MODULE 4

CHEMISTRY OF E-WASTE & ITS MANAGEMENT

Syllabus: E-Waste: Introduction, sources of e-waste, Composition, Characteristics, and Need of e-waste management. Toxic materials used in manufacturing electronic and electrical products, health hazards due to exposure to e-waste. Recycling and Recovery: Different approaches of recycling (separation, thermal treatments, hydrometallurgical extraction, pyro metallurgical methods, direct recycling). Extraction of gold from E-waste. Role of stake holders in environmental management of e-waste (producers, consumers, recyclers and statutory bodies).

Self-learning: Impact of heavy metals on environment and human health.

INTRODUCTION

Today's Electronic Gadgets, Tomorrow's E- Waste! In the new world of materials, usage of electrical and electronic items has been increasing rapidly year by year. These materials have lesser life span and also used for lesser duration due to fast change in features and the capabilities. Cumulative result of increased manufacturing, usage and discarding is rapid increase the amount of end-of- life electronics and electrical items. All electronic and electrical items which are discarded on completion of their useful life together is called as e-waste. There is rapid growth in e-waste generation since 1990s and will continue at faster rate in future.

What is E-Waste?

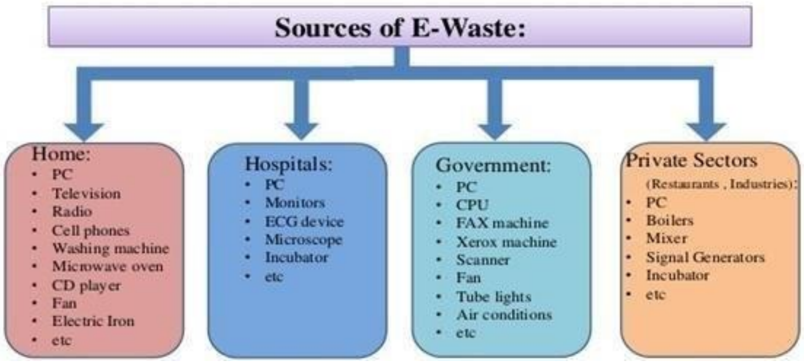
- Electronic Waste or E-Waste describes rejected electrical or electronic devices. All items of electrical and electronic equipment and its parts that have been discarded by the user as waste without the purpose of re-use or re-cycle is called Electronic Waste.

OR

- **Unwanted, discarded electrical and electronic devices which pollutes the environment and hazardous to human beings, plants and animals.**

SOURCES OF E-WASTE

- Computer peripherals: Monitor, key board, mouse, mother board, lap tops, CDs
- Telecommunication devices: phones, cell phones, routers, pagers, fax machine etc.
- Household appliances: TV, fridge, washing machine, video players, ovens etc.
- Industrial electronics: Sensors, medical devices, automobile devices etc.
- Electrical devices: switches, wires, bulbs etc.

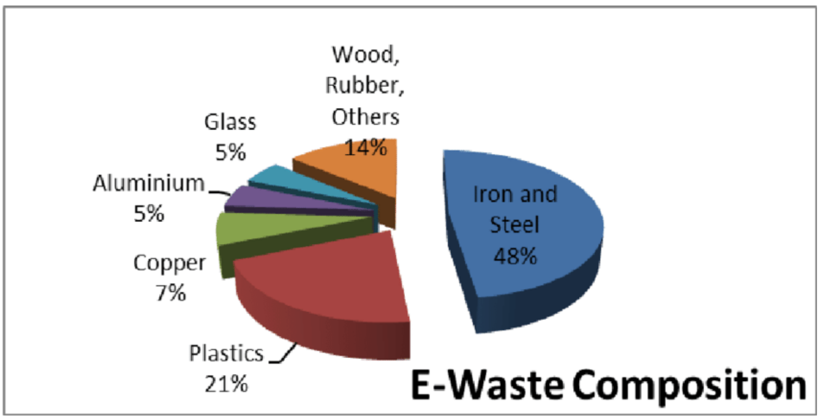


CAUSES OF E-WASTE

- Population - Due to the increase in population the use of electronic gadgets have also increased thus leading to generation of E-waste.
- Development - It is estimated that there are over a billion personal computers in the world. In developed countries these have an average lifespan of only 2 years. Due to development in technology the increase in the generation of E-waste has also increased.
- Falling prices of electronic items - As the new products come, old products are cheaper and the buying of the product increases.
- Advancement in Technology.
- Changes in style fashion and status.
- Not taking precautions while handling them.

