

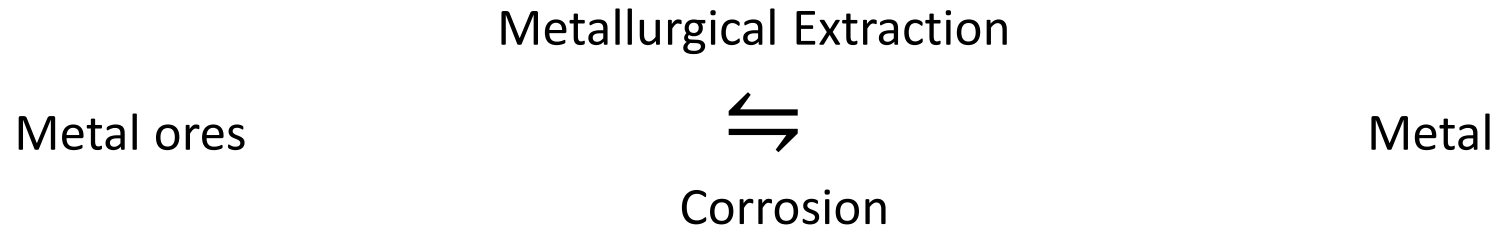
# Corrosion

## Module-2

# Introduction

## **Corrosion:**

Corrosion is defined as the destruction or deterioration and consequent loss of metals through chemical or electrochemical attack by the environment. e.g.: rusting of iron. In reality it is a transformation of pure metal into its undesired metallic compounds.



Metallurgical extraction is the reduction of the metal from its ore and it is an endothermic process, energy being supplied in the form of heat or electrical energy. Consequently, pure metals are at relatively higher energy state compared to their corresponding ores. Thus they try to revert back to their combined state.

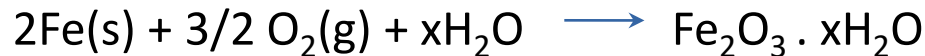
# Theory

Corrosion is based on two theories:

(1) Chemical theory and (2) Electrochemical theory.

## Chemical theory:

It is the deterioration of materials by chemical interaction with their environment.  
e.g.: rusting of iron exposed to atmospheric condition.



## Electrochemical theory:

- According to electrochemical theory, corrosion of metal takes place due to the formation of anodic and cathodic regions on the same metal surface or when two different metals are in contact with each other in presence of a conducting medium.
- At the anodic region oxidation reaction takes place and the metal gets converted into its ions with the liberation of electrons.  $\text{M} \longrightarrow \text{M}^{n+} + n\text{e}^-$

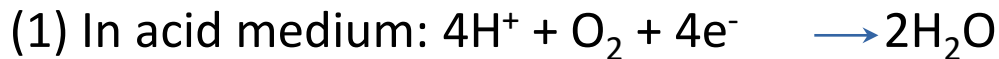
# Theory

- At the cathodic region reduction reaction takes place. Since the metal cannot be reduced further, so metal atoms remain unaffected at the cathodic region. Some constituents of the corrosion medium take part in the cathodic reaction.

(a) Liberation of hydrogen takes place in absence of oxygen.



(b) Absorption of oxygen takes place in presence of oxygen.



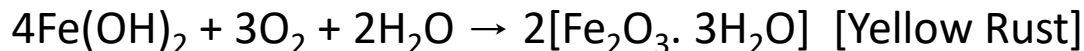
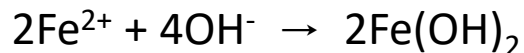
# Theory

- The electrons liberated at the anodic region migrate to cathodic region constituting corrosion current.
- The metal ions liberated at the anode and some anions formed at the cathode diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and cathode.
- **Example:** Rusting of an Iron in the presence of moist air

Anode reaction :  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Cathode reaction :  $\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow 2 \text{OH}^-$

(a) In an oxidising environment:  $\text{Fe}^{2+}$  and  $\text{OH}^-$  ions are obtained at the anode and cathode.



