

Module-3

CORROSION

Corrosion and its control:

Introduction, Electrochemical theory of corrosion, Types of corrosion - Differential metal and differential aeration (pitting and water line). Corrosion control: Anodizing – Anodizing of aluminum, cathodic protection - sacrificial anode method, Metal coatings – Galvanization. Corrosion Penetration Rate (CPR), numerical problems on CPR.

Course outcome (CO-3): Explain the fundamental concepts of corrosion, its control and surface modification methods namely electroplating and electroless plating.

Corrosion

Introduction:

The term corrosion is used to denote a change. A metal changes from its elementary state to the combined state when it comes in contact with liquid medium. This is actually due to the chemical interaction between the metal and the environment.

Definition: “The spontaneous deterioration and consequent loss of a metal/alloy due to chemical/electrochemical attack by the environment”.

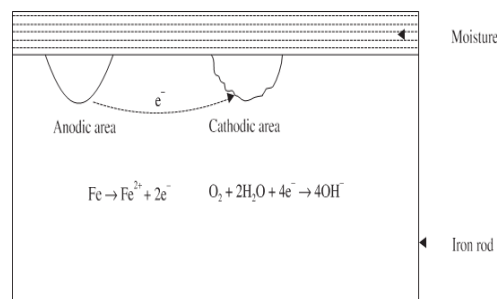
Example: When iron metal is exposed to the moist environment, the metal forms a hydrated ferric oxide called rust which is relatively non-protective.

Most of the corrosion cases are electrochemical in nature taking place by an electrochemical attack on the metal in the presence of air and moisture (H_2O) called **wet corrosion**. The mechanism of the wet corrosion is explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion:

According to this theory,

1. When a metal is in contact with moist air or when dissimilar metals are contact with each other in environment, large numbers of galvanic cells are formed with the existence of anodic and cathodic area on the metal.
2. In this corrosion, oxidation of the metal and reduction of species present in contact with the metal takes place.
3. The anodic part of the metal undergoes oxidation and suffers from corrosion, cathodic part undergo reduction and protected from the corrosion.
4. The electrons are transferred through the metal from anode to cathode.
5. During corrosion the following reactions takes place.



At anode (oxidation reaction) : $M \rightarrow M^{n+} + ne^{-}$

The reaction at cathode (reduction reaction) depends on the nature of the environment:

If the medium is acidic,

In the presence of dissolved oxygen : $2H^{+} + \frac{1}{2}O_2 + 2e^{-} \rightarrow H_2O$

In the absence of dissolved oxygen : $2H^{+} + 2e^{-} \rightarrow H_2 \uparrow$

If the medium is alkaline/neutral,

In the presence of dissolved oxygen : $H_2O + \frac{1}{2}O_2 + 2e^{-} \rightarrow 2OH^{-}$

In the absence of dissolved oxygen : $2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2 \uparrow$

Example: Rusting of an Iron in the presence of moist air

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

Cathodic reaction : $H_2O + \frac{1}{2}O_2 + 2e^{-} \rightarrow 2OH^{-}$

Products of anode & cathode : $Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$

In the presence of oxygen : $2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3 \cdot 2H_2O$
(Rust)

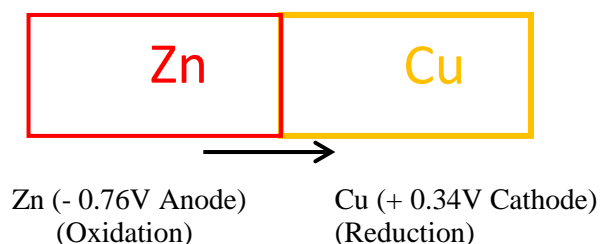
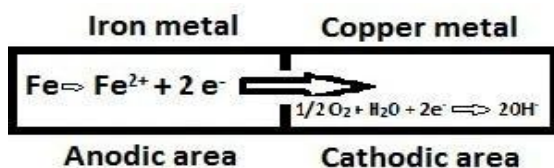
Types of corrosion: Corrosion can be classified into 3 types as follows

- 1) Differential metal corrosion (Galvanic corrosion)
- 2) Differential aeration corrosion

Differential metal corrosion (Galvanic corrosion)

- 1) When two dissimilar metals are in direct contact with one another and exposed to a corrosive medium, the metal with lower electrode potential becomes anode and suffers from corrosion, whereas the metal with higher electrode potential becomes cathode and protected from corrosion. This type of corrosion is known as differential metal corrosion or galvanic corrosion.
- 2) The rate of corrosion depends mainly on the difference in the position of the two metals in galvanic series.
- 3) Higher the difference, faster is the rate of corrosion.