COMPOSITION OF E-WASTE

- E-waste is characterized by more than 1000 hazardous and non-hazardous materials.
- E-waste contains about 65 % of iron, steel and other metallic materials including costly metals like platinum, gold, silver and toxic metals like lead, mercury, cadmium, chromium etc.
- E-waste contains about 21 % of polymeric non-biodegradable materials including Poly vinyl chlorides (PVCs), polychlorinated biphenyls, and brominated flame retardant plastics.
- E-waste also contains about 11.8% of CRT and LCD screens and other materials like glass, wood, plywood, and ceramics.



TOXIC MATERIALS USED IN MANUFACTURING ELECTRONIC AND ELECTRICAL PRODUCTS

Most electrical and electronic devices today are made with a variety of metals and chemicals. When this goes to the landfill – either domestically or abroad – the toxic chemicals that are inside of most of our electronics leach out into the environment, poisoning water and affecting animals, plants, and people. Some of the toxins found in electronic devices are given below:

- **Lead -** Almost all electronic devices contain lead, with old cathode ray tube (CRT) monitors and televisions weighing in at an average 4-5 lbs of lead each, and with smaller devices containing traces of lead from soldering. Collectively, some 58,000 tons of lead emissions are released from e-waste recycling every year.
- **Polybrominated Diphenyl Ethers (PBDEs) -** Most plastics used in electronics such as TVs and large appliances contain a variety of flame retardant chemicals, collectively known as PBDEs. These chemicals prevent devices from over-heating, and are found in laptops and computers as well. Electronics before 2000 are likely to have higher levels of PBDEs than more current electronics. Most PBDEs in a device are released during the dismantling process, with emissions also produced from crushing and sorting of plastics in the recycling process. PBDEs lack chemical bonds between them and the plastics they are applied to, so they are more likely to leach from surfaces during recycling.
- **Cadmium -** The greatest consumption of refined cadmium is for the production of nickel-cadmium batteries, which accounted for 81% of total refined cadmium globally in 2004. Burning or dismantling of cadmium products such as batteries, PCBs, CRT glass, toners, plastics, and infrared detectors can lead to cadmium dust or ash in the air.
- **Mercury -** Mercury can be found in fluorescent tubes, switches in thermostats, older computers, batteries, and more. When electronic waste containing mercury is sent to landfill sites or is burned in incinerators or open burning, mercury is released into the environment. 13.6 tons of mercury are released as emissions during e-waste recycling every year. Some electrical and electronic equipment that has no substitute for mercury, such as fluorescent lamps, will lead to an increase of mercury in obsolete electronics for the near future. Mercury used in electronics annually accounts for approximately 22 percent of all the world’s mercury consumption.
- **Chromium -** Chromium can be found in data tapes, floppy discs, and is used for coating and plating in many electronics to prevent rust. 198,000 tons of Chromium are produced as emissions from global processing of e-waste annually. Two different types of Chromium are used in electronics; Chromium (III) and Chromium (VI) are used in chrome plating, and Chromium (VI) is used as coating to prevent corrosion.