(b) In presence of limited oxygen:  $3\text{Fe}(\text{OH})_2 + \frac{1}{2}\text{O}_2 \rightarrow [\text{Fe}_3\text{O}_4 \cdot 3\text{H}_2\text{O}] \text{ [Black Rust]}$

- Corrosion of metal continues as long as both anodic and cathode reactions take place simultaneously.

## Dry Corrosion

Involves direct attack of atmospheric gases on metal in the absence of moisture liquid phase

Less prevalent

The corrosive media include vapors, gases, etc.

It is of various types: Oxidation corrosion, corrosion by other gases such as  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NO}_x$  and liquid metal corrosion

## Wet Corrosion

Involves electrochemical attack on metals in aqueous environments

More prevalent

The corrosive media is conducting liquid (aqueous) phase

It is of three types: differential metal corrosion, differential aeration corrosion and crevice corrosion

# Classification

**Differential metal corrosion**: It arises when two dissimilar metals (galvanic couples) are in contact with each other in a corrosive medium. The two metals differ in their electrode potential, the lower electrode potential or the more active metal (K, Na, Mg, Zn) acts as anode and the one with higher electrode potential (Cu, Ni, Sn) acts as cathode. The potential difference between the two metals is the cause or driving force for corrosion. The anodic metal undergoes corrosion and the cathode metal remains intact.

The following reactions occur during galvanic corrosion:

**Anode:**  $M \longrightarrow M^{n+} + ne^{-}$

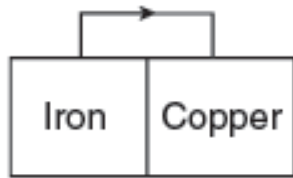
**Cathode:** Depending on the nature of the corrosion environment the cathode reaction may be either hydrogen evolution or oxygen absorption.

(a)  $2H^{+} + 2e^{-} \longrightarrow H_2(g)$  or (b)  $2H_2O + O_2 + 4e^{-} \longrightarrow 4OH^{-}$

Then give an example of rusting of iron with reaction as is given in the electrochemical theory (formation of  $Fe_2O_3 \cdot 3H_2O$ ).

# Classification

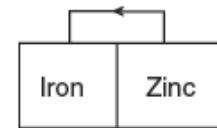
Example: (a) Steel screws/rivets in copper sheet. (b) Steel pipe connected to copper plumbing.



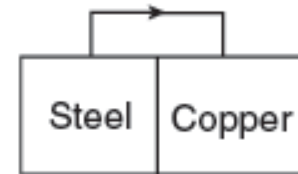
Bimetallic couple of iron and copper.



Fig. Galvanic corrosion between Steel and Brass.



Bimetallic couple of iron and zinc.



Bimetallic couple of steel and copper.

- **Preventive Measures:**

1. Placing a thin layer of an insulator between two metals or materials.
2. Selecting materials having very less potential difference.



# Classification

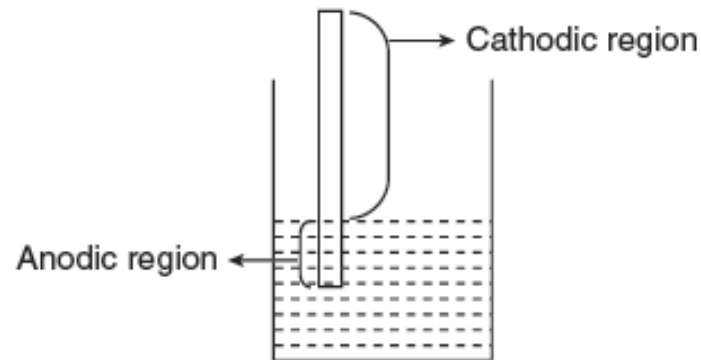
**Differential aeration corrosion**: It occurs when a metal surface is exposed to differential air or oxygen concentrations. The part of the metal exposed to higher concentration acts as cathodic region and rest of the metal part exposed to lower oxygen concentration acts as anodic region. The corrosion takes place at the anodic region. The reactions are as follows:

**Anode:**  $M \longrightarrow M^{n+} + ne^{-}$

**Cathode:**  $2H_2O + O_2 + 4e^{-} \longrightarrow 4OH^{-}$

Examples:

- a) Ocean going ships
- b) Steel storage tanks



Pure iron partially immersed in an aerated solution of NaCl.

