

MODULE 3: CORROSION SCIENCE AND E-WASTE MANAGEMENT

Corrosion chemistry: Introduction, electrochemical theory of corrosion, types-differential metal, differential aeration, corrosion control-galvanization, anodization and sacrificial anode method. Corrosion penetration rate (CPR) - introduction and numerical problem.

E-waste management: Introduction, sources, types of, effects of e-waste on environment and human health, methods of disposal, advantages of recycling, extraction of copper and gold from e-waste.

Corrosion chemistry

Definition: Metal when exposed to the atmosphere undergoes gradual destruction. Such destruction of metal is known as Corrosion. It's defined as the “destruction of metal or alloys from its surface by the surrounding environment through chemical or electrochemical changes”.

Eg. Rusting of Fe- A reddish brown scale formation on iron. It is due to the formation of hydrated ferric oxide, Green scale formed on Cu vessel- It is due to the formation of basic cupric carbonate ($\text{CuCO}_3 + \text{Cu(OH)}_2$)

Electrochemical theory of corrosion:

According to electrochemical theory, corrosion of the metal take place due to the formation of anodic and cathodic regions on the same metal surface in the presence of a conducting medium. At the anodic region oxidation reaction takes place and the metal gets corroded into ions liberating the electrons. Consequently metals undergo corrosion at the anodic region. At the cathodic region reduction reaction takes place. Metal ions in the cathodic region are unaffected by the cathodic reaction.

The electrons liberated at the anodic region migrate towards the cathodic region constituting corrosion current. The metal ions liberated at the anode and some anions formed at the cathode region diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and the cathode. Corrosion of metal continues as long as both the anodic and cathodic reactions take place simultaneously.

Corrosion reactions:

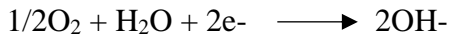
At the anodic region: At anodic region, iron is liberating Fe^{2+} ions and electrons,



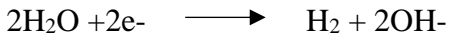
At the cathodic region:

The electrons flow from the anodic to cathodic area and at the cathodic region, reduction takes place. Since metal cannot be reduced further, metal atoms at the cathodic region are unaffected by the cathodic reaction. Some constituents of the corrosion medium take part in the cathodic reaction. There are three possible ways in which the reduction can take place.

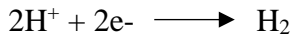
If the solution is aerated and almost neutral,



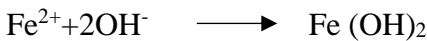
If the solution is deaerated and almost neutral:



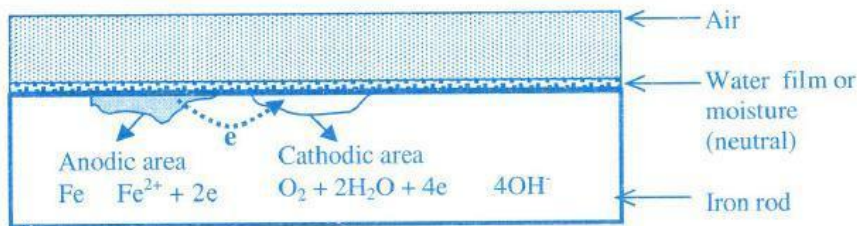
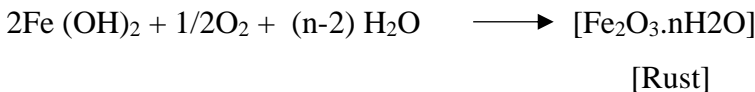
If the solution is deaerated and acidic:



The electrons liberated at the anodic region migrates to the cathodic region. Corrosion of iron produced Fe^{2+} ions and OH^- ions at the anode and cathode sites respectively. These ions diffuse towards each other and produce insoluble



In an oxidizing environment, it is oxidized to ferric oxide and the rust is hydrated ferric oxide.