HEALTH HAZARDS DUE TO EXPOSURE TO E-WASTE

- Exposure to lead can occur through air, dust, water, and soil. Exposure to lead can affect almost every organ and system in the human body, damaging the nervous system, causing weakness in extremities, and increases in blood pressure or anemia. At higher levels, lead can cause brain and kidney damage, miscarriages in pregnant women, lower sperm production in men, and can ultimately cause death. Children are more vulnerable to lead poisoning than adults, and persistent exposure can lead to smaller babies and decreased mental capacities. Long-term exposure to lead dust can lead to anemia, kidney damage, high blood pressure, nerve and brain damage, miscarriage, and birth defects.
- PBDEs do not dissolve easily in water, but stick to particles and settle to the bottom of rivers and lakes. They are also known to bio accumulate in fish, meat, and dairy products. PBDEs in high levels have been measured in the atmosphere, sediment, water and soil. High exposure can lead to abnormal changes in thyroid hormones and the functioning of the kidneys.
- Cadmium products that end up in landfills lead to acid leachate that can seep into groundwater. Fish, plants, and animals can take up cadmium from the environment. Breathing high levels of cadmium can severely damage lungs. Eating food or drinking water with high levels can irritate the stomach and lead to vomiting and diarrhea. Long-term exposure to lower levels can lead to buildup in the kidneys and lead to kidney disease. Lung damage and fragile bones are other long-term effects. Cadmium has also been associated with deficits in cognition, learning and neuromotor skills in children. Cadmium is a known human carcinogen, and is in most cases toxic to plants as well.
- Mercury exposure can lead to long-term damage to information processing, and psychomotor functioning, as well as increased depression and anxiety. Children have been shown to be particularly sensitive to mercury vapors, and newborns and infants can be at greater risk if they live near informal recycling industries Long-term exposure can lead to nerve and brain damage and birth defects. Mercury can also cause environmental problems, as it is known to bio magnify in aquatic food webs. Mercury uptake by fish can lead to a range of blood and behavioral abnormalities and can cause death.
- Chromium (III) is an essential element, helping the body use macronutrients. However, excessive intake can still lead to damage in the body. Chromium (VI) compounds are well-established environmental contaminants and are human respiratory carcinogens. High levels of Chromium exposure can lead to impaired motor function and irritation to linings of the nose and stomach, and some lab tests on animals suggest it can damage the male reproductive system and sperm.

NEED OF E-WASTE MANAGEMENT

- Discarded electronic devices can be kept out of the landfill if they are refurbished, reused and donated to a worthy cause.

- Recycling this material will save landfill space.
- Reclaiming valuable materials from the recycling process.
- Decreased demand for new raw materials.
- Using recycled material will also help reduce greenhouse gas emissions produced when manufacturing or processing new product known as “virgin material.”

RECYCLING AND RECOVERY OF E-WASTE

In E-waste, among various constituents, metals contribute to the significant economic value, and the efforts are focused on extracting those metals during recycling operations.

Recovery and Recycling Technologies

The recycling of E-waste is initiated with physical or mechanical pre-processes. First step is pre-treatment step. This involves physical removal of toxic materials and unwanted components and then manual dismantling and separation of components such as PCBs, monitors, batteries, etc. into various fractions like metals, ceramics, plastics, wood, and paper using hammers, screwdrivers, and conveyer beds for disassembling. The next step is the shredding of the materials mechanically through crushers and grinders to collect fragments of metal bearing components. Then the waste is passed through electrical separators to separate the metallic and non-metallic components and Magnetic separator is used to separate ferrous metals. Gravity separation is used to separate Al metal. Finally, after physical separation, various chemical techniques are employed to recover metals, Metals can be recycled any number of times and it contributes to conservation of the natural resources. And also recovery of metals from E-waste is more economical than extraction from their ores. E-waste contains 10 times more excessive concentration of gold compared to gold ores. It approximately contains 10-10,000 g of gold/ton, whereas the gold ore contains barely 0.5-13.5 g of gold/ton. Concentration of Copper in PCB is 20-40 times more than that is present in its ore.

