as silver whiskers, can form on circuit boards due to sulfur contamination. These whiskers create unintended conductive paths and are a clear warning sign of environmental contamination.

- **Creep Corrosion:** This occurs when corrosive residues spread across surfaces, bridging conductors and causing short circuits or signal interference.

Factors Affecting Corrosion in Electronics:

Environmental Factors

- **Particulate Contamination:** Dust can cause mechanical obstruction, chemical corrosion (especially if it contains sulfur or chlorine salts), and electrical interference by altering impedance or bridging conductors.
- **Microbial Growth:** Microorganisms can degrade materials and promote corrosion, especially in humid environments.
- **Heat and Solar Radiation:** Elevated temperatures accelerate chemical reactions and material fatigue.
- **Moisture and Humidity:** These enable electrochemical corrosion, especially when combined with conductive contaminants.
- **Corrosive Gases:** Sulfur-based gases aggressively attack metal surfaces and solder joints.
- **Dust Accumulation:** Trapped dust can retain moisture and contaminants, worsening corrosion.
- **Electrolyte Presence at Interfaces:** Electrolytes facilitate corrosion at metal junctions.
- **Improper Sealing and Packaging:** Poor protection allows ingress of moisture and pollutants.
- **Corrosion of Solder Joints:** Weakens electrical connections and can lead to circuit failure.
- **Contact Between Dissimilar Metals:** Metals like gold and aluminum can undergo galvanic corrosion when in contact.

Technical Factors

- **Power Supply Interruptions:** Can cause thermal cycling and stress on components.
- **Voltage Fluctuations:** May degrade protective coatings and accelerate corrosion.
- **Loose Connections and Mechanical Vibrations:** Lead to micro-cracks, exposing vulnerable surfaces to environmental attack.

Corrosion Prevention:

- Apply protective coatings or Volatile Corrosion Inhibitor (VCI) sprays to shield electronics from moisture and acid gases. VCI Vapor Capsules release protective vapors that prevent rust, especially in tight spaces like control panels.
- Use well-sealed enclosures with gaskets, O-rings, or potting compounds to block out dust and moisture.
- Select corrosion-resistant materials. Gold or palladium finishes on connectors offer extra protection.
- Maintain stable humidity and temperature. Use desiccant packs or VCI sachets to absorb moisture and protect metal parts.
- Clean electronics regularly to remove dust and contaminants. Use safe cleaning methods to avoid leaving corrosive residues.

By implementing these preventive strategies and considering specific environmental conditions, it is possible to minimize the impact of corrosion on electronic components, ensuring their long-term performance and reliability
(Potting compounds are protective materials (like epoxy or silicone) used to seal and shield electronic components. They block moisture, dust, and corrosive gases, provide insulation, and protect against vibration and heat.)

2.3 Different forms of Corrosion:

Learning Outcomes

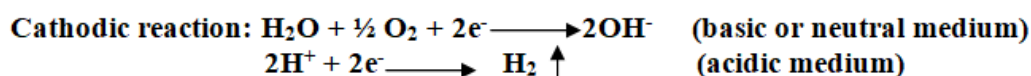
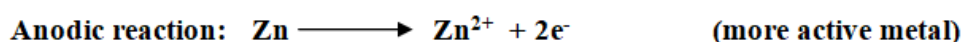
Upon completion of this topic, you will be able to,

- identify and classify corrosion types such as galvanic, differential aeration, and intergranular corrosion.

2.3.1 Galvanic Corrosion (Bimetallic Corrosion)

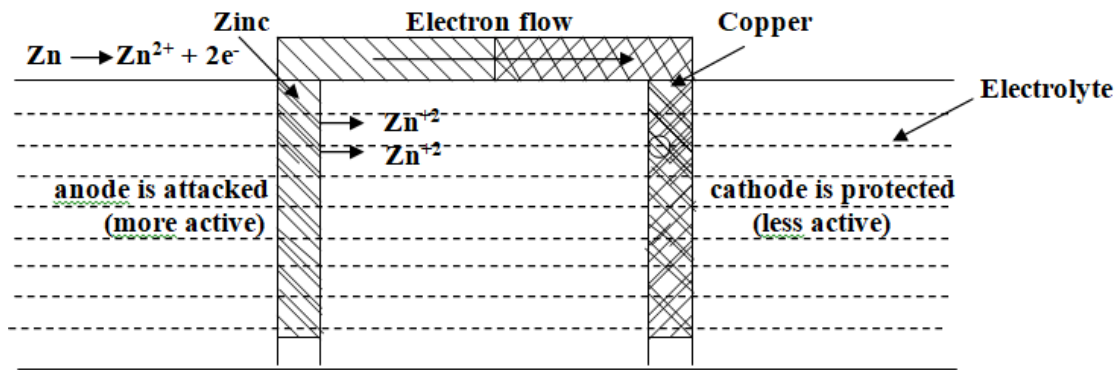
When two metallic materials (dissimilar metals) are electrically connected and exposed to an electrolyte, the metal with higher oxidation potential undergoes corrosion. This type of corrosion is called 'Galvanic corrosion'.

- Example: When two dissimilar metals such as Zinc and Copper are electrically connected and is exposed to an electrolytic medium, zinc which has a higher oxidation potential in the electrochemical series forms the anode and undergoes corrosion (get dissolved) while copper which is having lower oxidation potential in electrochemical series acts as the cathode.
- The type of cathode reaction depends upon the nature of medium around the dissimilar metals.
- In acidic solution the corrosion occurs by hydrogen evolution mechanism while in slightly alkaline or neutral solution the corrosion takes place by oxygen absorption mechanism. (The electrons flow from the anodic metal (Zn) to cathodic metal (Cu) where the electrons are intercepted by the positive ion deposited there.)



