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This is to certify that project work entitled "**Recovery of metallic values from Electronic Waste**" is prepared & submitted by **Ameya Dixit (903). Ishaan Karode (906) and Radhen Zalavadia (926)** for the partial fulfillments for the degree of bachelor of engineering in Metallurgical & Materials Engineering of the Maharaja Sayajirao University of Baroda, Vadodara has been carried out by them in the Metallurgical & Materials Engineering, Faculty of Technology and Engineering, the Maharaja Sayajirao University of Baroda, Vadodara under our guidance of supervision. The matter presented in this research work has not been submitted of any other degree or diploma anywhere.

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Abstract

Electronic Waste is becoming a crisis for the society. The technological developments in the electric, electronic industries have resulted in increase in consumption with past generation, which leads to significant increase in amount of waste comprising electrical and electronic products. The major and essential components of almost all these products is Printed Circuit Boards (PCB) which contains various elements like, gold, silver, platinum and some valuable base metals like copper, aluminum, lead, tin etc. hence, the recovery of these elements would be beneficial to converse scarce resources, reuse, electronic/electric components and eliminate environmental problems.

The present work is focused on the selective leaching of valuable metals like lead, tin, copper from soldering materials present on the outer layer i.e epoxy resin of waste PCB. Here the Nitric acid and the Hydrochloric acid were used as the leached solutions. This leaching process was subsequently followed with electrolysis using the leached solutions. It was found that the Hydrochloric acid is suitable as a leachant to dissolve lead and tin while the Nitric acid apart from lead and tin could also dissolve significant amount of copper. As the current density was increased during electrolysis tem out of copper deposition in nitric acid solution was increased.

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ABBREVIATIONS

CFCs	Chloroflurocarbons
CRT	Cathode ray tubes
EU	European union
GWP	Global warming potential
HCFCs	Hydrochlorofluorocarbon
UNEP	United nations environment programme
WEEE	Waste electrical and electronic equipment
PCB	Printed circuit boards
PM	Precious metals
BM	Base metals
UNU	United nations university
MCs	Metals of concern
SEs	Scarce metals
PGMs	Platinum group metals

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Chapter 1: Introduction

Chapter 1: Introduction

Advances in the field of science and Technology brought about industrial revolution in the 18th century which marked a new era in human civilization. In the 20th Century, the information and communication revolution has brought enormous changes in the way we organize our lives, our economies, industries and institutions. These spectacular developments in modern times have undoubtedly enhanced the quality of our lives. at the same time, these have led to manifold problems including the problem of massive amount of hazardous waste and other wastes generated form electric product.

Generation of huge amount of waste electrical and electronic equipments (WEEEs) is taking place globally, especially in industrialized countries such as USA, Europe, Korea, India, Greece, China, etc. (Jha et al., 2011) due to the rapid economical growth coupled with the swift change of technological advancement in the field of electrical and electronic equipments.

Printed circuit boards (PCBs) are employed in most of the electronic equipments to mechanically support and electrically connect electronic components using conductive pathways. The solder material containing lead and tin is employed to connect different electronic components on the surface of PCBs. Apart from the solder materials, PCBs contain several metals of interest like Au, Ag, Pt, etc. and some valuable base metals like Cu, Al, Fe, etc. and other materials viz. PVC plastics, heavy metals and brominated flame retardants (BFR). Average metallic analysis of a personal computer's PCB was found to contain 20.13% Cu, 3.59% Al, 2.78% Zn, 2.10% Pb, 3.27% Sn, 7.19% Fe and 0.66% Ni (Jha et al., 2010).

These metals are not harmful in solid form but when they come in contact with different liquid waste/sewage, hazardous solution is generated which seeps into the soil resulting in the contamination of water, plants as well as affect the human organs causing hormonal/genetic disorders. Therefore, the recovery/recycling of metals, particularly lead, from PCBs is essential to avoid the environmental pollution.

The traditional pyrometallurgical process of recyclingincludes different treatments at high temperature: incineration, meltingetc. (Choubey et al.,

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2010) and is also highly dependent on investmentand generates atmospheric pollution due to evolution of toxic dioxins,furan gasses and carcinogenic compounds (Kumari et al., 2010). However,metal recovery (or recycling) through hydrometallurgical technique isachieving significance as it is cost effective and affable to the environmentin comparison to other available recycling processes.

In the present work, leaching of PCB were carried out using conc. Nitric and Hydrochloric Acid, to recycle various Solder materials and some valuable Base metals. After leaching it has been subjected to electrolysis process, using the leached solutions containing various solder materials and some base materials. During electrolysis with conc. Nitric acid leached solutions, current density has been increased to study the effects on recovery of valuable metals at cathode. it was found that at higher current density more amount of copper will get deposited on cathode. The result of this research show that, the lead and tin is easily separated during leaching of Hydrochloric acid while, leaching with Nitric acid, apart from lead and tin some amount of copper also gets liberated from PCB.

Chapter 2:

Literature Review

Chapter 2: Literature Review

2.1) DEFINITION OF E-WASTE

There is no standard definition for WEEE or e-waste. E-waste or WEEE embraces various forms of EEE that have no value to their owners. The reported definitions of e-waste in literature are described here:

- ### European WEEE Directive

"Electrical or electronic equipment which is waste … including all components, sub-assemblies and consumables, which are part of the product at the time of discarding."

- ### Basel Action Network

"E-waste encompasses a broad and growing range of electronic devices ranging from large household devices such as refrigerators, air conditioners, cell phones, personal stereos, and consumers electronics to computers which have been discarded by their users.

The useful life of electrical and electronic equipment (EEE) has been shortened as a consequence of the advancement in technology and change in consumer patterns.

Every day the innovations in the field of electronics and computers cause the technology that was supposedly new just a week or a month ago to become obsolete. This leads to increase in the consumerism of techno-savvy and non-techno savvy consumers as well.

Electronic waste and the minimal regulations involving recycling have developed into aglobal problem. Discarded and unwanted electronics are finding their way into landfills andexported to third-world countries which use primitive recycling methods that have an impactonthe surroundings.

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These waste components are responsible for hazardous pollution of the Environment and affect the health of the population.

This has resulted in the generation of large quantities of electronic waste (e-waste) that needs to be managed. The handling of e waste including combustion in incinerators, disposing in landfill or exporting overseas is no longer permitted due to environmental pollution and global legislations.

Additionally, the presence of precious metals (PMs) makes e-waste recycling attractive economically.

The aim and objective of this project is tofind out how the process of recycling the different metals found in electronic waste can be refined and more productive in order to reduce its hazardous effects on living beings as well as to get maximum resource efficiency out of the process.