Most widely used techniques for metal recovery are:

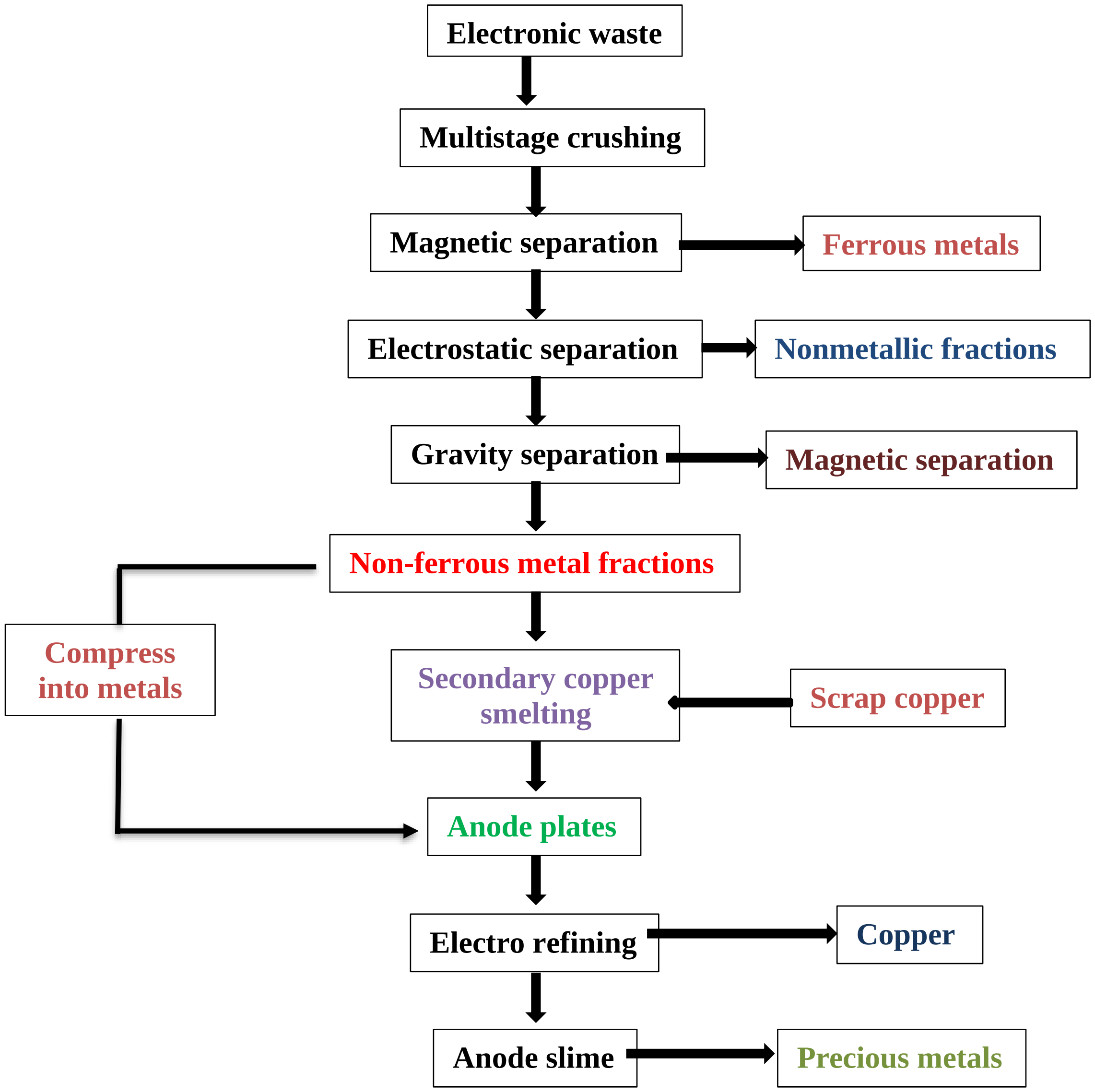
1) Pyrometallurgical process. 2) Hydrometallurgical process.