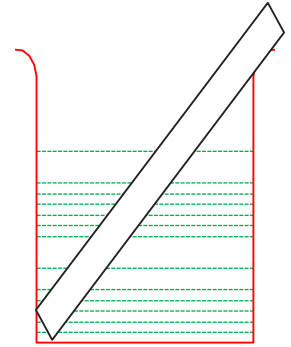
Example: 1. Electrode potential of iron (-0.44 V) is less than that of copper (0.34 V). Therefore when iron is in contact with copper, iron becomes anodic and undergoes corrosion, whereas copper becomes cathodic and protected from the corrosion.



Example: 2. when zinc is in contact with copper, zinc having lower reduction potential value acts as anodic and gets corroded, whereas copper metal with higher reduction potential value compared to zinc, acts as cathode and is protected from corrosion

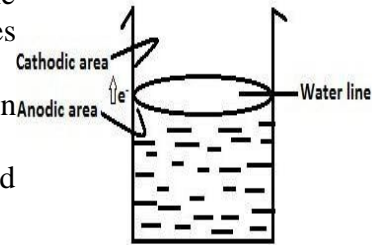
Differential aeration corrosion

- 1) When a metal is exposed to different concentration of air (O_2), part of the metal exposed to lower concentration of O_2 becomes anodic and undergoes corrosion.
- 2) Other part of the metal exposed to higher concentration of O_2 becomes cathodic and protected from the corrosion.
- 3) The difference in O_2 concentration produces a potential difference and causes corrosion. This type of corrosion is called differential aeration corrosion.



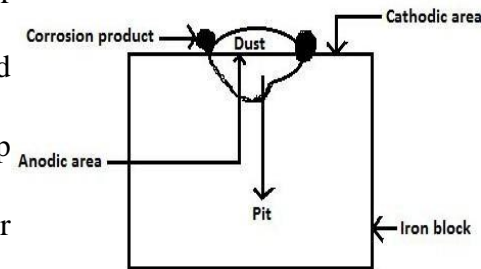
Example: 1 Water line corrosion

- 1) It is observed in steel or iron water tank partially filled with water. Part of the tank just below water level is exposed to lower concentration of O_2 becomes anodic and undergoes corrosion.
- 2) Part of the tank above the water line which is exposed to higher concentration of O_2 becomes cathodic and protected from the corrosion.
- 3) More corrosion is observed just below the water line; hence this type is called water line corrosion.



Example: 2 pitting corrosion

1. Pitting corrosion is observed when dust particles get deposited over the metal surface.
2. The portion of the metal covered by dust which is less aerated becomes anodic and suffers from corrosion.
3. Thus, metal is lost below the surface of dust particle forming a deep and narrow pit.
4. The adjacent area of the metal which is exposed to higher concentration of O_2 becomes cathodic and protected from corrosion.



Corrosion control

Inorganic coatings (Chemical conversion coatings)

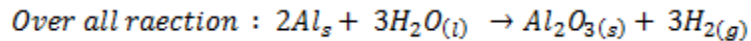
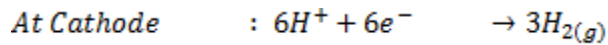
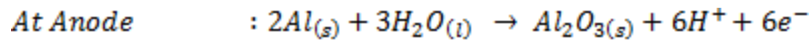
These coatings are produced at the surface of the metal by chemical/electrochemical reactions.
Examples: Anodizing and Phosphating

Anodizing:

Anodizing is the process of oxidation of outer layer of metal to its metal oxide by electrolysis. Oxide layer formed over the metal itself acts as protective layer.

Anode	: Aluminium
Cathode	: Steel or Copper
Electrolyte	: 5-10% chromic acid
Temperature	: 30-40 °C
Applied potential	: 0-40 V

Aluminum is made as anode and copper or steel is used as cathode. The electrodes are immersed in an electrolyte consisting of 5-10% chromic acid. The temperature is maintained at 30-40 °C. Potential of 0-40 V is applied which oxidizes outer layer of Al to Al_2O_3 and that get deposited over the metal. The reactions involved are as follows



The anodized coatings are thicker than the natural oxide film and possess improved corrosion resistance as well as resistance to mechanical injury.