Types of corrosion:

Depending upon the nature of the metal, environment, stress and strain on the material etc, the metal exhibit different types of corrosion, they are,

- (i) Differential metal corrosion or Galvanic Corrosion.
- (ii) Differential aeration corrosion E g: pitting corrosion, water line corrosion

Differential metal Corrosion: When two dissimilar metals are in contact with each other a potential difference is set up resulting in a galvanic current. The two metals differ in their tendencies to undergo oxidation, the one with lower electrode potential or the more active metal acts as anode and the one with higher electrode potential acts as cathode. The anodic metal undergoes corrosion and the cathodic metal is generally unattacked.

At the anode (less O_2 concentration), $Fe \rightarrow Fe^{2+} + 2e^-$

At the cathode (more O_2 concentration), $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

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

$2Fe(OH)_2 + \frac{1}{2} O_2 + H_2O \rightarrow [Fe_2O_3 \cdot 3H_2O]$ (rust)

Eg : Steel pipes joined to copper plumbing, undergo galvanic corrosion, Steel screws or rivets used on Copper sheet, or screws and washers of unlike metals, Steel propeller shaft in Bronze bearing.

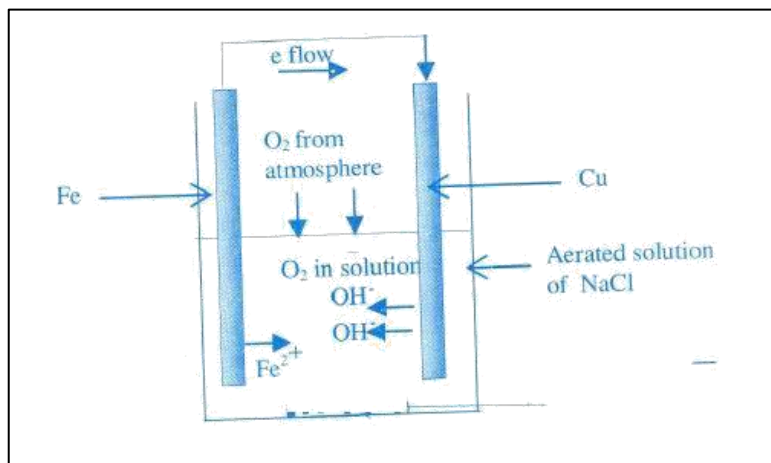


Fig. Differential metal corrosion:

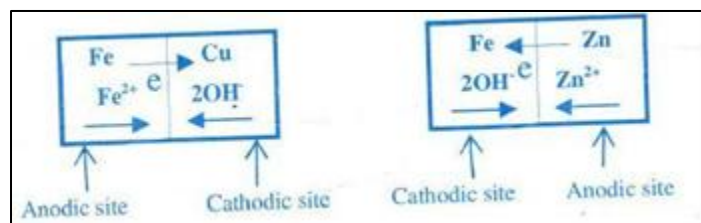


Fig. Corrosion in Bimetallic couple

Differential aeration corrosion: Differential aeration corrosion occurs when a metal surface is exposed to differential air concentrations of Oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as a cathodic region and the part of the metal exposed to lower oxygen concentration acts as anodic region.

Corrosion of metal arising as a result of the formation of an oxygen concentration cell due to uneven supply of air on the metal surface is known as differential aeration corrosion.

At the anode (less O_2 concentration), $Fe \rightarrow Fe^{2+} + ne^-$

At the cathode (more O_2 concentration), $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

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

$2Fe(OH)_2 + \frac{1}{2} O_2 + H_2O \rightarrow [Fe_2O_3 \cdot 3H_2O]$ (rust)

Eg. Part of the nail inside the wall, being exposed to lower oxygen concentration than the exposed part, undergoes corrosion. Paper pins inside the paper get corroded, and the exposed part is free from corrosion.

Metal under dirt, dust, scale or water undergoes corrosion.

(a) Water line Corrosion:

Water line corrosion is a case of differential aeration corrosion. The water line corrosion takes place due to the formation of differential oxygen concentration cells. The part of the metal below the water line is exposed only to dissolved oxygen (acts as anode) while the part above the water is exposed to higher oxygen concentration (acts as cathode) of the atmosphere. A distinct brown line is formed below the water line due to deposition of rust.