1. PYROMETALLURGICAL PROCESS

Pyrometallurgy technology is used to extract pure non-ferrous and precious metals from e-waste. The methods require elevated temperatures to reduce/extract metals, and therefore require high amount of energy input. Smelting, combustion, pyrolysis, and molten salt processes are the main pyrometallurgical methods employed for recovery of metals from E -waste. These methods are briefly given below:

a) Smelting

Copper smelting is commonly used for recovery of non-ferrous metal fractions from e- waste. The processed scrap after preliminary stage contains mainly iron (Fe). Aluminum (Al), copper (Cu), lead (Pb), tin (Sn), antimony (Sb), zinc (Zn), and precious metals as metallic constituents. This mixture is fed into copper smelters. During smelting, Pb, Sn. Sb, and precious metals are collected in the copper parent phase. This is casted in to anode slab and refined by electrometallurgy. Here, the anode is dissolved and pure (99.99 %) copper is deposited over cathode leaving a slurry residue. This slurry residue is called anodic slime and contains undissolved metallic fractions. It is rich in valuable metals like Au, Pt, lead, tin, and antimony. These metals are recovered from slurry with high recovery rates, of over 90% using hydrometallurgical techniques.



b) Combustion of e-waste

Combustion is a low-technology, low cost, straight forward operation focusing only on the recovery of valuable metals. Here, E-waste is subjected to open burning in uncontrolled manner which releases all sorts of pollutants in to atmosphere. Hence, this method is highly dangerous for the environment and also increases the health risk of the workers.

c) Incineration of e-waste

Incineration is a controlled combustion of the waste with suitable emission units. The incinerator has two connected furnaces. In the first furnace, e-waste is burnt at temperatures above 800°C and in the second stage for the gaseous products of the first incinerator are further oxidized above 1100°C. Heavy metals are collected in the bottom and fly ash. Hydro metallurgical processes are used for further recovery of metals. Both these methods are not advisable, due to pollutant gas emission and low metal recycling performance.

d) Pyrolysis of e-waste

Pyrolysis is a thermal decomposition of e-waste at higher temperatures in an oxygen-free environment. During pyrolysis, irreversible thermal decomposition reactions take place, leading to the formation of low-molecular products (gases and liquids) at temperatures between 450 and 1100°C. Pyrolysis gases, oils, and char have an economical value and can be used as fuel and chemical feedstock. The metallic components can be recovered easily by separation. Main danger with this process is release of toxic halogens into atmosphere with few gases.

e) Molten salt process

In this process, the e-waste is fed in with the salt, and salt is melted at the desired temperature under an inert atmosphere environment. The organic parts decompose in the molten salt forming carbonates and silicates and are trapped in molten salt. Halogens also react with the molten salt and are converted to alkali metal halides, which remain in the molten salt. Therefore, the flue gas contains a high content of He(g) that can be stored as a fuel. The metallic component is liberated by removing the organics, and is collected on the bottom of the furnace. After removing molten salt, mixture containing valuable metals is further treated to obtain pure metals. Various Molten mixtures of inorganic salts, such as sodium sulfate (NaSO1)-sodium carbonate (NaCO3) mixture, potassium hydroxide (KOH)-sodium hydroxide (NaOH) eutectic mixture, are used at different temperatures between 300 and 1100°C depending on the requirement

2. HYDROMETALLURGICAL PROCESS

Traditional hydrometallurgical process which have been used from so many years for metal extraction from mineral ores are used for the recovery of metals from E-waste.