Thus it is evident that corrosion occurs at the anodic metal, while the cathodic part is protected from attack.

Diagram: Galvanic Corrosion



Other examples:

- Copper sheet joined by iron nails.
- Steel pipe joined using copper coupler.
- Steel screw in marine brass hardware.

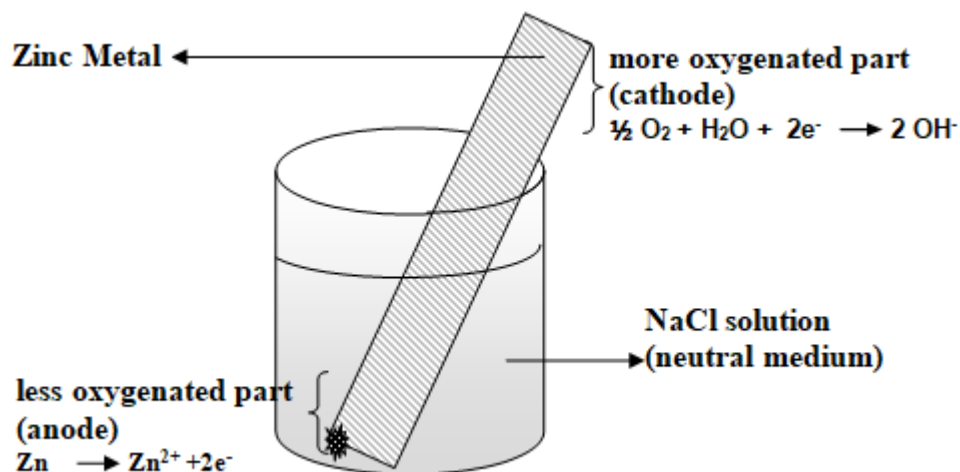
2.3.2. Concentration Cell Corrosion (Differential aeration corrosion)

Concentration cell corrosion arises due to differences in oxygen concentration on a metal surface in an electrolyte.

- Less aerated areas (deeper in solution) become anodic and undergo corrosion.
- More aerated areas (near the waterline/above) become cathodic and are protected.
- A potential difference forms between anodic and cathodic zones, causing current flow.
- Example: This type of corrosion is common in partially immersed metals in stagnant solutions. Zinc metal, the anodic part dissolves ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$) while at the cathodic part, oxygen accepts electrons and forms hydroxyl ions ($\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$).

The circuit is completed by migration of ions, through the electrolyte and flow of electrons through the metal from anode to cathode.

Diagram: Concentration Cell Corrosion



Anodic reactions: $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$ (less oxygenated part)

Cathodic reactions: $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2\text{OH}^-$ (more oxygenated part)

Other example:

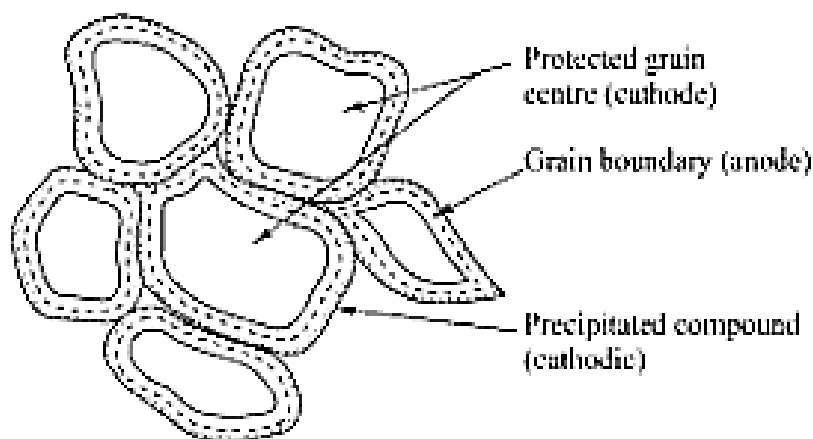
- In the similar way iron corrodes under drops of water (or salt solution). Areas covered by droplets having no access of oxygen, become anodic with respect to the other areas, which are freely exposed to air. It is therefore well evident that oxygen concentration cell increases the corrosion, but corrosion takes place where there is less access of oxygen.

2.3.3 Intergranular Corrosion (IGC)

During welding of stainless steel (under improper condition for heat treatment) when the molten metal solidifies, it forms tiny crystals called grains separated by areas of mismatch between them and these areas are called grain boundaries. Intergranular corrosion happens along these grain boundaries. In this case, chromium carbide forms at the grain boundaries.

- This causes nearby areas to lose chromium and become anodic (easily corroded), while chromium carbide areas become cathodic.
- The grain centers also stay cathodic.
- This difference causes corrosion to occur only along the grain boundaries, leading to weakening of the material.
- In most of the cases without any pre-warning sudden failure of material due to dislodging of the grains (occurs as cohesion between the grains is lost).

Diagram: Intergranular Corrosion



What Acts as Anode and Cathode:

- Anode (gets corroded): Chromium-depleted regions near the grain boundaries
- Cathode (protected): Chromium carbide and grain centers

How to Prevent IGC:

- Use proper heat treatment and quenching (fast cooling) to prevent carbide formation.
- Use stabilized steels (with Ti or Nb) to form stable carbides instead of chromium carbides.