At the anode (less O_2 concentration), $Fe \rightarrow Fe^{2+} + ne^-$

At the cathode (more O_2 concentration), $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

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

$2Fe(OH)_2 + \frac{1}{2} O_2 + H_2O \rightarrow [Fe_2O_3 \cdot 3H_2O]$ (rust)

Consider a strip of pure iron partially immersed in an aerated solution of NaCl as shown below.

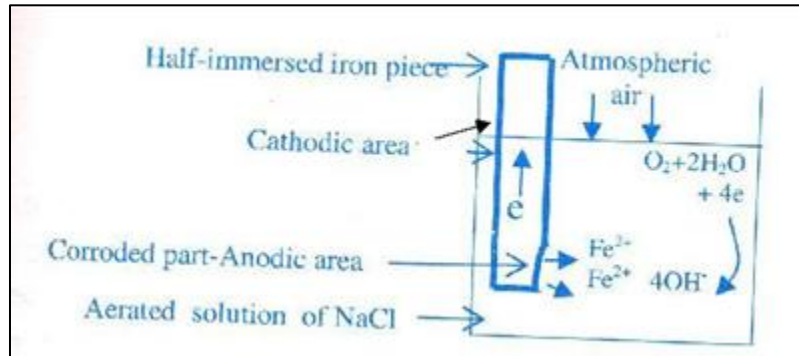
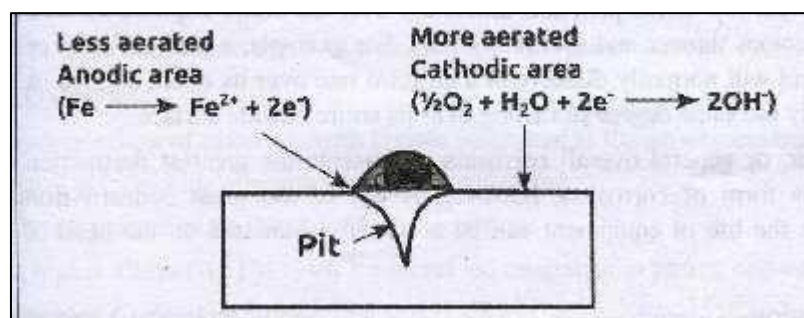


Fig. Differential aeration corrosion

The concentration of O_2 is high at the surface than that inside the solution. Since the cathodic reaction involves use of O_2 , the cathodic area tends to concentrate near the waterline. Therefore, the bottom portion of iron strip act as anode and corrosion commences here. The reactions are same as given above.

Ex: Partially buried pipe line in soil or submerged in water undergoes corrosion below the soil or water whereas the exposed part remains free from corrosion, Metal under dust, dirt or water undergoes corrosion

(b) Pitting Corrosion: Pitting corrosion is a localized and accelerated corrosion, resulting in the formation of pits or pin holes, around which the metal is relatively unattacked.