- c) Half-immersed iron plate in aqueous solution.

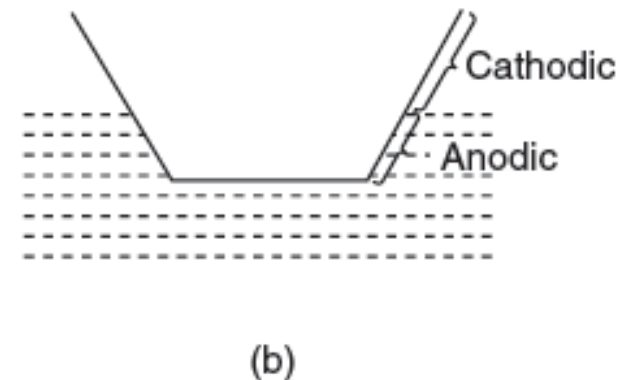
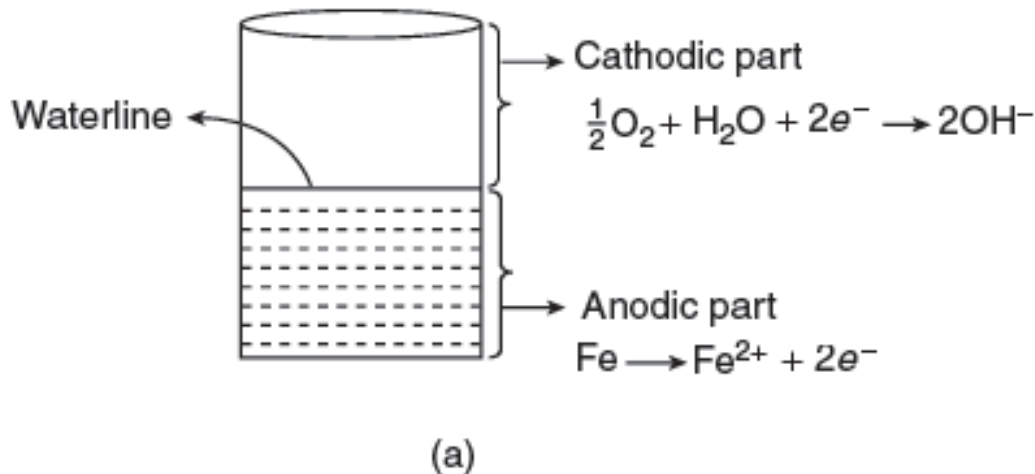
Then give an example of rusting of iron with reaction as is given in the electrochemical theory.

# Classification

## Preventive Measures:

1. Using metallic coating, electroless plating or chemical conversion methods.
2. Maintaining the material's own protective film.

**Waterline Corrosion**: a case of differential aeration corrosion. Give reaction as shown in the electrochemical theory (formation of  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ).



# Classification

**Example:** (a) Water storage tank and ocean going ships undergo this type of corrosion. (b) The metal portion just below the waterline is more anodic to portion above the waterline. (c) Ships sunk under water for several years do not undergo corrosion.

**Pitting Corrosion:** Pitting corrosion is a localized and accelerated form of corrosion, resulting in the formation of holes or small pits, around which the metal is relatively un attacked. It is one of the destructive forms of corrosion.