There are three stages in metal recovery by hydrothermal method:

a) Pre-treatment stage.
b) Chemical treatment stage.
c) Metal recovery stage.

a) Pre-treatment stage

Pre-treatment stage involves physical separation of metal components from e-waste as discussed above followed by smelting of the mixture in some cases. In hydrometallurgical process, main steps are chemical treatment and metal recovery steps. In chemical treatment stage, the metals are made to leach into solutions using different leaching reagents. In the metal recovery stage, metals are recovered from the leached solutions using through electro-refining, precipitation, cementation, adsorption, solvent extraction, and ion exchange methods. These techniques are briefly given below:

b) Chemical treatment stage

i) Cyanide Leaching

Even though, cyanide solutions are toxic, they are mainly used to leach gold metal, Alkali cyanide like KCN with 3-nitrobenzene sulfonic acid sodium salts are used to dissolve gold under aerated condition. Further, the same solution can be subjected to electroplating to obtain pure gold metal. Copper also readily dissolves in cyanide solutions.

ii) Acid and Alkaline Leaching

Nitric acids, sulfuric acids, and hydrochloric acids are the prominent mineral acids used for leaching of targeted metals. A few organic acids such as ascorbic acids, citric acids, and acetic acids are also used to leach light metals from spent batteries and mobile devices. Li is leached from Lithium ion battery waste by treatment with citric acids and hydrogen peroxide as reducing agent.

iii) Thiosulphate Leaching

Thiosulphate is used an alternative leaching agent to cyanide leaching agent for the recovery of precious metals like gold and silver. Solubilizing effect of thiosulfate reagent is better and its interference with the other cationic species is also very less. Ammonium thiosulfate solution is used to solubilize gold, silver, platinum, and other precious metals in the form of anionic stable complexes for a wide range of pH. This reagent is safe, non-toxic, non-corrosive and metal can be recovered readily from the complex.

iv) Thiourea Leaching

Thiourea is a sulfur-based organic complexing agent, that forms a cationic soluble complex with the target metal. Thiourea gives quick rates of leaching, less interference of ions, is environmentally friendly, and has a low cost. The leaching rates are up to 99% for this complex. Thiourea is not stable and decomposes easily in alkaline environment, hence the reaction requires an acidic media. In printed circuit boards, the gold and silver selectively forms a metal-thiourea cationic complex.

v) Halide Leaching

Chloride, bromide, and iodide ions can be used to leach gold from the PCB waste. They are employed as a replacement for cyanide leaching agents. They exhibit in high solubility, improved redox potentials, and high rates of leaching. They are cheaper, selective to the target, and ideal leaching agents.

c) Metal recovery stage

In this stage, pure metal is recovered from leached metal solution. A variety of methods such as solvent extraction, ion exchange, adsorption, precipitation, and cementation are available. Method employed depends upon the nature of leached solution. In majority cases, metal can be recovered selectively.

a) Solvent extraction

In this method, leaching solution is treated with an organic solvent in a separating funnel. It results in two phase system. Metal is extracted from leached solution phase to organic phase. Different extractants such as anionic, cationic, or solvating-type are employed. The anionic type like amides or amines are used for the extraction of vanadium, gold, indium, and sometimes rhodium and tungsten. Methyl-iso-butyl ketone is used as an extractant for gold. Amide extractant is used for chloride leached iridium found in electronic waste. Diamine extracts are used for platinum and palladium.

b) Electrodeposition

In this technique, pure metal is obtained from leached solution by electrodeposition. Pure metal same as metal to be extracted is taken as cathode and inert metal is used as anode. They are dipped in leaching solution. When current is applied, pure metal is electrodeposited on cathode. Electrodeposition techniques have the advantages of high efficiency, less use of auxiliary materials, low environmental impact, and cost-effectiveness. Lead, tin, and copper from PCs can be recovered by leaching followed by electrodeposition. With appropriate planning, both leaching step and recovery step can be clubbed together. For example, Copper can be leached from PCBs with simultaneous cathode electrodeposition from the leaching solution with 99.95 % efficiency leaving the residue rich in gold metal.

c) Ion Exchange

This is an improved version of solvent extraction method. Here, solvent extracting reagents are impregnated on polymer beads. The functional group of reagents act as chelating group and selectively bind to metal ions. Thus, they can be used for selective recovery of the desired metal ion. Some advantages of using ion exchange resins for recovery of metals are their ease to use, no loss of reagent, no separation of phases, low cost, use in low concentrations of metal ions and environmental safety.