Over the last decades the electronics industry has revolutionized the world: electrical and electronic products have become ubiquitous of today's life around the planet. Without these products, modern life would not be possible in (post-)industrialized and industrializing countries. These products serve in such areas as medicine, mobility, education, health, food-supply, communication, security, environmental protection and culture. Such appliances include many domestic devices like refrigerators, washing machines, mobile phones, personal computers, printers, toys and TVs.
The amount of appliances put on market every year is increasing both in (post-) industrialized and industrializing countries:
In the European Union (EU) the total weight of electronic appliances put on the market in 2005 ranged up to more than 9.3 million tons with a sensible growing rate, particularly in Eastern Europe. Electronic appliances put on the market included 44+ million large household appliances in EU15,
48 million desktops and laptops, Approximately 32 million TVs,
776 million lamps, In the United States of America (USA), in 2006, more than 34 million TVs and displays have been placed on the market, while more than 24 million PCs and roughly 139 million portable communication devices such as cell

phones, pagers or smart-phones have been manufactured. It has to be highlighted that in the last couple of years the highest growth rate has occurred in communication devices, less than 90 million were sold in 2003, whereas 152 million are expected to be sold in 2008, India had an installed base of about 5 million PCs in 2006, which is contributing to the 25% compounded annual growth rate in the Indian PC industry In China roughly 14 million PCs were sold in 2005, as well as more than 48 million TVs, nearly 20 million refrigerators and 7.5 million air conditioners in 2001, both growth rate and market penetration are increasing year by year,GSM Association estimates that 896 million mobile phone handsets were sold in 2006 worldwide Currently, the available data on e-waste arising is poor and insufficient and estimation techniques are required for extension of known data to regional-global coverage. United Nations University's estimations indicate that current e-waste arising across the twenty-seven members of the European Union amount to around 8.3 – 9.1 million tons per year; global arising are estimated to be around 40 million tons per year

Treatment processes of e-waste aim at either removing the hazardous items or at separation of as much as possible of the main recyclable materials (e.g. metals, glass and plastics), but achieving both objectives would be most desired. Although very limited information on e-waste treatment capacity in the EU Member States can be obtained, it is likely that the EU15 Member States should have had installed sufficient capacity to treat collected e-waste already by the middle of 2007. The situation in Central and Eastern Europe is likely to be different and it currently appears that a regional approach will be adopted. For example, Lithuania is planning to serve the Baltic States' needs and Hungary is expected to provide capacity for its neighboring countries, which will include Bulgaria and Romania.

Given the very limited data availability on amounts of e-waste collected and treated through "official" e-waste system channels, it is clear that the management of significant proportions of e-waste currently go unreported in Central and Eastern Europe. Moreover, the alarming and increasing reports on the e-waste situation in e.g. China, Nigeria, Pakistan and Ghana , in addition to the stocktaking of the situation in many more African and Latin American nations as part of the global "Solving the E-waste Problem (StEP)

Initiative", illustrate the urgent need to transfer and install appropriate and innovative technologies in the industrializing world.

2.2) Significance of e-waste recycling

E-waste is usually regarded as a waste problem, which can cause environmental damage if not dealt with in an appropriate way. However, the enormous resource impact of electrical and electronic equipment (EEE) is widely overlooked. Summarizing the lack of closing the loop for electronic and electrical devices leads not only to significant environmental problems but also to systematic depletion of the resource base in secondary materials.

Modern electronics can contain up to 60 different elements; many are valuable, some are hazardous and some are both. The most complex mix of substances is usually present in the printed wiring boards (PWBs). In its entity electrical and electronic equipment is a major consumer of many precious and special metals and therefore an important contributor to the world's demand for metals. Despite all legislative efforts to establish a circular flow economy in the developed countries/EU, the majority of valuable resources today are lost. Several causes can be identified: firstly, insufficient collection efforts; secondly, partly inappropriate recycling technologies; thirdly, and above all large and often illegal exports streams of e-waste into regions with no or inappropriate recycling infrastructures in place. Large emissions of hazardous substances are associated with this. Unfortunately, these regions with inappropriate recycling infrastructure are often located in developing and transition countries. At the moment the developing and transition countries are striving to implement technologies to deal with the recycling of e-waste and to establish circular flow economies.

Besides the direct impact of effective recycling on the resource base of the recycled metals, state of the art recycling operations 2 also considerably contribute to reducing greenhouse gas emissions. Primary production, i.e. mining, concentrating, smelting and refining, especially of precious and special metals has a significant carbon dioxide (Co2) impact due to the low concentration of these metals in the ores and often difficult mining conditions. "Mining" our old computers to recover the contained metals — if done in an environmentally sound or correct manner — needs only a fraction of energy compared to mining ores in nature.

a) Mobile phones: 1200 Million units x 250 mg Ag = 300 t Ag x 24 mg Au = 29 t Au x 9 mg Pd = 11 t Pd x 9 g CU =11,000 t cu 1200 M x 20 g/battery* x 3.8 g Co = 4500 t Co Li-Ion type	**b) PC &laptops:** 255 Million units x1000 mg Ag=255 tAg x 220 mg Au = 56 t Au x 80 mg Pd = 20 t Pd x = 500 g Cu = 128,000 t Cu =100 M laptop batteries* x 65 g Co = 6500 t Co Li-Ion type is > 90% used in modern laptops	**World Mine a + b Production share** Ag: 20,000 t/y = 3% Au: 2,500 t/y =3% Pd:230 t/y =13% Cu:16 **Mt/y= 1%**

Figure 2: Impact of phones and PCs on metals demand, based on global sales 2007

Table 1: Important metals used for electric and electronic equipment

Metal	Primary production (t/y)	By-product from	Demand for EEE (t/y)	Demand/ production %	Price (USD/kg)	Value In EEE (106 USD)	Main applications
Ag	20000	(Pb, Zn)	6000	30	430	2.6	Contacts, switches, solders...
Au	2500	(Cu)	300	12	22 280	6.7	Bonding wire, integrated circuits...
Pd	230	PGM	33	14	11 413	0.4	Multilayer capacitors, connectors
Pt	210	PGM	13	6	41 957	0.5	Hard disk, thermocouple, fuel cell
Ru	32	PGM	27	84	18 647	0.5	Hard disk, plasma displays
Cu	15000000		4500000	30	7	32.1	Cable, wire, connector...
Sn	275000		90000	33	15	1.3	Solders
Sb	130000		65000	50	6	0.4	Flame retardant, CRT glass
Co	58000	(Ni, Cu)	11000	19	62	0.7	Rechargeable batteries
Se	1400	Cu	240	17	72	0.02	Electro-optic, copier, solar cell
In	480	Zn, Pb	380	79	682	0.3	LCD glass, semiconductor
Total			**4670000**			**45.4**	

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Taking into account the highly dynamic growth rates of all the other electronic devices such as liquid crystal display (LCD)-TVs and monitors, MP3 players, electronic toys and digital cameras, it becomes clear that electrical and electronic equipment is a major driver for the development of demand and prices for a number of metals as shown in Table 1. In particular the booming demand for precious and special metals is linked to increasing functionality of the products and the specific metal properties needed to achieve these. For example, electronics make up for almost 80% of the world's demand of indium (transparent conductive layers in LCD glass), over 80% of ruthenium (magnetic properties in hard disks (HD)) and 50% of antimony (flame retardants).

Some of these metals are also important for renewable energy generation: selenium (Se), tellurium (Te) and indium (In) are used in thin film photovoltaic panels; platinum (Pt) and ruthenium (Ru) are used for proton exchange membrane (PEM) fuel cells. Some metal price increases, which we have observed over the last years are directly connected to the developments in the electronic industry. The monetary value of the annual use of important "electrical and electronic equipment metals" represents USD 45.4 billion at 2007 price levels.

The metal resources used yearly for electrical and electronic equipment are added to the existing metal resources in society of the devices in use. These metal resources become available again at final end-of-life of the devices. As mentioned earlier this is a potential material resource of 40 million tons each year. Effective recycling of the metals/materials is crucial to keep them available for the manufacture of new products, be it electronics, renewable energy applications or applications not invented yet. In this manner primary metal and energy resources can be conserved for future generations.

2.3 ENVIRONMENTAL ISSUE RELATED TO E-WASTE RECOVERY:

Primary production (mining) plays the most important role in thesupply of metals for electrical and electronic equipment applications since secondary metals (recycling) are only available in limited quantities so far. The environmental impact/footprintof the primary metal production is significant, especially for precious and special metals which are mined from ores in which the precious and special metal concentration is low.