2.4 Corrosion Protection Methods:

Learning Outcomes

Upon completion of this topic, you will be able to,

- evaluate and select appropriate corrosion prevention and control methods for different applications.
- apply principles of corrosion protection to design systems using coatings, lubricants, and cathodic protection techniques.

Corrosion is one of the major causes of increasing maintenance cost of all the industries therefore either prevention or subsequent control of corrosion becomes all the more important. The methods for corrosion control vary from condition to condition.

The following are the methods which can be used either singly or in combination in order to protect the metals from corrosion.

Methods to Control Corrosion

- Material Selection
- Design Consideration
- Non-Metallic Coatings : Acrylic, Epoxy Coatings
- Anti-Rust Lubricants, Corrosion Inhibitors in Engine Oils
- Metallic Protective Coatings: Galvanization and Tinning
- Surface Treatment: Anodizing
- Cathodic Protection: Sacrificial anode and Impressed Current Systems

2.4.1 Material Selection:

Proper selection of material for manufacturing machine parts or joining different parts to construct a unit helps tremendously to avoid or control corrosion. Thus selection of right type of material is the main factor for corrosion control. The choice of metal should be made not only on its cost and structure but also on its chemical properties and environment. This can be done by taking following precaution.

- *The contact of dissimilar metals should be avoided especially if the working environment is corrosive.*
- *If it is unavoidable to choose two dissimilar metals, then area of anodic metal should be larger than that of cathodic metal.*
- *If two dissimilar metals are to be selected, then metals should be chosen in such a way that they are as close as possible in the Galvanic series.*
- *When two dissimilar metals are required to be joined then their direct contact should be avoided by inserting a piece of hard plastic or rubber which acts as an insulator between the joints.*
- *When two dissimilar metals are used in contact the anodic metal should not be painted or coated. Any crack in the coating can lead to rapid localized corrosion.*

2.4.2 Design Considerations:

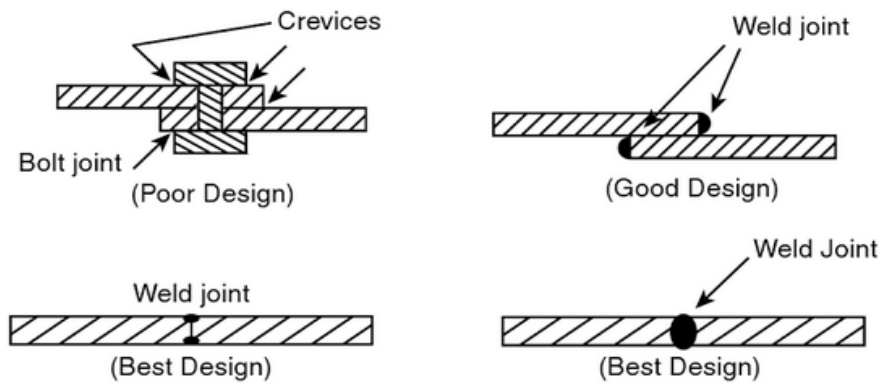


Figure2(g): Welded joints for prevention of corrosion

Corrosion resistance of metal parts or machines can be improved by improving the design. The design of the metal should be such that corrosion even if it occurs is uniform and does not result in intense and localized corrosion.

- a) *Welded joints should be preferred over riveted or bolted lap joints to prevent the formation of crevices that can lead to differential aeration corrosion.*
- b) *A better design should always avoid sharp bends, corners, lap joint, projected parts, recesses etc. because these favor the formation of stagnant area and accumulation of solids.*
- c) *The surfaces of two joining parts should be as smooth as possible, which avoids accumulation of the corrosive liquids, suspended particle, dust, dirt, grit, stagnation of water e*

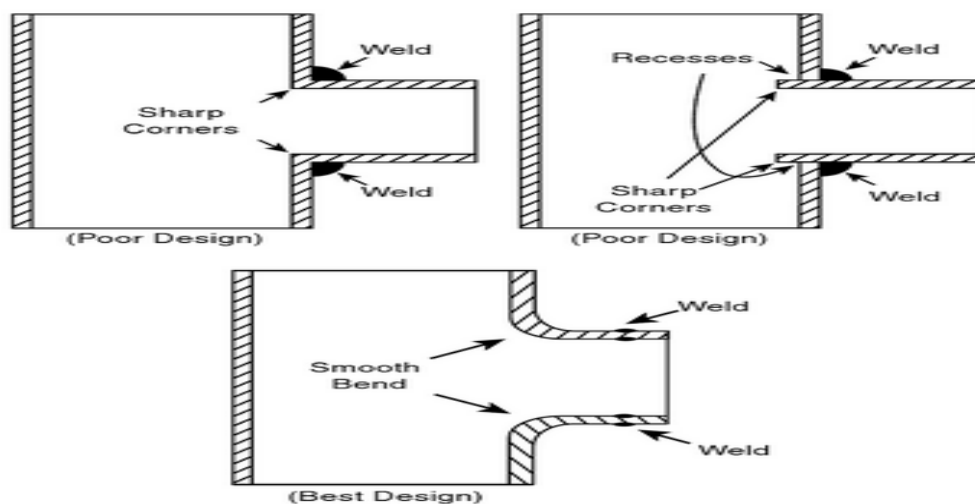


Figure2(h): Smooth bends for prevention of corrosion

- d) *The equipment should be kept free from dust and dirt to reduce corrosion due to pitting or differential aeration effect.*
- e) *Wherever possible the equipment should be supported on legs instead on large block to allow free circulation of air and prevent the formation of stagnant pool or damp areas.*