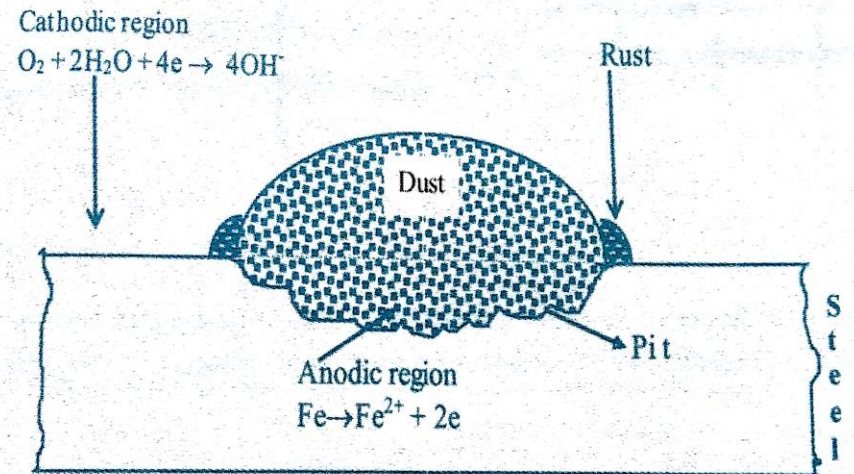
This corrosion arises when a small portion of the metallic surface is defective (with cracks) or occupied by dust/scale/sand/water drop i.e. presence of extraneous impurities embedded on the surface of the metal. The portion covered by the dust will be less aerated compared to the exposed surface. Thus covered surface becomes anodic with respect to the exposed surface. In presence of moisture, corrosion starts beneath the dust resulting in a pit. Once the pit is

# Classification

Corrosion takes place rapidly. This is because of the formation of small anodic area (pit) compared to a large cathodic area (surface).

**Example:** (a) Less aerated areas in a machinery. (b) Less aerated areas in metals e.g. cracks. Give reaction as shown in the electrochemical theory (formation of  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ).

**Preventive Measures:** (a) Preparing surfaces with best possible finish. Mirror-finish resists pitting best. (b) Removing all contaminants, especially free-iron by passivation (putting a thin film on the surface of the metal and the film is insoluble, non-porous and of self-healing nature). (c) Designing and fabricating to avoid trapped and pooled liquids.



# Corrosion control

## **Module 2**

# Cathodic Protection

- Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode.
- **Principle:** Metals normally undergo corrosion by electrochemical process with the formation of anodic and cathodic regions in contact with each other. The corrosion of metal takes place at the anodic region whereas the metal remains unaffected at the cathodic region. Therefore corrosion can be restricted by eliminating the anodic sites and converting the entire metal into cathodic area.
- By two ways it can be achieved: (a) Sacrificial anode (b) Impressed current.

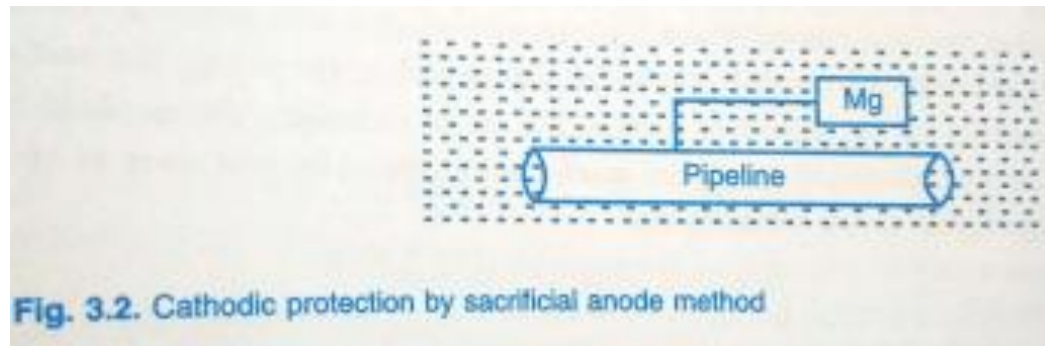
# Cathodic Protection

**Sacrificial anode:** Sacrificial anode method involves the conversion of the metal structure (complete metal) into cathode by connecting it into a more active metal, which acts as an auxiliary anode. The most commonly used metals as auxiliary anodes are Zn, Mg and aluminium. These metal being more active, act as anode and undergo preferential corrosion, thus protecting the metal structure. Since metal used as auxiliary anode are sacrificed to protect the metal structure, this method is known as sacrificial anode method.