Considerable amounts of land are used for mining, waste water and sulfur dioxide (So_2) is created and the energy consumption and Co_2 emissions are large. For example, to produce 1 ton of gold, palladium or platinum, Co_2 emissions of about 10,000 tons are generated. Conversely the production of copper has only an emission of 3.4 co_2 per ton metal.

Combining these numbers with the metal usage in electrical and electronic equipment (given in Table 1) enables calculation of the Co_2 emissions associated with the primary production of the metals as shown in the table 2.

For example, the annual demand for gold in EEE is some 300 t at average primary generation of almost 17,000 tons Co_2 per ton of gold mined, which leads to gold induced emissions of 5.1 million tons in total. In the case of copper, the specific primary emissions are 3.4 t/t which are relatively low, but the high annual total demand in EEE leads to 15.3 million tons of Co_2 emissions

As shown in table 2, the cumulated values of the metals listed account for an annual Co_2 emission level of 23.4 million tons, almost 1/1000 of the world's Co_2 emissions.

Important EEE Metals	Demand for EEE t/a (2006)	data for primary production [t CO_2/t]	Co2 emissions [Mt]
Copper	4 500 000	3.4	15.30
Cobalt	11 000	7.6	0.08
Tin	90 000	16.1	1.45
Indium	380	142	0.05
Silver	6 000	144	0.86
Gold	300	16 991	5.10
Palladium	32	9 380	0.30
Platinum	13	13 954	0.18
Ruthenium	6	13 954	0.08
Co_2 total W			23.4

Table 2: Co2emissions of primary metal production

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Recovering metals from state-of-the art recycling processes generates only a fraction of these Co2 emissions and also has significant benefits compared to mining in terms of land use and hazardous emissions . For example, production of 1 kg aluminum by recycling uses only 1/10 or less of the energy required for primary production, and prevents the creation of 1.3 kg of bauxite residue, 2 kg of Co2 emissions and 0.011 kg of So2 emissions as well as the impacts and emissions associated with the production of the alloying elements used in aluminum.

Furthermore, the salt slag created during the recycling process is treated to recover salt flux for the recycling industry, inert oxides for cement industry and aluminum metal . For precious metals the specific emissions saved by state-of-the-art recycling are even higher.

The substances contained in the devices can also have an impact on the environment. Cooling and freezing equipment for example, employ ozone depleting substances (ODS) in the refrigeration system. These substances, such as CFCs and HCFCs, have a huge global warming potential . It must be mentioned that particularly the older devices are those which contain ODS with a high global warming impact; the newer devices use alternative substances. As a consequence it is important to ensure accidental release to the atmosphere because of damages during collection or improper recycling treatment is not taking place. It is in this manner that high environmental impact during end-of-life can be avoided.

On a more local level, uncontrolled discarding or inappropriate waste management/recycling generates significant hazardous emissions, with severe impacts on health and environment. In this context, three levels of toxic emissions have to be distinguished:

Primary emissions: Hazardous substances that are contained in e-waste (e.g. leads,
mercury, arsenic, polychlorinated biphenyls (PCBs), fluorinated cooling fluids etc.),

Secondary emissions: Hazardous reaction products of e-waste substances as a result of improper treatment (e.g. dioxins or furans formed by incineration/inappropriate smelting of plastics with halogenated flame retardants),

Tertiary emissions: Hazardous substances or reagents that are used during recycling (e.g. cyanide or other leaching agents, mercury for gold amalgamation) and that are released because of inappropriate handling and treatment.

It needs to be understood that legislative approaches to restrict the use of hazardous substances (e.g. European Union's Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment ROHS [4]) can address only primary emissions and partly secondary emissions. However, even the 11 cleanest/greenest" products cannot prevent tertiary emissions if inappropriate recycling technologies are used. The latter is the biggest challenge in particular in developing and transition countries, where "backyard recycling" with open sky incineration, cyanide leaching, "cooking" of circuit boards etc. lead to dramatic effects on health and environment.

2.4Classification and Composition of E-Waste:

Generally, metals in e-waste can be grouped into PMs, platinum group metals (PGMs), BMs, metals of concern (MCs), and scarce elements (SEs),:

- PMs: Gold (Au), Silver (Ag);
- PGMs: Palladium (Pd), Platinum (Pt), Rhodium (Rh), Iridium (Ir) and Ruthenium (Ru);
- BMs: Copper (Cu), Aluminum (Al), Nickel (Ni), Tin (Sn), Zinc (Zn) and Iron (Fe);
- MCs(Hazardous): Mercury (Hg), Berylium (Be), Indium (In), Lead (Pb) , Cadmium (Cd), Arsenic (As) and Antimony (Sb);

- SEs: Tellerium (Te), Gallium (Ga), Selenium (Se), Tanatalum (Ta) and Germanium (Ge).

2.5 E-Waste Facts And Figures:

Trashed computers, TVs and other gadgets make up the fastest-growing municipal waste stream in the U.S., according to a report published by the Environmental Protection Agency in June 2011. As much as 80% of electronic waste goes out with the trash, the EPA estimates, while only about 20% is properly recycled.

It is reported that 80% of all Asian children have elevated levels of lead in their systems due to the unceremonious dumping of e-waste.

The Indian city of Bangalore produces some 20,000 tonnes of e-waste per year, the Association of Chamber of Commerce and Industry of India. This figure is rising at a rate of 20% per year.

300 million computers and 1 BILLION cell phones are put into production each year. This global mountain of waste is expected to continue growing 8% per year, indefinitely (BCC Research).

In A 2011 report, "Ghana E-Waste Country Assessment", found that of 215,000 tons of electronics imported to Ghana, 30% were brand new and 70% were used.

Of the used product, the study concluded that 15% was not reused and was scrapped or discarded. This contrasts with published but uncredited claims that 80% of the imports into Ghana were being burned in primitive conditions.

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Fig-1) Characterization & Quantification of E-waste

2.6 Source of metals and their general processing:

Printed circuit boards (PCBs) are found in electrical and electronics appliances (televisions, computers, mobile phones and laptops).

Generally, PCBs are composed of 40% metals, 30% plastics and 30% ceramics. PCBs are coated with base metals (BMs) (tin, silver or copper) to make them conductive.

There are two types of PCBs, which are used in mobile phones and personal computers. These types of PCBs are made of a multilayer of fiberglass coated with copper are used for small electronic equipment (mobile phones) or are made of a single layer of fiber glass or cellulose paper or phenolic material that is also coated with a copper layer.

PCBs of FR-4 types and FR-2 are used for larger appliances (computers and television). Polymers and industrial plastics are other major constituents of PCBs that contain polyethylene, polypropylene, epoxies and polyesters.

Sampling is difficult for e-waste composition analysis due to the inhomogeneous and composite nature of the materials. Large numbers and various kinds of small components are attached to PCBs.

Generally, PCBs are crushed into smaller sizes (less than 1–2 mm) and various techniques including magnetic, electrostatic, electrowinning, and selective dissolution are implemented to separate the components.

Yamane et al. investigated the composition of spent PCBs from mobile phones and personal computers.

Preprocessing included crushing and then separation by magnetic and electrostatic techniques. Chemical analysis was conducted using aqua regia leaching, loss on ignition and inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The results showed that PCBs from mobile phones had higher (34.5%) copper contents compared to personal computers (20%).

2.7General Driving Force for E-Waste Processing

There are three general reasons for e-waste processing: environmental concerns, energy savings and resource efficiency. These are explained in more detail in the following subsections.