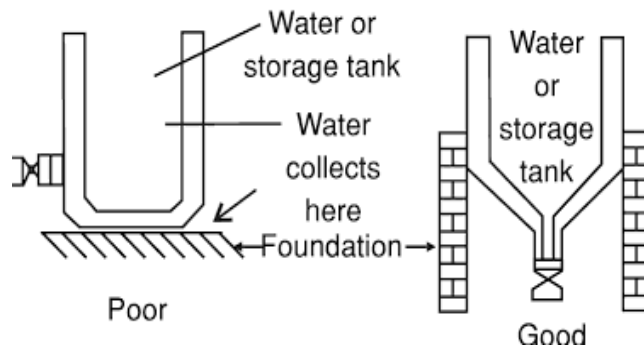


Figure2(i):
Support legs for prevention of corrosion

Use of alloys or pure metals:

If the metal used to manufacture machine parts is 100% pure, the corrosion resistance is more as compared to the impure metal. This is because, impurities cause heterogeneity. Thus, use of pure metal or purifying the metals prevents corrosion. This method is useful only if corrosion proceeds by electrochemical mechanism.

Corrosion resistance of metal can be improved by alloying the metals. Alloying can help to greater extent, if it gives homogenous product.

Examples: Iron can be alloyed with chromium and carbon to give stainless steel, which has better corrosion resistance, since its film is self-healing. Thus, steels containing 13% chromium are used in cutlery, surgical instruments, springs, etc., while high percentage of chromium such as 25% are used to prepare turbine, brackets, heat resisting parts etc.

Brass is an alloy of copper and zinc. Individually these are less resistant to corrosion, but alloy brass has better corrosion resistance.

2.4.3 Non-Metallic Coatings: Acrylic, Epoxy Coatings

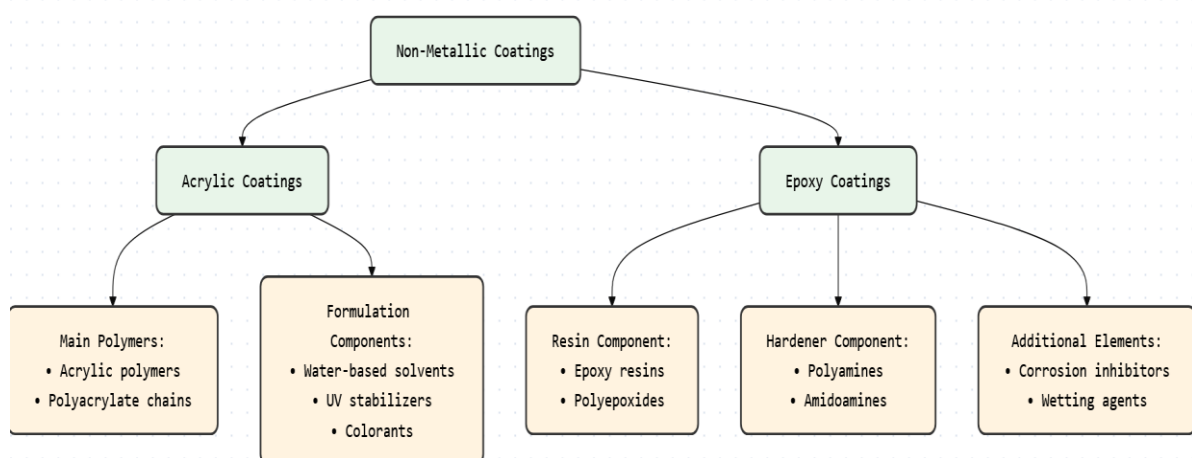


Figure-2(j)-non metallic coatings-Types

Mechanism of Protection: Acrylic and Epoxy Coatings These coatings act as barriers that shield the metal from moisture, oxygen, and corrosive chemicals. Here's how each works:

a) Acrylic Coatings

- 1) **Barrier Protection:** Acrylic forms a thin, flexible film that blocks water and air from reaching the metal.
- 2) **UV Resistance:** It resists sunlight and weathering, making it great for outdoor use.
- 3) **Quick Drying:** Acrylic dries fast and is easy to apply, often used in spray paints and decorative finishes.
- 4) **Eco-Friendly Options:** Water-based acrylics are low in VOCs (volatile organic compounds), making them safer for the environment.

b) Epoxy Coatings

- 1) **Strong Adhesion:** Epoxy bonds tightly to metal, creating a tough, durable layer.
- 2) **Chemical Resistance:** It resists acids, oils, and solvents—ideal for industrial and marine environments.
- 3) **Corrosion Blocking:** Epoxy forms a thick, impermeable film that stops corrosive ions from reaching the metal.
- 4) **Enhanced with Additives:** Nanoparticles or phosphate monomers can be added to improve strength and corrosion resistance.

c) Hybrid coatings. They combine acrylic and epoxy to get the best of both:

- 1) Acrylic adds flexibility and UV resistance.
- 2) Epoxy adds strength and chemical protection.
- 3) Together, they form a hybrid coating that's tough, long-lasting, and environmentally friendly.