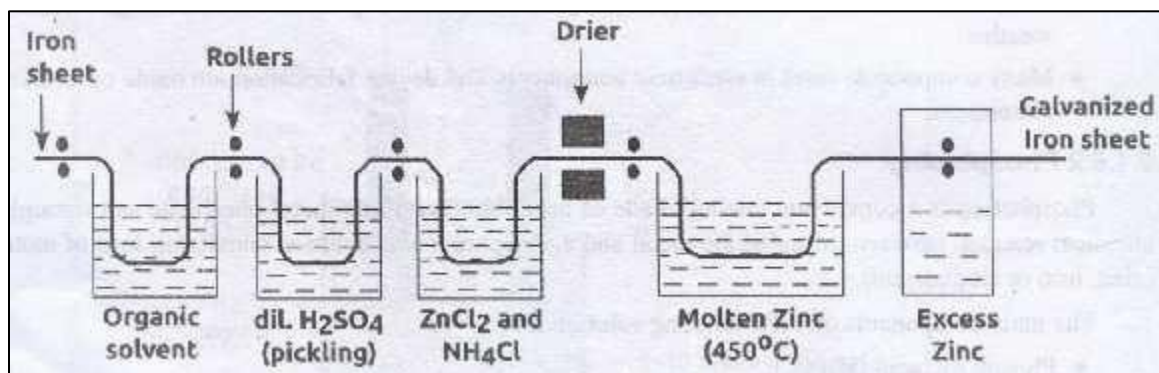


Pitting corrosion results when small particles of dust get deposited on a steel surface. The portion covered by the dust will not be well aerated compared to the exposed surface. The covered portion acts as anode with respect to the surface exposed. Once a pit is formed the rate of corrosion increases. This is because of the formation of small anodic area. The cathode induces the small anodic area to corrode faster by accepting electrons from the anodic area resulting in the enlargement of the pit.

Eg.: Less aerated part of the machinery, cracks in metals which are not well aerated

Corrosion Control: Following methods are used to control the corrosion of the metal.

Galvanisation: It is a process of coating a base metal surface with Zinc metal by hot dipping method.



The galvanization process involves the 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 dilute 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 – 430 °C and covered with a flux of ammonium chloride to prevent the oxidation of molten Zinc.
- 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.

Uses:

Galvanization is used to protect roofing sheets, water pipes, barbed wire, buckets etc.

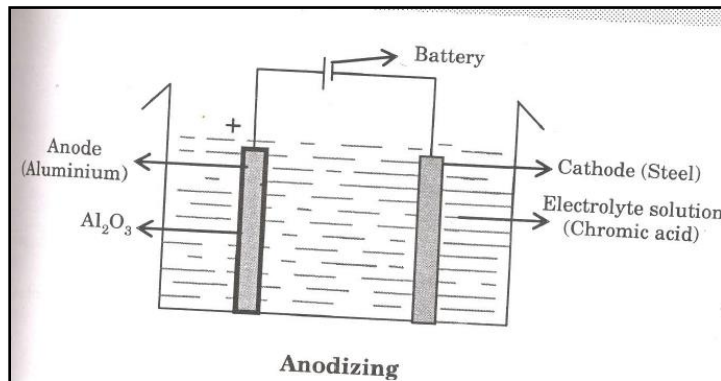
Galvanised articles are not used for preparing and storing foodstuffs, since Zinc dissolves in dilute acids producing toxic Zinc compounds.

Anodization: Anodization is a process in which a protective passive oxide film is artificially (chemically or electrochemically) produced on certain metals. It is also called as anodic oxidation process. Anodized coating is generally produced on non ferrous metals like Al, Zn, Mg and their alloys by anodic oxidation process.

In anodization of aluminium, clean, polished aluminium is taken as anode and immersed in an electrolytic cell containing chromic acid or sulphuric acid. Inert electrodes like lead is generally used as cathode. The anodic oxide film formed on Al as aluminium oxide, which is porous. The pores are finally sealed by dipping in hot water to produce $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which acts as a non-porous protective layer preventing corrosion.

Anode reaction: $2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$

Cathode reaction: $6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2$



Advantages:

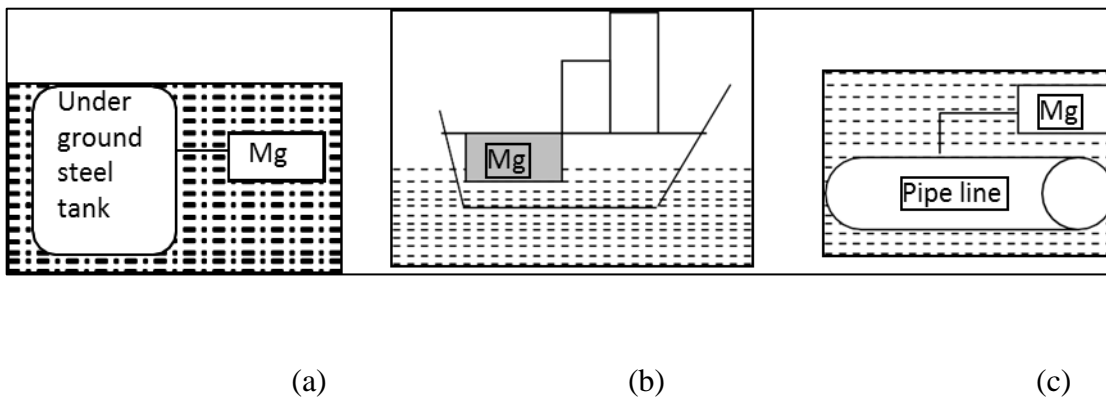
1. Anodised aluminium products have a protective layer; they have harder and durability than normal aluminium.
2. The anodized surface show good adhesion to paint and gives a colored appearance.
3. The thick outer coating produced, along with the proper sealing, increases the corrosion resistivity of the surface as it prevents further oxidation.