- Environmental Concerns

E-waste is composed of a large number of components of various sizes, shapes and chemistry. Some of them contain hazardous metals including Hg, Pb and Cd. Such components are removed through separate treatment and recycling processes.

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- Energy and Resource Conservation

Recycling of e-waste for metal recovery is also important from the perspective of saving energy. The U.S Environmental Protection Agency has identified seven main benefits for using recycled Fe and steel over their virgin materials. One of the major benefits is a significant energy saving using recycled materials compared to virgin materials.

Moreover, processing of e-waste will reduce burden on mining ores for primary metals. Therefore, scarce resources especially for PMs could be conserved, e.g., metals that exist at low concentrations in primary ores and consume significant energy during extraction.

Factually, e-waste is a rich source of PMs compared to their primary ores. The amount of gold recovered from one ton of e-waste from personal computers is more than that recovered from 17 ton of gold ore.

The processes for recovering PMs from electronic scrap, in limited cases are easier than their primary ores. If PMs and SEs are unrecovered, it will be a significant loss of precious resource.

Mobile Phones: Then and Now

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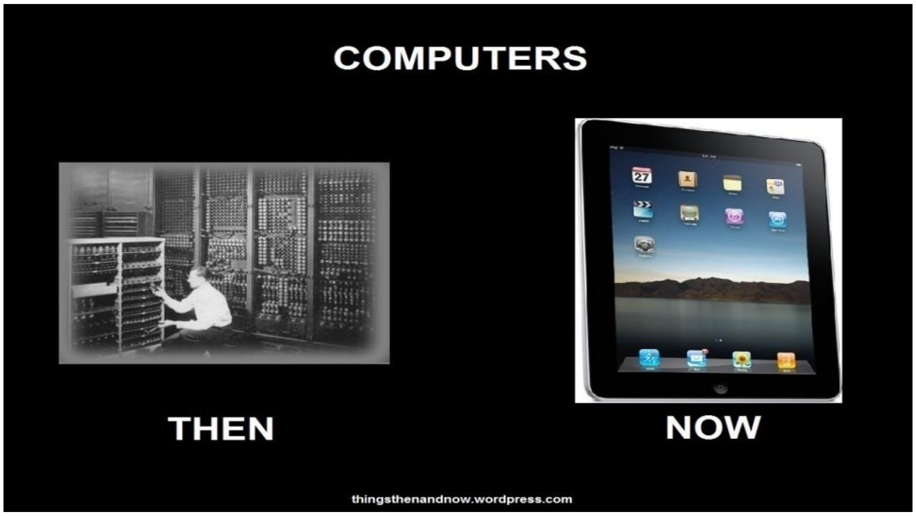

- Economic Value of Selected PMs

The recovery of precious and base metals is important for e-waste management, recycling, sustainability and resource conservation. The value distribution of PMs in PCBs and calculators is more than 80%. After PMs, copper is the next highest value metal to be extracted from e-waste It is worth noting that sustainable resource management demands the isolation of hazardous metals from e-waste and also maximizes the recovery of PMs. The loss of PMs during the recycling chain will adversely affect the process economy. The extraction of PMs (Au, Ag and Pd) and BMs (Cu, Pb and Zn) from e-waste is a major economic drive due to their associated value.

2.8ROUTES OF E-WASTE RECOVERY

E-waste recycling consists of three main steps: **Collection, Preprocessing and End Processing**. Each step is critical for the recovery of metals and recycling economy. E-waste collection is facilitated by appropriate government policies, effective advertisement for public awareness, and by installing separate collection facilities at public places. End of life electronic components are sorted at the collection facility where useable components are returned to the consumer supply chain.

Preprocessing of e-waste is one of the most important steps in the recycling chain. The expired equipments are manually dismantled at collection facilities and individual components are tested and isolated from e-waste.

During the early stage, housing, wiring boards and drives, and other components are liberated. Mechanical processing is an integrated part of this stage where e-waste scrap is shredded into pieces using hammer mills. Metals and non-metals are separated during this stage using techniques similar to that used in the mineral dressing, e.g., screening, magnetic, eddy current and density separation techniques.

The final stage in the recycling chain of e-waste is the end processing, where the non-metal and metal fractions of e-waste are further processed.

There have been a number of studies on the recycling and utilization of the non-metals fractions from e-waste, for example from wasted PCBs that contain >70% of non-metallic fractions.

In general, the non-metallic fractions of PCBs are mainly composed of thermoset resins and glass fibers. Thermoset resins cannot be re-melted due to their chain structure.

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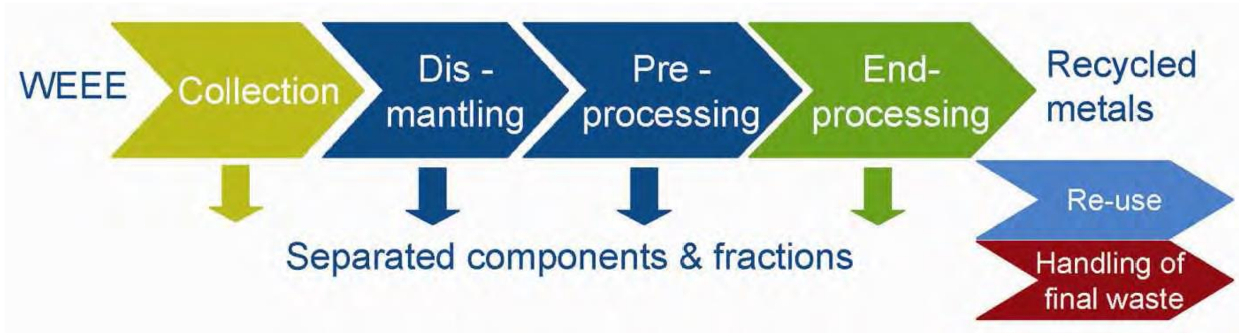

Fig-2) Flowchart for recycling of metals

Collection of e-waste is of crucial importance as this determines the amount of materialthat is actually available for recovery. Many collection programs are in place but theirefficiency varies from place to place and also depends on the device.

Improvement of collection rates depends more on social and societal factors than oncollection methods as such, but should be considered when discussing innovative recyclingtechnologies/systems.

When no devices are collected, the feed material to dismantling, preprocessing and end-processing facilities is lacking and a recycling chain cannot beestablished.

The collected equipment is sorted and then enters a pre-treatment step.

The aim of **dismantling and pre-processing** is to liberate the materials and direct themto adequate subsequent final treatment processes. Hazardous substances have to beremoved and stored or treated safely while valuable components/materials need to be takenout for reuse or to be directed to efficient recovery processes.

This includes removal ofbatteries, capacitors etc. prior to further (mechanical) pre-treatment. The batteries from the
devices can be sent to dedicated facilities for the recovery of cobalt, nickel and copper.

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For devices containing ODS such as refrigerators and air-conditioners, the de-gassingstep is crucial in the pre-processing stage as the refrigerants used (CFC or HCFC in oldermodels) need to be removed carefully to avoid air-emissions.

For CRT containingappliances (e.g. monitors and TVs) coatings in the panel glass are usually removed as well before end-processing. LCD monitors with mercury-containing backlights need specialcare too, as the backlights need to be carefully removed before further treatment.

The circuit boards present in ICT equipment and televisions contain most of the preciousand special metals as well as lead (solders) and flame retardant containing resins.

They canbe removed from the devices by manual dismantling, mechanical treatment (shredding and sorting) or a combination of both. Manual removal of the circuit boards fromtelecommunication and information technologies (IT) equipment prior to shredding willprevent losses of precious and special metals and offers advantages, especially indeveloping and transition countries with rather low labour costs.