Acrylic, Epoxy, and Hybrid Coating Applications

Coating Type	Applications
Acrylic Coating	Outdoor surfaces: metal structures, fences, signage (UV resistant)
	Decorative finishes: spray paints, wall coatings
	Concrete protection: sidewalks, driveways, parking lots
	DIY & crafts: art projects, hobby use
Epoxy Coating	Industrial floors: factories, warehouses, garages (durable, chemical resistant)
	Marine & automotive: corrosion and chemical protection
	Structural adhesives: construction, aerospace, electronics
	Countertops & surfaces: glossy, hard finish for kitchens and labs
Hybrid Coating	Bridges, tunnels, infrastructure: protective finishes
	High-performance needs: combines flexibility of acrylic with toughness of epoxy

Table-No 2- Acrylic, Epoxy, and Hybrid Coating Applications

2.4.4 Lubricants: Introduction

A 'Lubricant' is a substance introduced to reduce friction between two moving surfaces. In addition to industrial applications, lubricants are used for many other purposes. Other uses include cooking (oils and fats in use in frying pans, in baking to prevent food sticking), bio-medical applications on humans (e.g. lubricants for artificial joints), ultrasound examination, etc.

Significance:

If the oil to be used as a lubricant contains free carboxylic-acids, then they bring about corrosion of metal-surfaces. The corrosion results in the increase of friction and wear. Free-acids are not present in lubricants unless refining has been done in a faulty manner

Definition:

A Lubricant is defined as “a substance which when applied to moving parts of machines reduces the friction between the surfaces and thereby minimizes their wear and tear”.

Chemical Tests for Lubricants: Acid Value

Acid value is defined as “ the number of milligrams of KOH required to neutralize free-acid present in 1 gm. of lubricating oil”. It is also called as 'Neutralization-number', an indication of the acidity.

Significance of Acid Value: A good lubricant should possess low acid-value. High acid-value leads to corrosion and sludge-formation .

The Acid value is calculated by the formula;

$$\text{Acid-Value} = \frac{\text{Volume of KOH in ml.} \times \text{Normality of KOH} \times 56}{\text{Weight of oil in grams}}$$

$$\text{Weight of oil} = \text{Volume of Oil} \times \text{Density}$$

2.4.5 Numerical Problems on Acid Value

- 1) Find the acid value of an used oil sample whose 7 ml. required 3.8 ml. of N/50 KOH during titration. (Density of oil = 0.88g/cc)

Solution: -

$$\begin{aligned}\text{Weight of Oil} &= \text{Volume of oil} \times \text{Density of oil} \\ &= 7 \times 0.88 \\ &= 6.16 \text{ g}\end{aligned}$$

n

$$\text{Normality of KOH} = \text{N}/50 = 1/50 = 0.02 \text{ N}$$

$$\text{Acid-Value} = \frac{\text{Volume of KOH in ml.} \times \text{Normality of KOH} \times 56}{\text{Weight of oil in grams}}$$

$$\text{Acid Value} = \frac{3.8 \times 0.02 \times 56}{6.16}$$

$$= 0.691 \text{ mg of KOH /g of oil}$$

Problems for practise :-

1. A sample of vegetable oil purchased was tested for acid value. 10 gm. of the oil was titrated against N/40 KOH and burette reading was found 2.6 ml, state whether the oil is proper for lubrication or not from acid-value.
2. 5 ml. of an oil taken out from a gear-box takes 2.1 ml. of 0.02N KOH for titration. Find its acid-value. (Density = 0.91 gm/ml.)
3. Find the acid number of a resin sample weighing 1.1 gm which reading 280 ml. of 0.11 N KOH to bring about the end point.
4. A 2 gm. sample of cod liver oil reading 4.5 ml. of 0.02 N KOH in the titration of free fatty-acid. What would be the acid-number of an oil ?
5. 2.5 gm. of an oil sample required 2.5 ml. of N/100 KOH to neutralize free fatty-acids in oil. Find the acid-value. (0.56 mg/gm.)

2.4.5 Corrosion inhibitors in engine oils:

Corrosion inhibitors in engine oils are additives designed to protect metal engine components from rust and degradation. These additives protect metal engine parts from rust and degradation by forming a barrier, neutralizing acids, and preventing electrochemical reactions. They are essential for engine health, especially in the presence of moisture and contaminants that can enter the lubricant system. By reducing corrosion, they help extend engine life and ensure reliable performance

Types of Inhibitors:

- Oil-soluble Corrosion Inhibitors:

These are dissolved in the engine oil and form a protective layer on metal surfaces

- VCIs (Vapor Corrosion Inhibitors): Release vapors to protect enclosed areas like engine crankcases during storage.
- Detergents: Many detergents used in engine oils keep deposits suspended, preventing corrosion indirectly.

Examples

Amines: Form protective salts with acids.

Phosphates: Create corrosion-resistant layers on metal.

2.4.6 Metallic Coatings: Galvanization and Tinning

The protective metallic coating can be applied by the following methods:

Hot dipping : a) Galvanization and b) Tinning

a) Galvanizing:

Applications:

- The process of galvanizing is commonly used for coating the iron or steel sheets, tubes, pipes, screws, nuts, bolts and wires for protection against corrosion.