Cathodic Protection:

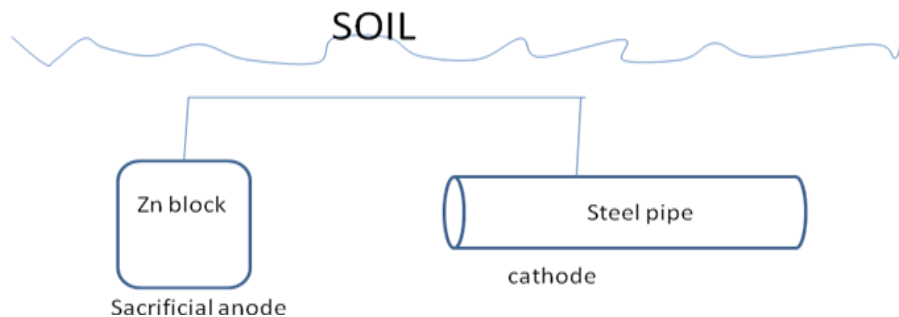
The principle is to force the metal to be protected to behave as cathode. There are two types of cathodic protections namely,

- 1) Sacrificial anodic protection.
- 2) Impressed current method

Sacrificial anodic protection:

- 1) The metal to be protected is connected to a more anodic metal using a metallic wire.
- 2) The more active metal gets corroded while the parent structure is protected from corrosion.
- 3) The more active metal so employed is called sacrificial anode.
- 4) The sacrificial anodes to be replaced by fresh ones as and when it is required.
- 5) Commonly used sacrificial anodes are: Mg, Zn, Al etc.

Example: steel pipe is protected by connecting it to a block of Zn. In such cases steel acts as a cathode and is unaffected or protected from corrosion and Zn act as anode and undergoes sacrificial corrosion

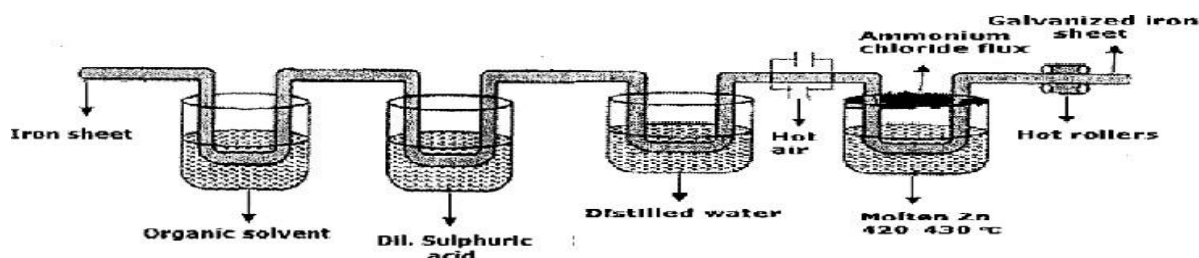


Metal coatings:

Metal coatings can be applied on the base metal by hot dipping process. This method is used for producing a coating of low melting metals such as Zn, Al, Sn etc, on iron/steel metals which have relatively high melting point. Example: Galvanizing and Tinning

Galvanization:

Coating of zinc on iron or steel by hot dipping process is called galvanizing. (M.P of Zn=419 °C)
It is carried out as follows,



- 1) The iron sheet is subjected to pretreatment by degreasing with organic solvent.
- 2) The sheet is passed through dilute H_2SO_4 to remove any rust.
- 3) Washed with distilled water and dried by supplying hot air.
- 4) Then iron sheet is dipped in molten bath of Zn at 419°C and surface is covered with NH_4Cl flux which prevents the oxidation of Zn metal.
- 5) The excess of coated metal is removed by passing through a pair of hot rollers and cooled gradually.

Corrosion Penetration Rate (CPR)

The corrosion penetration rate (CPR) is defined as “the speed at which any metal in a specific environment deteriorates due to chemical reactions when it is exposed to a corrosive environment” or the amount of corrosion loss per unit time in thickness or the speed at which corrosion spreads to the inner portions of a material. Corrosion rate depends on the metal and the environmental condition.