Intensive mechanical preprocessing such as shredding and automated sorting to remove circuit boards should beavoided, because significant losses of precious and special metals can occur.
One of the causes is unintended co-separation of trace elements such as precious metals with majorfractions such as ferrous, Aluminum or plastics due to incomplete liberation of the complex materials.

An intermediate approach to the removal of hazardous andvaluable components can be a very coarse crushing to liberate the components (circuitboards, batteries etc.) as a whole followed by removal of the components by hand picking.

It has to be noted that pre-processing of e-waste is not always necessary. Small, highlycomplex electronic devices such as mobile phones, MP3 players

etc. can (after removal ofthe battery) also be treated directly by an end-processor to recover the metals.

2.9 Metallurgical Processes for the Extraction of Metals from E-Waste

The metal fractions separated from e-waste during preprocessing can be further processed using hydrometallurgical, pyrometallurgical, electrometallurgical, biometallurgical processes, and their combinations.

The hydrometallurgical and pyrometallurgical processes are the major routes for processing of e-waste. These routes may be followed by electrometallurgical/electrochemical processes (for example electrorefining or electrowinning) for selected metal separation and recovery.

2.9.1 Pyrometallurgical Processes

Pyrometallurgical processes for recovering metals from various waste materials have been used during the last two decades. Smelting in furnaces, incineration, combustion and pyrolysis are typical e-waste recycling processes.

Pyrometallurgical processes work with the steps of liberation, separation/upgrading and purification that are fundamentally similar to those of mechanical or hydrometallurgical routes.

However, the liberation of valuable metals is not achieved by leaching, crushing or grinding but by smelting in furnaces at high temperatures. In these processes, metals are sorted by exploiting their chemical and metallurgical properties, e.g., PMs are segregated into a solvent metal phase (copper or lead)

Chapter 2: Literature Review

The metal fractions separated during the preprocessing of e-waste are composed of Fe, Al, Cu, Pb and PMs. After Fe and Al, Cu and Pb are the main constituents of a typical e-waste.

Therefore, it is logical to send e-waste to smelters that accept copper/lead scrap. Currently, copper and lead smelters work as e-waste recyclers for the recovery of Pb, Cu and PMs.

In these pyrometallurgical processes, e-waste/copper/lead scrap is fed into a furnace, whereby metals are collected in a molten bath and oxides form a slag phase.

Fig-3) Conventional recovery of metals

2.9.1.1 Limitations of Pyrometallurgical Processes

Pyrometallurgical routes are generally more economical, eco-efficient and maximize the recovery of PMs, however, they have certain limitations that are summarized here:

- Recovery of plastics is not possible because plastics replace coke as a source of energy;
- Iron and aluminum recovery is not easy as they end up in the slag phase as oxides;
- Hazardous emissions such as dioxins are generated during smelting of feed materials containing halogenated flame retardants. Therefore special installations are required to minimize environmental pollution;
- A large investment is required for installing integrated e-waste recycling plants that maximize the recovery of valuable metals and also protect the environment by controlling hazardous gas emissions;
- Instant burning of fine dust of organic materials (e.g., non-metallic fractions of e-waste) can occur before reaching the metal bath.
- In such cases, agglomeration may be required to effectively harness the energy content and also to minimize the health risk posed by fine dust particles;
- Ceramic components in feed material can increase the volume of slag generated in the blast furnaces, which thereby increases the risk of losing PMs from BMs;
- Partial recovery and purity of PMs are achieved by pyrometallurgical routes. Therefore, subsequent hydrometallurgical and electrochemical techniques are necessary to extract pure metals from BMs;
- Handling the process of smelting and refining is challenging due to complex feed materials. The expertise in process handling and the thermodynamics of possible reactions will be difficult.

2.9.2 Hydrometallurgical Processes

Various investigators studied the extraction of PMs, copper, lead and zinc from e-waste using hydrometallurgical routes. These routes are based on traditional hydrometallurgical technology of metals extractions from their primary ores.

Chapter 2: Literature Review

This method can be broken down in general categories as:

1) Leaching

Similar steps of acid or caustic leaching are employed for selective dissolution of PMs from e-waste. The pregnant solution is separated and purified for the enrichment of metal content thereby impurities are removed as gangue materials.

The isolation of metal of interest is conducted through solvent extraction, adsorption and ion exchange enrichment processes. Finally, metals are recovered from solution through electrorefining (electrometallurgy) or chemical reduction processes

Solvents especially halides, cyanides, thiourea and thiosulfates are used for the leaching of PMs from their primary ores. Process factors including pH, temperature and stirring control the dissolution of metals from their primary ores.

2) Separation and Purification

The leachate solutions then go through separation and purification processes in order to concentrate the valuable metals and separate impurities) Metal Recovery

Recovering metals from leached solution can be done via electrodeposition, electrorefining processes, chemical reduction or recrystallization.. Similar techniques could be employed for extracting metals from e-waste, however, its complex nature makes the process complicated compare to natural ores.