Applications:

- (i) Anodization is used for aluminium pressure cookers and cooking pots.
- (ii) Aluminium window frames are anodized.

Sacrificial Anode Method: The protected metal structure is converted into a cathode by connecting it to a more active metal. This active metal acts as an auxiliary anode Zn, Mg and Al are the common auxiliary anodes and are more reactive undergo corrosion, protecting the metal structure. Since the anodic metals are sacrificed to protect the metal structure, the method is known as sacrificial anode method. Exhausted sacrificial anodes are replaced by new ones as and when required.

- Eg. (a) A magnesium block connected to a buried oil storage tank
 (b) Mg bars are fixed to the sides of ocean going ships to act as sacrificial anodes.
 (c) Mg blocks are connected to buried pipe lines.



Sacrificial anode method

Advantages: (i) The method is simple.
 (ii) Low installation cost and low maintenance.
 (iii) Does not require power supply.

Disadvantage: Replacement of consumed anodes

Corrosion Penetration Rate (CPR)

The corrosion penetration rate (CPR) is defined in three ways:

- The speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment.
- The amount of corrosion loss per year in thickness.
- The speed at which corrosion spreads to the inner portions of a material.

The speed or rate of deterioration depends on the environmental conditions and the type and condition of the metal under study.

Corrosion penetration rate may also be known as corrosion rate. Several pieces of data must be collected to calculate the corrosion penetration rate for any given metal:

- The weight lost (the decrease in weight of the metal during the period of reference).
- The density of the metal.
- The total surface area initially present.
- The time taken for the metal to corrode.

The CPR is calculated as follows:

$$\text{CPR} = (k \times W) / (D \times A \times T)$$

where k = a constant depends on unit used.

when K = 534 the mpy will be used. when K = 87.6, mm/yr will be used.

W = total weight lost ($m_o - m$) m = weight after corroded m_o = weight before corroded

T = time taken for the loss of metal

A = the surface area of the exposed metal

D = the metal density in g/cm^3

The corrosion penetration rate is best expressed in terms of thickness or weight loss where the surface of the metal corrodes uniformly across an area.

This method involves the exposure of a weighed piece of test metal or alloy to a specific environment for a specific time. This is followed by a thorough cleaning to remove the corrosion products and then determining the weight of the lost metal due to corrosion.

The rate may vary if the rate expressed by the formula above is used to compare corrosion rates for a period of time longer than one year with rates calculated over short periods. This is because the short time periods are prone to fluctuating environmental changes from season to season and also from day to day

E-waste management

Introduction: E-waste or electronic waste means discarded electrical or electronic devices or components. This includes working and broken items that are thrown in the garbage or donated to a charity reseller, their components, consumables, parts, and spares. E-waste management is defined as a holistic method of cutting down E-waste from the earth to prevent its harmful toxic to deteriorate earth. It recycles and reuses the e-waste that is no longer needed.

Sources of e-waste: The common sources of e-waste are as follows.