**Example:** Magnesium block connected to underground pipelines.

**Advantages:** (a) The method is simple. (b) Low installation cost. (c) Minimum maintenance cost.

**Limitations:** (a) Involves recurring expenditure for replacement of consumed anodes.



# Cathodic Protection

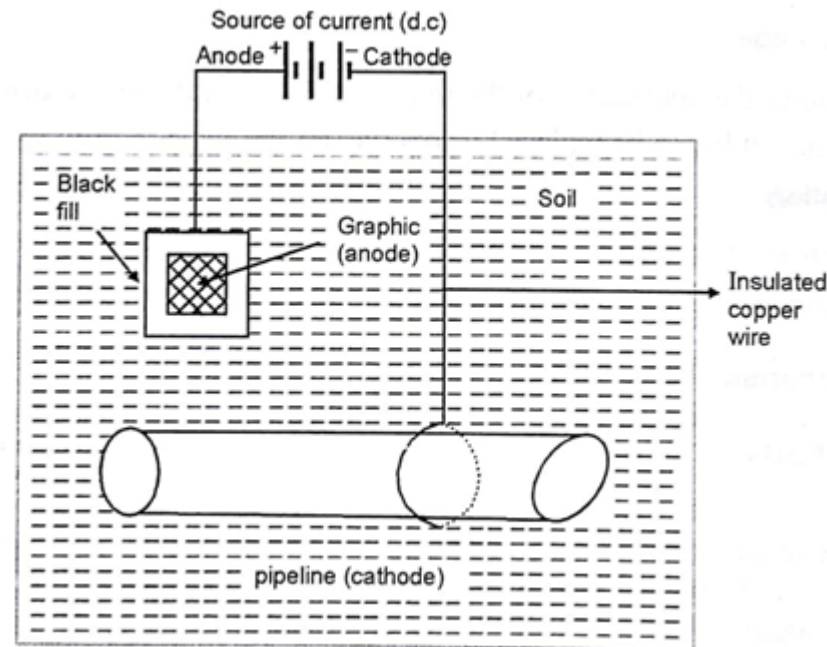
## Impressed Current Method:

- For larger structures, galvanic anodes can't economically deliver enough current to provide complete protection.
- Another method of providing cathodic protection is by applying a direct current larger than the corrosion current in opposite direction to nullify the corrosion current. The metal is protected by connecting it to a negative terminal of the DC source and making it cathodic.
- The anode of the source is connected to an inert electrode.
- To increase electrical contact with itself and the surrounding soil the anode is buried in back fill (gypsum).
- The metal source being cathode does not undergo corrosion. Anode being inert is remain intact. Graphite, stainless steel or scrap iron are widely used as the inert anode in this method which are buried in soil. Silicon-iron alloy, platinised Ti are also used as anode.



# Cathodic Protection

- **Example:** It is used for protecting marine structures, water storage tanks and oil pipe lines.
- **Advantages:** (a) one installation can protect large area of metals. (b) Low maintenance cost.
- **Limitations:** (a) Rather expensive, since it requires high current for safe protection of structure. (b) If the impressed current is not uniform on the entire surface of the protected structure, localized corrosion may takes place.



## **Protective Metal Coatings:**

### **Cathodic Coating:**

(a) Cathodic coatings are produced by coating a base metal with a more noble metal which is cathodic. The metals such as copper, tin, nickel is commonly used as cathodic coatings on steel. These coating metals are less reactive than the base metal and are less susceptible for corrosion.

(b) The cathodic coating provides protection only when it is undamaged, continuous and non-porous. When the coating is discontinuous, an intense localized corrosion of the base metal (small anodic region) occurs due to electrochemical corrosion.

(c) **Tinning** is a process of coating a base metal with tin. The process is carried out by hot dipping method and the process involves following steps:

(i) The sheet is first washed with organic solvents to remove grease or oil deposits.

(ii) Then treated with dilute sulphuric acid to remove rust and scale deposits. Finally, it is washed well with water and air dried.

(iii) The clean and dry sheet is passed through molten zinc chloride flux. The flux helps the molten metal to adhere on the metal surface.

(iv) It is then passed through a tank that contains molten tin.

(v) Finally passed through series of rollers immersed in palm oil. The rollers wipe out excess tin deposit and produces a continuous, thin coating on the sheet. The oil prevents the oxidation of the tin coated surface.

(vi) The tin layer prevent corrosion as long as the layer is continuous and completely covering the base metal surface.

### **Anodic Coating:**

(a) Anodic coatings are produced by coating a base metal with more active metals (e.g., Zn, Mg, Al) which are anodic to the base metal.