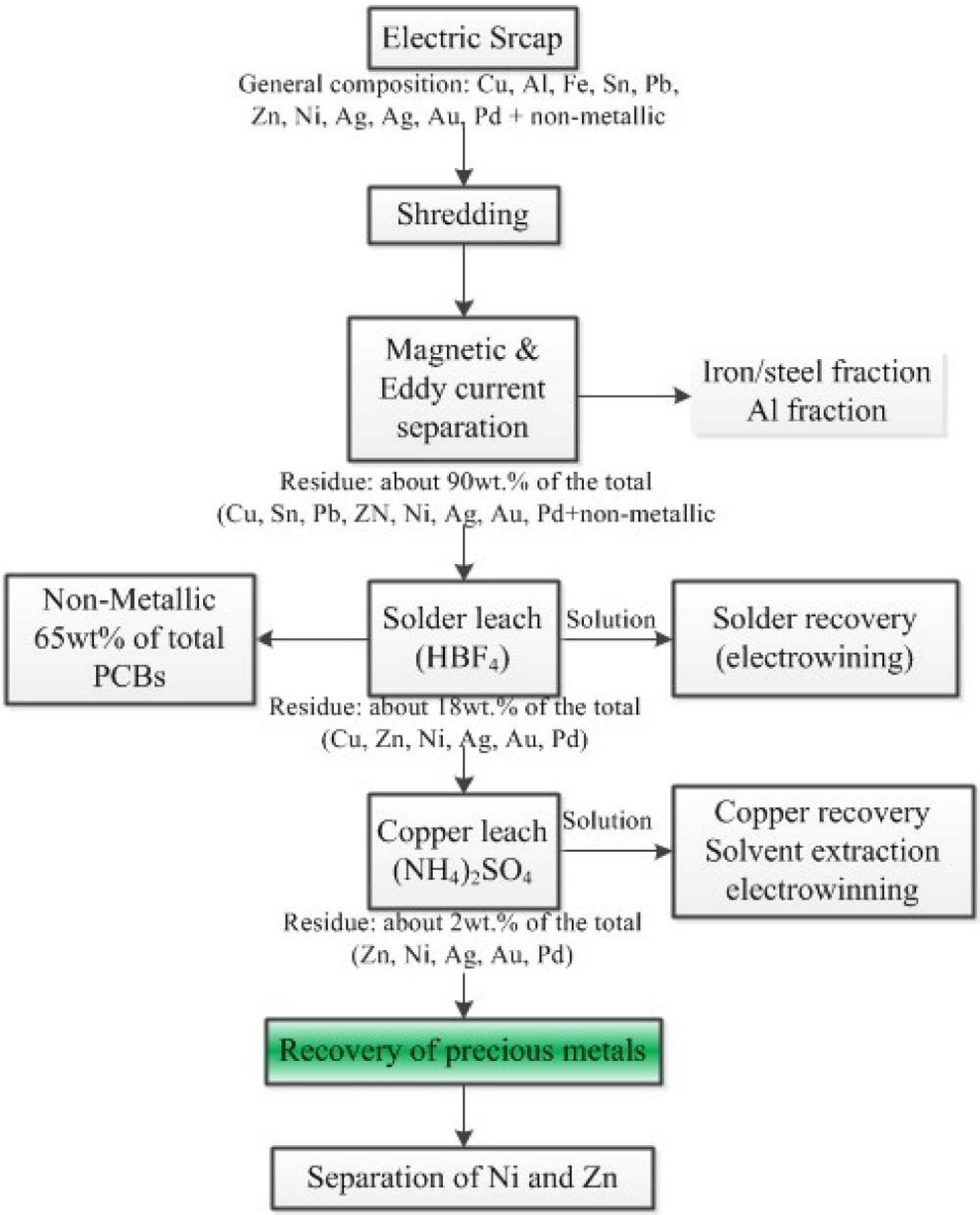


Fig-4) Separation of precious metals from base metals

2.9.2.1 Limitations of Hydrometallurgy Route

Hydrometallurgical routes have been successfully used to recover PMs from e-waste. However, these processes are associated with certain disadvantages that limit their application on the industrial scale. Some common limitations of hydrometallurgical methods for recovering PMs from e-waste are listed here:

- Overall, hydrometallurgical routes are slow and time consuming and impact recycling economy. There are concerns regarding the economy of hydrometallurgical routes compared to pyrometallurgical processes for the extraction of PMs from e-waste.
- Mechanical processing of e-waste takes longer to reduce size for efficient dissolution. It is reported that 20% PM is lost by mechanical force during the liberation process that contributes to a significant loss in the overall revenue.
- Cyanide is a dangerous leachant and should therefore be used with high safety standards. It can cause contamination of rivers and seawater, especially near gold mines, which poses serious health risks to the inhabitants.
- Halide leaching is difficult to implement due to strong corrosive acids and oxidizing conditions. Specialized equipment made of stainless steel and rubbers is required for leaching of gold using halide agents from e-waste.
- The use of thiourealeachants is limited in gold extraction due to its high cost and consumption. Moreover, further developments are required to improve the current technology of thiourea-based gold leaching.
- The consumption of thiosulfate is comparatively higher and the overall process is slower, which limits its application for gold extraction from ores as well as from e-waste.
- There are risks of PM loss during dissolution and subsequent steps, therefore the overall recovery of metals will be affected.

Sr. No.	Metal	Leaching Agent
1	Base metals(Lead , tin or nickel)	Hydrochloric acid
2	Copper	Sulphuric acid or aqua regia
3	Gold And Silver	Thiourea or cyanide
4	Palladium	Hydrochloric acid

Table 3-Some Leaching agents used in hydrometallurgy

2.9.3 Electrometallurgy

These processes are carried out as a part of the 'End-processing' of the waste. The mixture of metals obtained either by pyrometallurgy or hydrometallurgy is subjected to electrometallurgy methods to get the final product.

For e.g. After the dissolution of tin and lead by a concentrated chloride solution (generally HCl), the remaining parts now contain metals like Copper and Zinc.

This copper and zinc is in the form of solid layers on the surface of the circuit plate or in a melted state if pyrometallurgically separated.

The pyrometallurgically separated copper and zinc is cast as an anode and separated using any electrometallurgy technique.

For hydrometallurgically separated copper and zinc, they are separated by electrodeposition.

2.9.3.1 Some Basic Steps for Electrometallurgy Process

First leaching of solder material is done with either nitric acid or hydrochloric acid so solder material gets dissolve in solution and all the components like capacitors, relays, oscillators, inductors etc. gets separated.

Then leaching for various other base metal and precious metal is carried out using appropriate leaching agent

Electrolysis process is carried out for different metals with suitable setup which generally involves the solution containing metal as electrolyte and stainless steel as cathode and varyinganode for different metals.

2.10 Industrial Processes for the Recovery of Metals from E-Waste

Industrial processes for recovering metals from e-waste are based on combined pyrometallurgical, hydrometallurgical and electrometallurgical routes.

In pyrometallurgical processes, e-waste is blended with other materials and incorporated into primary/secondary smelting processes (e.g., into copper or lead smelters).

Copper smelting is the dominating route for e-waste recycling where PMs are collected in copper matte or black copper.