The CPR is given by

$$\text{CPR} = \frac{k \times W}{D \times A \times T}$$

Where k = a constant

W = total weight lost

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 expressed in terms of thickness or weight loss when 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 metal after corrosion.

The rate may vary if the rate expressed by the formula above is used to compare corrosion rates for a period 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 from day to day.

Note:-

1. Unit of CPR is mils per year if W is in mg, A in Inch², D in g/cm³, t in hrs and k value will be 534. (1mil = 0.001 inch)
2. Unit of CPR is mm per year if W is in mg, A in cm², D in g/cm³, t in hrs and k value will be 87.6. (1inch = 2.54 cm)
3. If CRP is less than 20m/year or 0.5 mm/year, it is acceptable for most of the application.

Numerical Problems on CPR

1. A steel of area 100 inch² is exposed to air near the seashore. After 1 year it was found that the steel sheet has lost 485g due to corrosion. What is the value of CPR in mils/year and in mm/year? Can such steel sheet be applicable for the construction purpose where the steel sheet is exposed?

Given - Area (A) = 100 inch², total weight lost (W) = 485g = 485 x 10³ mg, T = 1 year = 1 x 365 x 24hrs, D = 7.9g/cm³ and k=534.

$$\text{CPR} = \frac{k \times W}{D \times A \times T}$$

$$\text{CPR} = \frac{534 \times 485000}{7.9 \times 100 \times 365 \times 24}$$

$$\text{CPR} = 37.42 \text{ mils/year}$$

Area = 100 inch² = 100 x 2.54 x 2.54 cm² (1 inch = 2.54 cm) and k = 87.6

$$\text{CPR} = \frac{k \times W}{D \times A \times T}$$

$$\text{CPR} = \frac{87.6 \times 485000}{7.9 \times 100 \times 2.54 \times 2.54 \times 365 \times 24}$$

$$\text{CPR} = 0.9516 \text{ mm/year}$$

Since CPR is not less than 20m/year or 0.5 mm/year, it is not applicable for the construction purpose.

E-WASTE MANAGEMENT

Electronic waste or e-waste is a term for electronic products that have become unwanted, non-working or obsolete and have essentially reached the end of their useful life. Because technology advances at such a high rate, many electronic devices become trash after a few short years of use.

Sources

E-waste refers to the generation of waste from the engineering world which is dominated by the use of electronic / electrical devices and equipment.

- (a) Waste generated from the products used for data processing such as computers, computer devices like monitor, speakers, keyboards, printers, calculators, phones, digital / video cameras, radios.
- (b) Calculators, electronic devices used for entertainment like TV, DVDs, CD players, VCRs and MP3 players.
- (c) Equipment or devices used for communication like phones, landline phones, fax etc.
- (d) Laboratory with equipment's such as calorimeters, hot plates, microscopes.
- (e) Household equipment's such as vacuum cleaner, microwave ovens, washing machines, air conditioners etc.

Characteristics:

- (a) Hazardous components in e-waste: Electronic waste consists of a large number of components of various sizes and shapes some of which contain hazardous component that need to be removed for separate treatment.
- (b) Material composition of e-waste: E-waste contains a mixture of various metals, particularly copper, aluminium and steel attached to, covered with or mixed with various types of plastics and ceramics. Precious metals have a wide application in the manufacture of electronic appliances serving as contact material due to their high chemical stability and their good conducting properties. Platinum group metals are used among other things in switching contacts.

It is obvious that the copper and precious metals make-up more than 80 % of the value for most of the e-waste samples. Recovery of precious metals and copper remain as the major economic driver for a long time.

Types of e-waste

Any appliance that runs on electricity has the potential to cause damage to the environment if it is not disposed of in a responsible way. Common items electronic waste are:

- Large household appliances (refrigerators/freezers, washing machines, dishwashers)
- Small household appliances (toasters, coffee makers, irons, hairdryers)
- Information technology (IT) and telecommunications equipment (personal computers, telephones, mobile phones, laptops, printers, scanners, photocopiers)

- Consumer equipment (televisions, stereo equipment,
- Lighting equipment (fluorescent lamps)
- Electrical and electronic tools (handheld drills, saws, screwdrivers)
- Toys, leisure and sports equipment
- Medical equipment systems (with the exception of all implanted and infected products)
- Monitoring and control instruments
- Automatic dispensers.