(b) The coated metal can prevent corrosion of the base metal even if the coated layer is ruptured. The exposed surface of the base act as a cathode in presence of the remaining metal layer.

(c) **Galvanization note is provided in the Corrosion control notes.**

# Metal Coating

- **Galvanization:** Galvanization is a process of putting metallic coating which are anodic to the base metal. For example, iron is coated with anodic and more active metals such as zinc, magnesium and aluminium. The one of the important characteristics of anodic coating is that, even if the coating is ruptured, the base metal does not undergo corrosion. The exposed metal surface is cathodic with respect to the coating metal and the coating metal preferentially undergoes corrosion. It involves following steps:
  - The metal surface is washed with organic solvents to remove organic matter on the surface.
  - Rust and other deposits are removed by washing with sulphuric acid.
  - Finally the article is well washed with water and air dried.
  - The article is then dipped in a bath of molten zinc, maintained at 425-430C and covered with a flux of ammonium chloride to prevent oxidation of molten zinc.

# Metal Coating

- The excess zinc on the surface is removed by passing through a pair of hot rollers, which wipes out excess of zinc coating and produces a thin coating.
- Galvanization is used extensively to protect iron from corrosion in the form of roofing sheets, fencing wire buckets etc. Galvanized steel reinforcements are used in building construction, where high degree of corrosion resistance is required.

# **E-waste (Module:2)**

## **E-waste:**

- Basically, includes electronic or electrical goods which can no longer be used. They may contain hazardous or toxic material which cannot be disposed with other solid waste.
- It includes mobile phones, batteries, telephones, switch, socket, cable wires, computer hardware and other electronic products which are not of use.

## **Types of e-waste:**

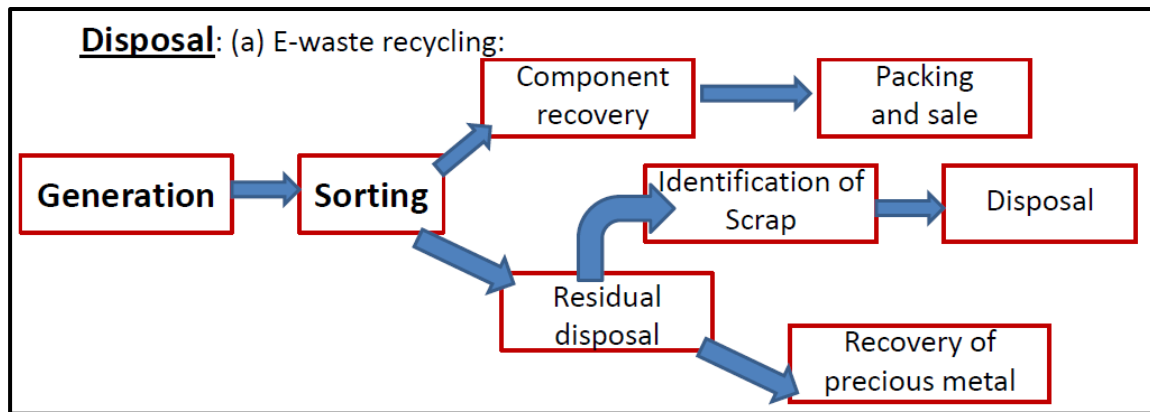
- Fridges, freezers and other cooling equipment.
- Computers and telecommunications equipment.
- Consumer electronic devices and solar panels.
- TVs, monitors and screens.
- LED bulbs.
- Vending machines.

## **Effects of e-waste on environment and human health:**

- E-waste can be toxic, contains various types of toxic metals (lead, mercury, nickel, cadmium, lithium etc.), which can get accumulated in the environment, in the soil, air, water. This can cause a long term damage in the environment and also to the human health.
- It also contains biodegradable materials. Their disposal techniques also harmful for the environment and living beings. For example, open-air burning and acid baths being used to recover valuable materials from electronic components release toxic materials leaching into the environment.
- The improper disposal of lead acid batteries and alkaline batteries also causes contamination of toxic chemicals with the soil and water.