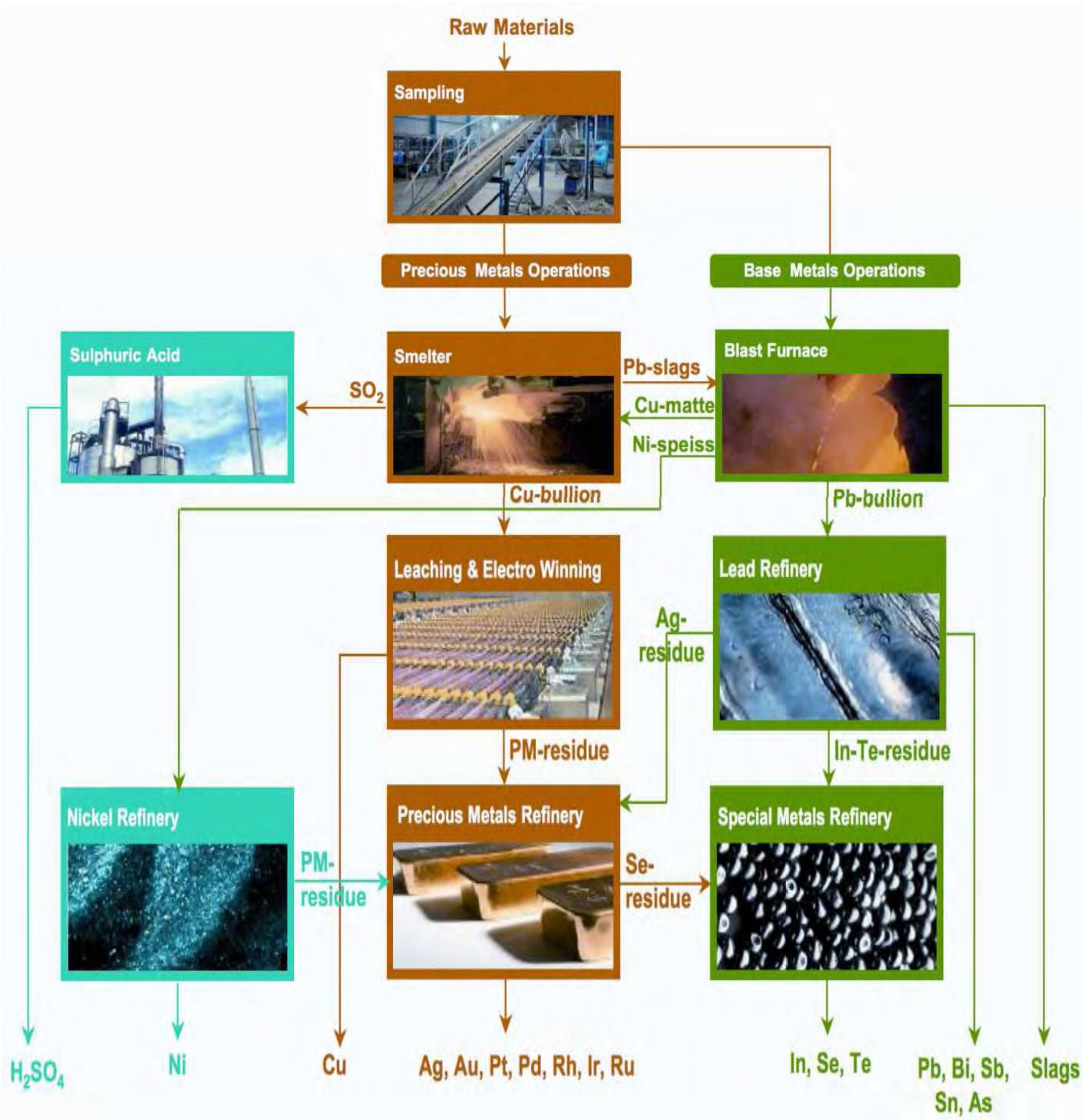


Figure 5 - Industrial method for the recovery of metals from E-waste

2.11 Aim and Scope of E-waste Recovery

To recycle the different metals found in electronic waste in order to reduce its hazardous effects on living beings as well as to get maximum resource efficiency out of the process

- The hydrometallurgical and pyrometallurgical processes are the major routes for processing of e-waste. These routes may be followed by electrometallurgical /electrochemical processes (for example electro refining or electro winning) for selected metal separation and recovery.

- As pre-processing is necessary step for pyrometallurgical processes our project is strictly focused on hydrometallurgical process .

Our project deals with combination of hydrometallurgy and electrometallurgy routes. In hydrometallurgy route generally leaching of PCB was carried out in nitric acid and hydrochloric acid. The important parameter in leaching process is leaching time which governs the amount of metal dissolved in solution. the second part involve electrodeposition process in which stainless steel was taken as cathode and graphite rod as anode, here the solution obtained after leaching serves as electrolyte. The important parameters in electrodeposition method are current, voltage and deposition time.

Hydrometallurgy route for e-waste recovery is followed by first allowing the PCBs to leach in the Nitric or Hydrochloric acids.

Hydrochloric acid dissolves just the Tin and lead while the Nitric acid dissolves significant amount of copper in addition to the solder metals, tin and lead.

The leached solutions are then used for electrodepositon, with the electrodes used being Stainless Steel Plates and Graphite Rods. Stainless steel is the Cathode and Graphite Rod is the anode.

Chapter 2: Literature Review

Objectives:

1) Establishment of process parameters to separate solder metals by leaching process.
2) Study effect of acid solution on dissolution behavior of solder materials.
3) To study effect of current density on electrodeposition of metals during electrodeposition.

Chapter 3:

Experimental Work

Chapter 3: Experimental Work

3.1) PRECLEANING of PCB:

The printed circuit boards (PCB) was properly cleanedwith running water in order to remove dirt or any other unwanted material from the surface of PCB.

3.2) LEACHING process for extraction of metals from PCB

3.2.1) LEACHING process for extraction of metals from PCB in concentrated nitric acid

The acid leaching was employed for selective dissolution of solder materials which allows the components like capacitors, relays, oscillators, inductors etc. to get separated from PCB. In the present research work, leaching of solder material was carried out with nitric acid for about one hour at room temperature using a bath containing concentrated 500 ml solution of nitric acid. The experimental set up is shown infigure-6while the experimental parameters of leaching with nitric acid solution are tabulated in table no-4

Figure 6- Leaching Process with nitric acid

Table 4- Dissolution of metals in concentrated nitric acid solution

SR NO	LEACHING SOLUTION (500ML)	LEACHING Time (MIN)	CURRENT (Ampere)	VOLTAGE (VOLTS)	DEPOSITION TIME(MINS)	Current Density (Ampere/m^2)
1	HNO_3	60	1.5 -1.8	2.5-3.0	20	450
2	HNO_3	60	1.7 -1.9	2.8-3.5	20	500

3.2.2) LEACHING process for extraction of metals from PCB in concentrated hydrochloric acid

The acid leaching was employed for selective dissolution of only solder material (Tin & Lead). In the present research work, leaching of solder material was carried out with hydrochloric acid for about thirty minutes at room temperature using a bath containing concentrated 500 ml solution of hydrochloric acid. The experimental set up is shown in figure-7 while theexperimental parameters of leachingwith hydrochloric acid solution are tabulated in table no-5

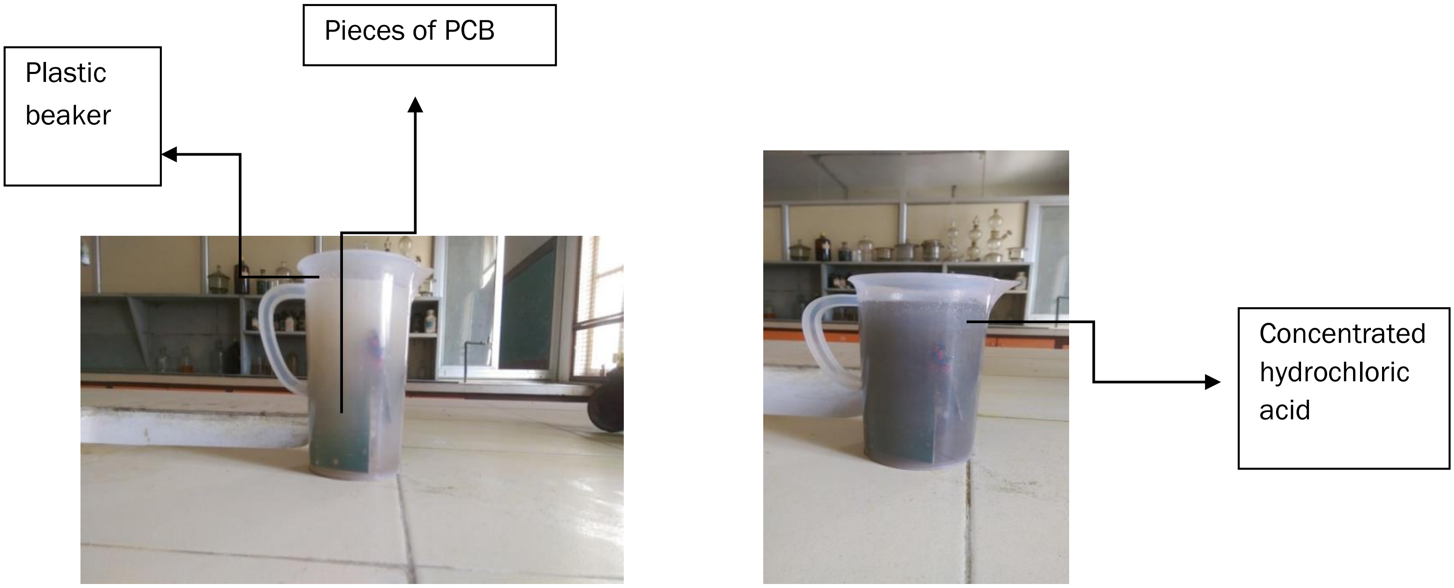


Figure 7-Leaching process with hydrochloric acid

Table 5- Dissolution of metals in concentrated hydrochloric acid solution

SR NO	LEACHING SOLUTION (500 ml)	LEACHING TIME (MINS)	CURRENT (AMPERES)	VOLTAGE (VOLTS)	DEPOSITION TIME(MINS)	Current density
1	HCL	25	1.3 - 1.5	2.1-2.3	15	400

3.3) ELECTROLYSIS:

The electrolysis process was carried out to recover the metallic value from leaching solution using graphite as anode and Stainless Steel plate as cathode & DC source , as shown in figure-8. This process was performed for both leach solution i.e. hydrochloric & nitric acid.