This method was first used for uranium recovery. However, with the development of new chelating and impregnated ion exchange resins, their use became widespread. It is used for recovery of palladium group metals in hydrochloric acid. In aqueous solutions, the cation exchange resin KB-2 and the anion exchange resin AN-108, synthesized with long-chain cross-linking agents can completely remove Mn(II) and Cr(VI) respectively. Ion exchange resins have found to be effective in recovering gold from cyanide and thiosulfate leach solutions.

d) Adsorption

Metals can be recovered from leached solutions by adsorption on appropriate adsorbents. Activated carbon is found to be effective adsorbent. The adsorption of gold on activated carbon from cyanide solutions is an efficient, cost-effective process. It is commercially called as carbon-in-leach (CIL) technology. Adsorption of gold-thiourea complex on activated carbon is also effective. Freundlich and Langmuir isotherms are used for modelling of adsorption of single-component metal systems. Pt, Au, Ag, and Cu metals were removed from their cyanide solutions with 95 - 100 % efficiency. Thus, using appropriate combination of pyro metallurgical and hydrometallurgical techniques metals can be extracted economically from e-waste. This will not only prevent leaching of metals into ecosystem, it will also contribute to environment sustainability.

EXTRACTION OF GOLD FROM E-WASTE.

Gold metal has good electric conductivity and chemical stability, and hence it is used for making integrated circuits of electronic devices, coating for contacts and connectors. Electronic industry uses over 300 tons of gold each year. E-waste contains 10 times more excessive concentration of gold compared to gold ores. It approximately contains 10-10,000 g of gold/ton, whereas the gold ore contains barely 0.5-13.5 g of gold/ton. Usage of electronic gadgets is increasing day by day and their life span is very short. Hence, there is a rapid surge in e-waste generation. Presently, more than 50 million metric tons of e-waste is generated globally every year out of which only 17 % is processed to recover precious metals. Hence, e-waste can act as a vital source of precious metals and can satisfy their demand in various industries. Among the e-waste, PCBs are rich in metals. It contains around 35% Cu, 0.16% silver, and 0.13% gold, by weight. Several techniques such as pyrometallurgy, hydrometallurgy, biometallurgy, microwave treatment, and plasma technology are employed to recover precious metals from e-waste. Among these, recovery of metals using hydrometallurgical route is more economical.

The hydrometallurgical method

There are three stages in metal recovery by hydrothermal method:

(1) Pre-treatment stage.

(2) Chemical treatment stage.

(3) Metal recovery stage.

Pre-treatment stage

In the pre-treatment step, 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 separation are used to separate metals from other fractions.

Chemical treatment stage

In the chemical treatment step, targeted metals are leached in to solution by treating with appropriate chemical reagents. Several leaching agents such as thiosulfate, alkali cyanide, and many acids such as hydrochloric acid, sulfuric acid, and nitric acid can be used to leach gold in to solutions. Cyanide leaching is the most common method used to extract gold metal. Sodium salt of 3-nitrobenzene sulfonic acid with Potassium cyanide (KN) in the presence of oxygen is used as leaching agent. A water-soluble dicyanoaurate gold complex is obtained in the process.

Metal recovery stage

In the last step, metal is recovered from leach solutions. Varieties of methods like electro-deposition, solvent extraction, ion exchange, adsorption, precipitation, and cementation are used to recover metals from leached solutions. Selective recovery is possible for most processes.

Gold can also be extracted from leaching solution by electrodeposition of gold from dicyanoaurate gold complex. Pure gold metal taken as cathode and inert anode are dipped in leached solution. When current is applied, gold is electrodeposited on cathode.

DIRECT RECYCLING OF E-WASTE

In the previous sections, various methods available for scientific processing of e-waste to recover useful chemical components from it were discussed. These techniques are used to prevent disposal of e-waste by means of dumping or landfilling. Because, this results in waste of valuable materials and can also cause environmental problem due to contamination by heavy metals. But, all those processes require lot of energy and money. Another cost effective method for recycling of e-waste is by direct recycling.