## **Disposal:**

## E-waste (Module:2)



- **Landfilling:** A landfill site, also known as a tip, dump, rubbish dump, garbage dump, or dumping ground, is a site for the disposal of waste materials. By this the technique, the e-waste are to be disposed scientifically, so that the soil and water resources doesn't get effected in the nearby area.
- Incineration (decomposing the waste material by burning) and pyrolysis (heating at high temperature and decomposing the product) are one of the coming techniques to dispose the e-waste.
- The electronic waste are required to be recycled and reused in a scientific way.
- **Plastic Waste:** Products made from plastics such as keyboards, casing, front or rear panel. Miscellaneous parts encased in plastics – disposed by shredding and melting method.
- **Printed Circuit Board Waste:** Used in electronic parts such as motherboard, TV internal circuits, etc. need to be disposed by desoldering and open burning to remove metals.
- Lead acid batteries and alkaline batteries should be disposed properly, so that the toxic metals, harmful chemicals like acid and base should not get contaminated with air and water sources.

### Extraction of gold from E-waste:

When electronic products, such as computers, cell phones, televisions, VCRs, stereos, copiers, fax machines, internal chips and other relating parts, reach the end of their lifetime, they become electronic waste, otherwise known as “e-waste.” E-waste can often comprise of several hazardous components which can include heavy metals like mercury and lead. Despite this reality, gold, as well as

# E-waste (Module:2)

other precious metals, also make up a significant amount of e-waste, and its extraction could have advantageous properties for the gold industry.

## 1. Gold Extraction by Cyanide:

Since its introduction into the mining industry during the 1870s, the use of cyanide in gold leaching has been a useful, but dangerous technique of metal extraction. This extraction process involves the chemical reaction between the pulverized e-waste and sodium cyanide, which produces a soluble gold cyanide solution that allows for easier extraction of the precious metal. While useful, gold cyanidation remains a controversial technique that is prohibited in several countries around the world.

## 2. Acid Treatment:

The combination of hydrochloric acid and nitric acid have been found to be useful chemicals in the extraction of gold from e-waste. Other mild acids have also been successful in their extraction of gold, as these acids can successfully dissolve gold while limiting their potential to cause adverse effects to the environment.

## 3. Bioleaching:

Microbiological processes have been proposed over the last decade as possible alternatives to extracting precious metals such as copper, gold and other heavy metals. Bacteria such as *Aspergillus niger* and *Chromobacterium violaceum* are two microorganisms that have been found as suitable and sustainable methods of extracting gold from gold plated electronic devices.

**4.Solvent Extraction:** The solvent extraction method is known to one of important method regarding the extraction of copper from e-waste. This process comprises the liberation of the metallic fractions from downsized PCB's, a two-step acid leaching process to provide a bulk separation of copper from the other metals present. Then it is followed by subsequent purification of the copper containing solutions by solvent extraction using highly selective phenolic oxime and amide extractants, respectively.

## Extraction of copper from E-waste:

1. **Acid Treatment:** The crushed printed circuit boards are allowed to react with the acidic solutions like  $\text{HNO}_3$ ,  $\text{HCL}$ , and  $\text{H}_2\text{SO}_4$ . The concentrations of the acidic solutions are kept at proper proportion. It was found that the metal present in the sample get dissolved into solution with appropriate amount at different concentration of acids.

## E-waste (Module:2)

2. **Solvent Extraction:** The solvent extraction method is known to one of important method regarding the extraction of copper from e-waste. This process comprises the liberation of the metallic fractions from downsized PCB's, a two-step acid leaching process to provide a bulk separation of copper from the other metals present. Then it is followed by subsequent purification of the copper containing solutions by solvent extraction using highly selective phenolic oxime and amide extractants, respectively.
3. **Bioleaching:** Microbiological processes have been proposed over the last decade as possible alternatives to extracting precious metals such as copper, gold and other heavy metals. Bacteria such as *Thiobacillus ferrooxidans* and *T. thiooxidans* have been documented to successfully extract copper.
4. **Supercritical method:** Supercritical CO<sub>2</sub> with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> was efficient to Cu recovering from PCBs. It was found that the supercritical extraction was 9 times faster, compared to atmospheric pressure extraction.