Diagram:

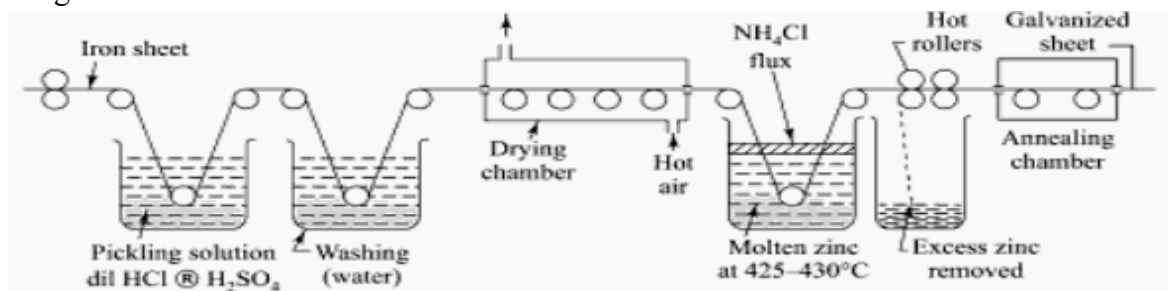


Figure-:2(k)-Hot Dipping-Galvanizing

Advantages:

Zinc offers better protection against corrosion because even if any cracks are developed over the film of deposit, at a later stage, zinc being more reactive than iron or steel, undergoes corrosion keeping the base metal article unaffected.

Disadvantages:

Galvanized zinc coated utensils or containers cannot be used for preparing or storing food stuffs, particularly those which are acidic in nature. This is because zinc dissolves to form poisonous zinc compounds which are injurious to human health.

- b) Tinning:** Tinning is defined as the process of coating iron or other metals with a layer of tin to protect them from corrosion and enhance their durability

Diagram:

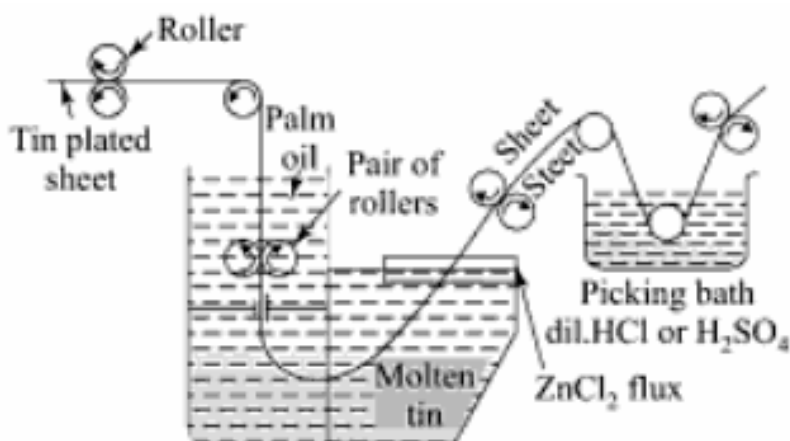


Figure-:2(l)-Hot Dipping-Tinning

Advantages:

Tin coated containers can be used for preparing and storing food stuffs as tin does not form any poisonous products with such acidic materials.

Disadvantages:

Tin only provides a mechanical protection against corrosion. It acts as a cathode to more active metal like iron and so. If any cracks are developed in the protective layer, then more rapid corrosion takes place the underlying exposed metal becomes anode.

Distinction between galvanizing and tinning

Galvanizing (Anodic coating)	Tinning (Cathodic Coating)
1) It is the process of coating iron or steel sheets with a thin coat of zinc by hot dipping to prevent them from rusting.	1) It is a process of coating steel sheets with a thin layer of tin to prevent them from corrosion.
2) Zinc metal protects iron as it is more anodic to iron.	2) Tin protects the base metal as it is less electropositive than iron. It is more resistant to chemical attack.
3) Zinc continues to protect the metal by Galvanic action, even if the coating is broken.	3) Tin protects the metal till the coating is perfect. A break in coating causes rapid corrosion.
4) Galvanized container cannot be used for storing acidic food stuffs, as acids react with zinc to form poisonous compounds.	4) Tin containers can be used for storing acidic food stuffs as tin does not form any poisonous products.

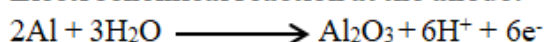
Table-No 3-Differences anodic and cathodic coating

2.4.7 Electrochemistry of Anodizing

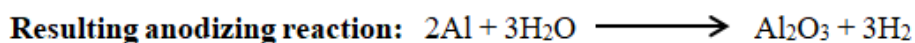
Anodizing process occurs in an electrochemical cell, in which the anode is the anodized part and the cathode is a plate/rod made of a material chemically inert(eg-carbon, Stainless steels) in the acidic electrolyte .

Anodizing is an electrolytic passivation process that enhances the natural oxide layer on metals—especially aluminum. Unlike paint or plating, the anodized layer is grown from the metal itself, making it highly durable and integrated into the surface.

Electrochemical reaction at the anode:



Electrochemical reaction at the cathode:



In aqueous solutions aluminum oxide may form various hydrates



How the Process Works:

Surface Preparation

- Metal is cleaned and degreased to remove contaminants.

Electrochemical Reaction

- The metal part is submerged in an acid electrolyte bath.

- It becomes the anode in an electric circuit.
- Oxygen ions from the electrolyte react with the metal surface, forming a porous oxide layer.

Coloring (Optional)

- Dyes or metal salts can be introduced into the pores for vibrant, fade-resistant colors.

Sealing

- The porous layer is sealed to improve corrosion resistance and prevent staining or scratching.