Pollutants in e-waste

Pollutants or toxins in e-waste are typically concentrated in circuit boards, batteries, plastics, and LCDs (liquid crystal displays). Pollutants and their occurrence in waste electrical and electronic equipment are:

Pollutants	Occurrence
Arsenic	Semiconductors, diodes, microwaves, LEDs (Light-emitting diodes), solar cells
Barium	Electron tubes, filler for plastic and rubber, lubricant additives
Brominated flame- proofing agent	Casing, circuit boards (plastic), cables and PVC cables
Cadmium	Batteries, pigments, solder, alloys, circuit boards, computer batteries, monitor cathode ray tubes (CRTs)
Chrome	Dyes/pigments, switches, solar
Cobalt	Insulators
Copper	Conducted in cables, copper ribbons, coils, circuitry, pigments
Lead	Lead rechargeable batteries, solar, transistors, lithium batteries, PVC (polyvinyl chloride) stabilizers, lasers, LEDs, thermoelectric elements, circuit boards
Liquid crystal	Displays
Lithium	Mobile telephones, photographic equipment, video equipment (batteries)
Mercury	Components in copper machines and steam irons; batteries in clocks and pocket calculators, switches, LCDs
Nickel	Alloys, batteries, relays, semiconductors, pigments
PCBs (polychlorinated biphenyls)	Transformers, capacitors, softening agents for paint, glue, plastic
Selenium	Photoelectric cells, pigments, photocopiers, fax machines
Silver	Capacitors, switches (contacts), batteries, resistors
Zinc	Steel, brass, alloys, disposable and rechargeable batteries, luminous substances

Effect of e-waste on environment and human health:

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 and end up in landfills, toxic chemicals are released, impacting the earth's air, soil, water and ultimately, human health.

The Negative Effects on Air:

Contamination in the air occurs when e-waste is informally disposed 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. E-waste of little value is often burned, but burning also serves a way to get valuable metal from electronics, like copper. 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. Higher value materials, such as gold and silver, are often removed from highly integrated electronics by using acids, desoldering, and other chemicals, which also release fumes in areas where recycling is not regulated properly.

The air pollution caused by e-waste impacts environment. Over time, air pollution can hurt water quality, soil and plant species, creating irreversible damage in ecosystems.

The Negative Effects on Soil and water:

When improper disposal of e-waste in regular landfills or in places where it is dumped illegally, heavy metals such as mercury, lithium, lead, and barium and flame retardants can seep directly from the e-waste into the soil, causing contamination of soil and 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.

When large particles are released from burning, shredding or dismantling e-waste, they quickly re-deposit to the ground and contaminate the soil and water as well. The amount of soil contaminated depends on a range of factors including temperature, soil type, pH levels and soil composition.

Through these pathways, acidification and toxification are created in the soil and water, which is unsafe for animals, plants and human beings.

Brominated flame retardants:

Brominated flame retardants (BFRs) have routinely been added to consumer products for several decades in a successful effort to reduce fire-related injury and property damage. The widespread production and use of BFRs strong evidence of increasing contamination of the environment, wildlife, and people; and limited knowledge of potential effects heighten the importance of identifying emerging issues associated with the use of BFRs.

These do not decompose easily in the environment, and long term exposure can cause impaired memory function and learning. Pregnant women exposed to brominated flame retardants have been shown to give birth to babies with behavioural problems as it interferes with oestrogen and thyroid functioning.

As mentioned, 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.

Lead: Lead is a naturally-occurring element that can be harmful to humans when ingested or inhaled, particularly to children under the age of six. Lead found in most computer monitors and televisions, lead exposure leads to intellectual impairment in children and serious damages to human reproductive systems, the nervous system and blood. Lead poisoning can cause a number of adverse human health effects, but is particularly detrimental to the neurological development of children.

Cadmium: The kidney is the critical target organ for the general population as well as for occupationally exposed populations. Cadmium is known to accumulate in the human kidney for a relatively long time, from 20 to 30 years, and, at high doses, is also known to produce health effects on the respiratory system and has been associated with bone disease. Found in rechargeable batteries for laptop computer and other electronic devices, can cause damage to kidneys and bones.