- Large household appliances like refrigerators/freezers, washing machines, dishwashers, televisions.
- Small household appliances which include toasters, coffee makers, irons, hairdryers.
- Information Technology (IT) and Telecommunications equipment namely personal computers, telephones, mobile phones, laptops, printers, scanners, photocopiers etc.
- Lighting equipment such as fluorescent lamps.
- Electronic or Electrical tools i.e. handheld drills, saws, screwdrivers etc.
- Toys, leisure and sports equipment.
- Monitoring and control instruments.
- Automatic dispensers.

Types of e-waste:

It is categorized into 21 types under two broad categories:

- Information technology and communication equipment.
- Consumer electrical and electronics.

Due to rapid technology changes large amount of electronic or electrical devices are turning into waste. Some of the common e-waste elements are mobile phones, computers, laptops, hard drives, fans, microwaves, DVD, printers, lamps, etc.

Effects of e-waste on environment and human health: E-waste is a serious issue for our environment because it releases harmful toxic chemicals from the metals due to chemical reactions and these toxic chemicals harm our environment, therefore they must be handled with care when no longer wanted or needed.

Electronic scrap components, such as CPUs, contain potentially harmful materials such as lead, cadmium, beryllium, or brominated flame retardants. Improper disposal of e-waste is highly dangerous to the global environment involving significant risk to the health of workers and their communities

The consequences of improper e-waste disposal in landfills or other non-dumping sites pose serious threats to current public health and can pollute ecosystems for generations to come. When electronics are improperly disposed of and end up in landfills, toxic chemicals are released, impacting the earth's air, soil, water, and ultimately, human health.

Effects on Air quality: Contamination in the air occurs when e-waste is informally disposed of by dismantling, shredding, or melting the materials, releasing dust particles or toxins, such as dioxins, into the environment that cause air pollution and damage respiratory health. Chronic diseases and cancers are at a higher risk to occur when burning e-waste because it also releases fine particles, which can travel thousands of miles, creating numerous negative health risks to humans and animals. The air pollution caused by e-waste impacts some animal species more than others, which may be endangering these species and the biodiversity of certain regions that are chronically polluted. Over time, air pollution can hurt water quality, soil, and plant species, creating irreversible damage to ecosystems.

Effects on Soil: When the improper disposal of e-waste in regular landfills or in places where it is dumped illegally, both heavy metals and flame retardants can seep directly from the e-waste into the soil, causing contamination of underlying groundwater or contamination of crops that may be planted nearby or in the area in the future. When the soil is contaminated by heavy metals, the crops become vulnerable to absorbing these toxins, which can cause many illnesses and doesn't allow the farmland to be as productive as possible.

Effects on Water: After soil contamination, heavy metals from e-waste, such as mercury, lithium, lead, and barium, then leak through the earth even further to reach groundwater. When these heavy metals reach groundwater, they eventually make their way into ponds, streams, rivers, and lakes. Through these pathways, acidification and toxicity are created in the water, which is unsafe for animals, plants, and communities even if they are miles away from a recycling site. Clean drinking water becomes problematic to find.

Effects on Humans: Electronic waste contains toxic components that are dangerous to human health, such as mercury, lead, cadmium, polybrominated flame retardants, barium, and lithium. The negative health effects of these toxins on humans include brain, heart, liver, kidney, and skeletal system damage. It can also considerably affect the nervous and reproductive systems of the human body, leading to disease and birth defects.

Methods of disposal of E-waste:

To avoid the toxic effects of e-waste, it is crucial to dispose them in proper manner, so that items can be recycled, refurbished, resold, or reused.

Following methods are used to dispose e-waste:

Landfills: This is the most commonly used method of disposing e-waste. In this method, large trenches are made in the soil to bury e-waste. But this is not a good method to dispose e-waste because e-waste contains toxic substances like lead, mercury, etc., that leak into the earth and harm the underground water and soil.

Incineration: It is also the most commonly used method to dispose of e-waste. In this method, the e-waste is burned at high temperatures in specially designed incinerators. Due to which the volume of e-waste is reduced and the energy produced by this method is also utilized separately. But this is also not a good method because when the e-waste burns, it releases harmful gases which harm our environment.