Purpose and Advantages of the Porous Structure:

- **Coloring and Dye Absorption** The pores act like tiny channels that absorb dyes. This allows manufacturers to add vibrant, long-lasting colors to anodized parts.
- **Sealing Capability** After dyeing, the pores are sealed—usually by boiling water or steam—which hydrates the oxide and closes the pores. This improves corrosion resistance and locks in the color.
- **Adhesion for Coatings** The porous surface provides excellent grip for paints, adhesives, and lubricants, making it ideal for layered coatings or composite materials.
- **Template for Nanostructures** In advanced applications, the pores can be used as templates for growing nanowires or nanotubes, especially in electronics and sensor technology easy

Characteristics of Anodized Surfaces

- Porous structure allows for dyeing and sealing.
- Non-conductive and weather-resistant.
- Harder than the base metal, but can be brittle under thermal stress.
- Microscopic texture changes, improving adhesion for paints and glues.

Applications:

Industry	Use Case
Aerospace	Lightweight, corrosion-resistant components
Architecture	Window frames, curtain walls
Electronics	Smartphone casings, laptop bodies
Automotive	Trim parts, wheels
Consumer Goods	Cookware, sporting equipment

Table-No 4-Anodizing-Applications

Advantages:

- Long-lasting protection
- Scratch and abrasion resistance
- UV-stable colors that don't peel or fade
- Environmentally safe and non-toxic process

Schematic for Anodizing Process:

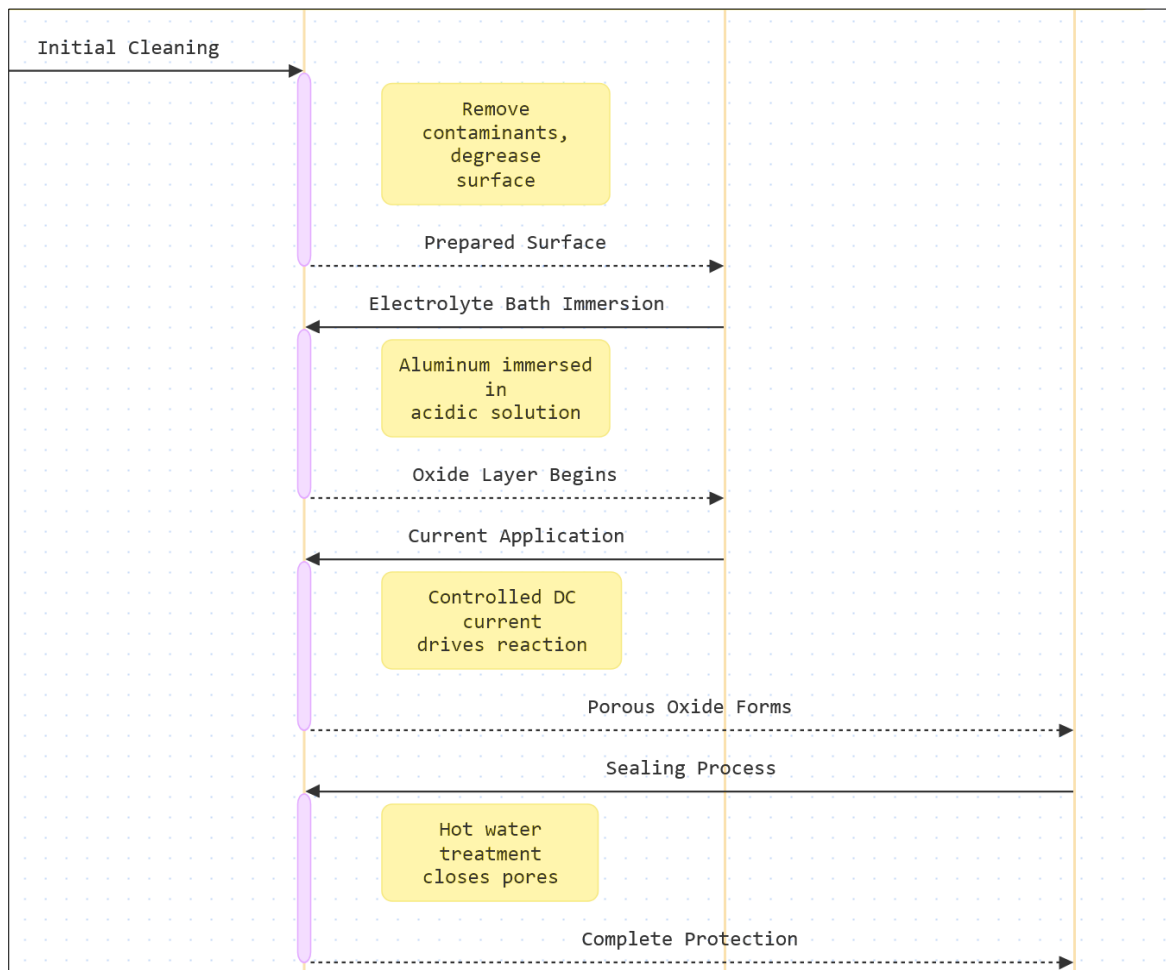


Figure:2(l)- Schematic for Anodizing Process:

2.4.8 Cathodic protection

Principle: The structure to be protected is forced to act as cathode

Cathodic protection is the method in which an impressed or galvanic current is used to reduce or prevent corrosion of a metal in an electrolyte by forcing the metal to be protected to become the cathode of a corrosion cell.