Mercury: Elemental and methyl mercury are toxic to the central and peripheral nervous systems. The inhalation of mercury vapour can produce harmful effects on the nervous, digestive and immune systems, lungs and kidneys, and may be fatal. The inorganic salts of mercury are corrosive to the skin, eyes and gastrointestinal tract, and may induce kidney toxicity if ingested.

Neurological and behavioural disorders may be observed after inhalation, ingestion or dermal exposure of different mercury compounds. Symptoms include tremors, insomnia, memory loss, neuromuscular effects, headaches and cognitive and motor dysfunction. Kidney effects have been reported, ranging from increased protein in the urine to kidney failure. Mercury (Hg), which is used in lightening devices in flat screen monitors and televisions can cause damage to the breast milk.

Plastic compounds: Poly vinyl chloride (PVC) cabling is used for printed circuit boards, connectors, plastic covers and cables. When burnt or land-filled, these PVCs release dioxins that have harmful effects on human reproductive and immune systems.

Disposal methods

Land filling: This is the most common methodology of e-waste disposal. Soil is excavated and trenchers are making for burying the e-waste in it. However, landfill is not an environmentally sound process for disposing off the e-waste as toxic substances like Cd, Pb and Hg are released inside the soil and ground water.

Incineration: This is a controlled way of disposing off the e-waste and it involves combustion of electronic waste at high temperature in specially designed incinerators. This e-waste disposal method is quite advantageous as the waste volume is reduced extremely and energy obtained is also utilized separately. However it is also not free from disadvantages with the emission of the harmful gases, mercury and cadmium in the environment.

Reuse: Reuse of electronic equipment has first priority on the management of e-waste because the usable lifespan of equipment is extended to secondary market, resulting in a reduced volume of waste stream encompassing treatment.

Re-manufacturing: It is a process in which used products are disassembled, cleaned, repair or refurbished, reassembled and qualified for new or like - new equipment.

Recycle: Recycling of e-waste can be broadly divided into three major steps.

- Dis-assembly • Upgrading
- Refining

Advantages of Recycling E-Waste

The top 5 benefits of recycling e-waste include the following:

- Reduces Landfill Sites
- Preserves Natural Resources
- Prevents Toxic Chemicals from Polluting the Ecosystem
- Creates New Business & Employment Opportunities
- Promotes Mindful Consumerism.

Extraction of Gold and Copper from PCB's (e-waste)

E-waste contains 10 times more excessive concentration of gold compared to ores. Concentration of copper in PCB is 20-40 times more than that is present in the ore. Hence, e-waste can act as a vital source of precious metal and can satisfy their demand in various industries.

There are three stages in metal recovery by hydrothermal method

- 1) Pretreatment stage
- 2) Chemical treatment stage
- 3) Metal recovery stage

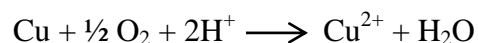
Pretreatment stage

In the pretreatment stage, e-waste is manually dismantled to separate various fractions like metals, ceramics, plastics, wood and paper. Techniques such as gravity separation, electrostatic separation, Magnetic separation and eddy current separations are used to separate metals from other fractions.

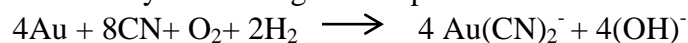
Chemical treatment stage

In the chemical treatment step, targeted metals are leached into solution by treating with appropriate chemical reagents.

Acid leaching is the most common method used to extract copper. H_2SO_4 / HNO_3 in the presence of oxidizing agent H_2O_2 is used in the process.



Cyanide leaching is the most common method used for to extract gold metal. Sodium salt of 3-nitrobenzene sulfonic acid with Potassium cyanide (KCN) in the presence of oxygen is used as leaching agent. A water-soluble dicyanoaurate gold complex is obtained in this process.



Metal recovery stage

In this step, metal is recovered from leach solutions. Copper metal can be recovered by electrodeposition. Pure copper metal taken as cathode and inert anode are dipped in leaching solution. When current is applied, copper is electrodeposited on cathode.

Gold can also be extracted from leaching solution by electrodeposition of gold from dicyanoaurate gold complex. Pure gold metal is taken as cathode and inert metal like stainless taken as anode. Both are dipped in leaching solution containing gold cyanide complex. Under approximate electroplating conditions, gold from the leached solution is electrodeposited on cathode.