Acid Bath: In this method, the e-waste is soaked in powerful sulphuric, hydrochloric, nitric acid solutions that remove the metal from the e-waste. The recovered metal is further reused to create other products. This method also has drawbacks, like the acid solutions sometimes dumped into the water resources which is harmful for living things.

Recycling: This is the most efficient method and also environmentally friendly. Recycling involves dismantling, processing and end processing. In this method, separation is done to recover used circuit boards, ICs, motherboard, etc from the e-waste and recycle them. Precious metals like copper, lead, etc., are separated from the e-waste using a PCB recycling machine without harming the environment.

Re-use: It includes direct second hand use or use after slight modifications to the original functioning equipment like Inkjet cartridge is used after refilling. Old working computers can be donated to schools or organization working in the field of education. Computers beyond repairs can be returned back to the manufacturers. This can considerably reduce the volume of E-Waste generation converted into less hazardous compounds.

Advantage of Recycling:

- Saves landfills: Recycling the e-waste helps to manage solid waste effectively and reduces waste sent to landfills and incinerators.
- Conserves natural resources: Recycling recovers valuable materials from old electronics that can be used to make new products. As a result, we reduce pollution, reduce greenhouse gas emissions and save natural resources by extracting fewer raw materials from the earth
 - Protects Environment: E-waste recycling provides proper handling and management of toxic chemical substances like mercury, lead and cadmium contained in the e-waste stream. Nowadays, e-waste contributes to more than 70% of the environmental pollution, hence recycling of e-waste can reduce environmental pollution.
 - Save Energy: Reduces consumption of energy by minimizing product development lifecycle
 - Creates Jobs: E-waste recycling creates new jobs for professional recyclers and creates a second market for the recycled materials and hence produce economic benefits.

Extraction of copper and gold from e-waste:

The electronic waste also contains fair percentage of precious metals like Cu, Ag, Au, Pd, Rh etc. These metals can be recovered from E-waste at cheaper cost than from the usual ores. The recycling of metals such as gold and copper from discarded e-waste is an important aspect to develop the environmental friendly manufacturing processes. Techniques such as Pyrometallurgy, Hydrometallurgy and Biohydrometallurgy are used to recover precious metals like copper, silver and gold.

The extraction of copper and gold from e-waste using hydrometallurgical route comprises the liberation of the metallic fractions from downsized PCBs, a two-stage acid leaching process to provide a bulk separation of copper and gold from the other metals present, and subsequent purification of the copper and gold-containing solutions by solvent extraction using highly selective phenolic oxime and amide extractants, respectively.

Following steps are involved in the process.

1. Pre-processing: After collection of e-waste, it is segregated, delaminated, cleaned with water and acetone and treated with *N,N*-dimethylacetamide (DMA) to remove the organic components (epoxy resins) present in the e-waste. This pretreated e-waste is shredded into small pieces and powdered, further it is subjected to recovery of precious metals. The metals were dissolved in acid and non-metallic component such as plastic and ceramic is separated by filtration.
2. Leaching: The liberated metallic fraction collected from the pre-processing step was leached in two stages to provide a bulk separation of copper and gold from the other metals present.
 - (i) First stage leaching process involves the selective dissolution of copper over gold. The samples were dissolved in dilute nitric acid, which almost exclusively leached the copper.
 - (ii) The filtered residue was then subjected to a second stage leaching process using sulfuric acid and halide salts (NaCl, NaBr) to selectively dissolve, silver and tin.
3. Solvent extraction:
 - (i) Recovery of Cu: Distilled water and ammonia solution was added to the leach solutions obtained after stage-one leaching process. To selectively recover the copper, the phenolic oxime dissolved in kerosene was used as the extractant. The Cu metal loaded organic phase was separated from the acidic aqueous leach liquor and washed with either sulfuric acid or nitric acid.
 - (ii) Recovery of Au: In the second-stage solvent extraction, an organic amide diluted in toluene was used as the extractant. The gold-loaded organic phase was then separated from the aqueous phase and stripped of the metal using either water or sodium hydroxide.