There are two types of cathodic protections:

- Sacrificial anode method
- Impressed current method

a) Sacrificial anode method:

- In this protection method, the metallic structure (base metal) to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal.
- The more active metal itself gets corroded slowly: while the metallic structure is protected.
- This results in the corrosion of the piece of more active metal connected, thereby saving the base metal from corrosion.
- Since the more active metal sacrifices itself, by undergoing corrosion and protects the base metal, the method is known as Sacrificial anode method.

- When the piece of more active metal gets corroded completely, it is simply replaced by new piece. Most of the common sacrificial anodes are based on the alloys of magnesium, zinc and aluminium.

Diagram: Sacrificial Anode Method

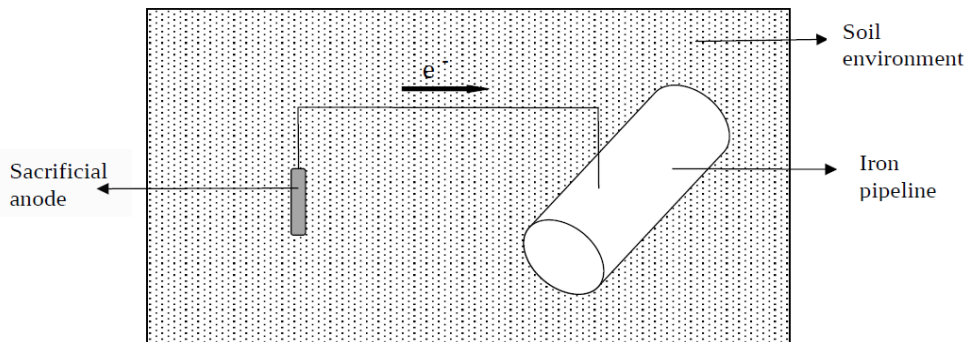


Figure:2(m)-i- Sacrificial Anode Method

Applications of this method is seen in

- 1) protection of cables or iron pipelines, by connecting them to Mg- block:
- 2)marine structures, ships protected by using Zn-plates
- 3)water tanks, boilers are protected by Zn metal.

b) Cathodic protection by impressed current :-

In this method, an impressed current is applied in opposite direction to that of corrosion current, thereby nullify the effect of corrosion current, and converting the metal to be protected from anode to cathode.

Such an impressed current is obtained by using D.C. source such as battery or dry cell along with an insoluble anode such as platinum, stainless steel, graphite.

The anode is usually kept in backfill made up of gypsum or any such material, which can help in increasing electric contact with soil.

The anode may be single (as in simple applications) or many anodes depending on the application.

Diagram: Impressed Current Method

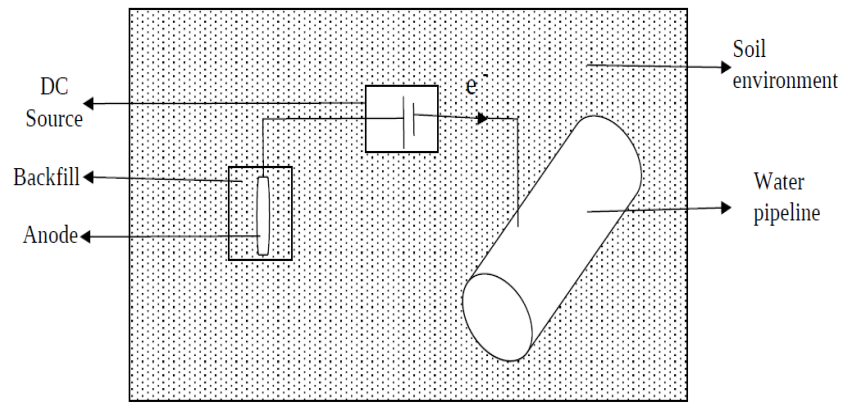


Figure:2(n)-i- Impressed Current Method

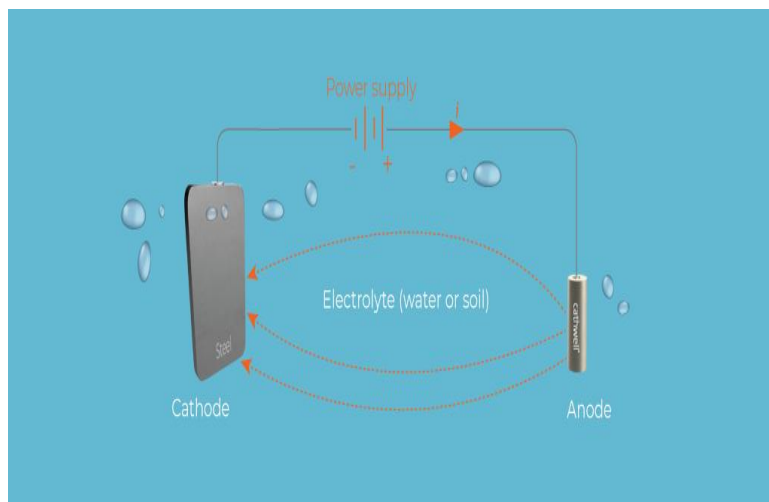


Figure:2(n)-ii- Impressed Current Method

Applications:

Impressed current systems are appropriate for protection of larger structures and are more effective in handling the more complicated corrosion problems than are sacrificial anodes. They can be automatically controlled which reduces the maintenance and operating costs.

This type of cathodic protection by impressed current is applied to open water box coolers, water tanks, buried pipelines, condensers, transmission line towers, laid-up ships etc