Direct Recycling means harvesting electronic components directly from e-waste without breaking them further into small components. Harvested materials are further processed with healing methods to regenerate recycled materials. The regenerated materials have performance equivalent to originally manufactured materials. Thus, in this method, all the complicated chemical and metallurgical steps involved in conversion of e-waste components into original chemicals are avoided. Recycling loop is shortened. Hence, it requires less amounts of energy and reagents and hence it is then most environmentally friendly method. However, there are few problems associated with direct recycling method. Direct regeneration of components depends on state-of- health of used electronic materials. Defects and impurities accumulated during usage could affect the quality of the refurbished active material. And also direct recycling may not restore the initial properties of pristine active materials.

Presently, direct recycling of lithium ion batteries is studied extensively. Here, the battery is discharged first to avoid short circuiting and self-ignition of battery and dismantled to separate anode, cathode, electrolyte and separated. These components are not dismantled further, but each component is regenerated by appropriate process to recover its function. These components are reassembled for reuse.

ROLE OF STAKE HOLDERS IN ENVIRONMENTAL MANAGEMENT OF E-WASTE (PRODUCERS, CONSUMERS. RECYCLERS, AND STATUTORY BODIES).

Basically there are four stakeholders in environmental management of the e-waste.

They are:

1. Statutory Government Regulatory bodies
2. Producers (Manufacturing units)
3. Recyclers (Recycling units and Collection units)
4. Consumers

The E-waste management program is designed by statutory Government regulatory bodies. The members of the body frame the policies and execute it for protection of environment. To achieve the plan of management of e-waste a green tax is collected from /consumer through manufacturer. Penalties are implied on manufacturer and consumers when green tax is not paid. Manufacturing units must support the agenda of e-waste management by doing dismantling, processing of e-wastes, management of /scrap materials and reselling of recycled materials. The presence of collection units for door to door collection of e-waste. Consumer must pay green tax and be aware of importance of e-waste management. All four stake holders must work in tandem form effective e-waste management.

1. Statutory Government Regulatory bodies

The statutory bodies play a pivotal role in management of e-waste. Main roles of statutory bodies are:

a) To collect the green tax from consumer though producer.

b) Apply some extra charges on the producers (manufacturing units) in the form of penalty when no proper recycling of e-waste is assured from manufacturing units.

c) Provide the incentives in the form of subsidy to recyclers and collectors when recycling of e-waste is monitored properly.

d) To conduct the programs of awareness in the society about importance of e-waste recycling in reduction of hazardous substances.

2. Producers (Manufacturing units)

The main roles of producers in management of e-waste are:

a) The accountability to collect green tax.

b) Charging an additional amount on consumer during sell of e-products and returning it with interest at the time of exchange of e-product.

c) Forming the group of manufactures who monitor and encourage the recycling of e-waste.

d) Bearing the transportation cost and collection fees to ease the collection process.

e) Purchase the recycled material at fixed value and using of recycled e-waste during manufacturing.

f) Giving discount to consumer on the basis of e-waste generated from gadget.

3. Recyclers (Recycling units and Collection units)

The main roles of recyclers in management of e-waste are:

a) The accountability of recycling units is dismantling, recycling processing of e-waste materials, management of scrap materials (like incineration) and reselling of recycled materials.

b) Establish the collection units and the group of people who can ensure return back of e-products by consumer in exchange offer or directly approach consumer for door to door collection.

c) Collect the e-waste from the collection units, dealer or retailer.

d) Providing incentives when proper collection of e-waste assured by collection units.

4. Consumer

The main roles of consumer in management of e-waste are:

a) The accountability to pay green taxes.

b) Develop self-awareness on e-waste management and involve in awareness programs.

c) Returning back of e-waste to collection units.