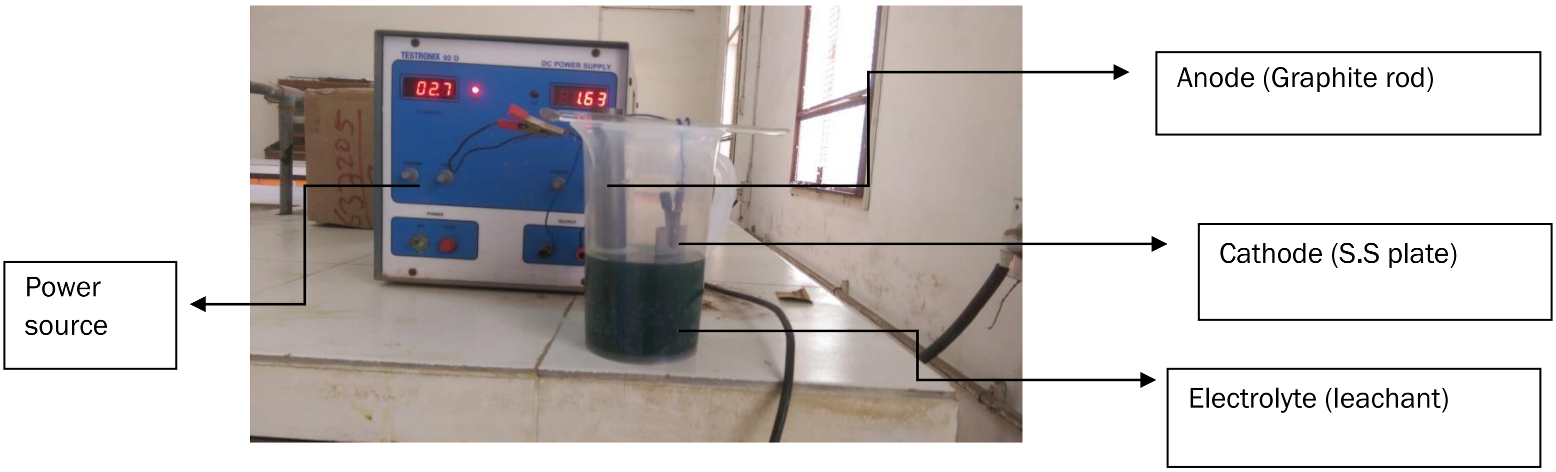


Figure 8-Set-up for electro deposition for nitric acid

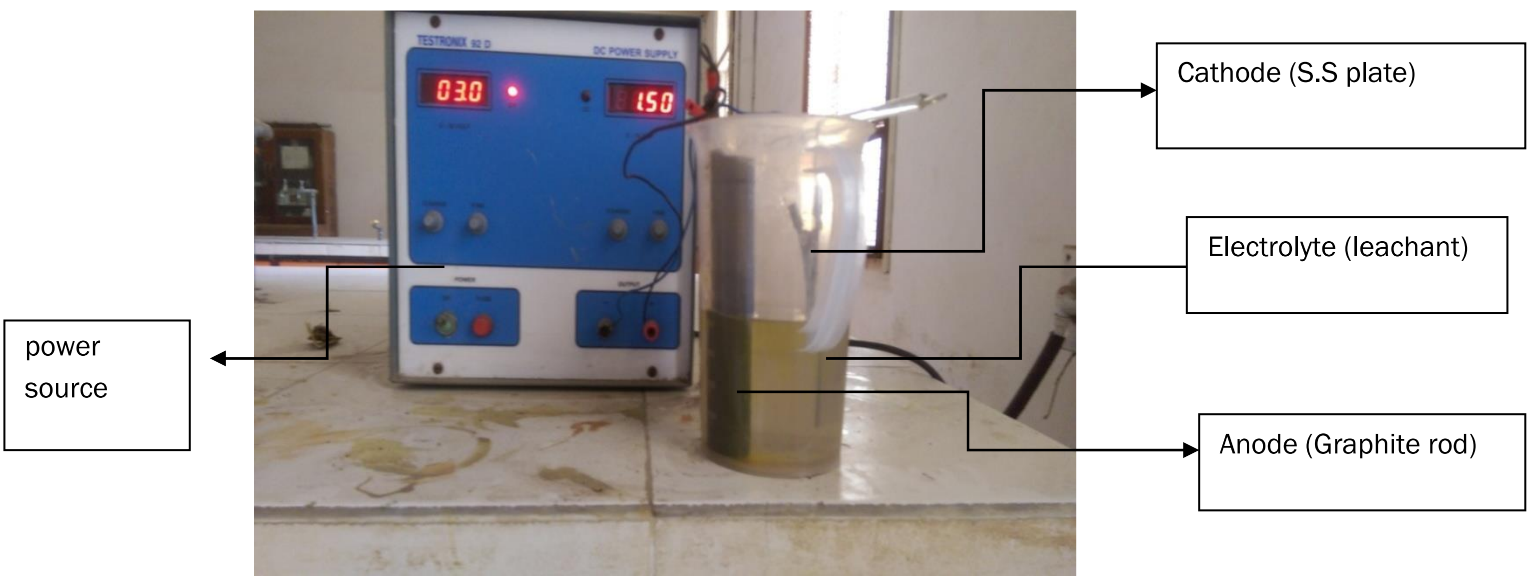


Figure 9- Set-up of electro deposition process for hydrochloric acid.

Chapter 4: Results And Discussion

Chapter 4 Results And Discussion

1) Results of electrodeposited metals from various acid solutions

1.1) Results of electrodeposited metals from Nitric acid

Table no 6: Chemical analysis of electrodeposited metals from Nitric acid

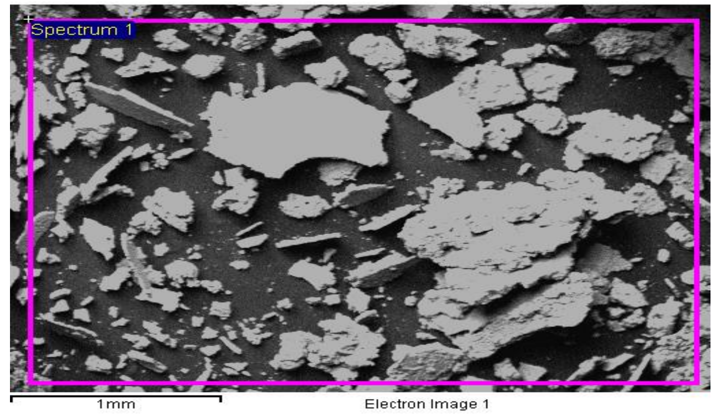
LEACHING SOLUTION (500ML)	LEACHING TIME (IN MINS)	CURRENT (IN AMPERES)	VOLTAGE (IN VOLTS)	DEPOSITION TIME (IN MINS)	% WEIGHT CONTENT		
					COPPER (CU)	TIN (SN)	LEAD (Pb)
HNO_3 Sample 1	60	1.5 -1.8	2.5-3.0	20	51.74	2.70	
HNO_3 Sample 2	60	1.7 -1.9	2.8-3.5	20	57.64	2.74	

Results of chemical analysis of electrodeposited metals from Nitricacid obtained shows thatwith increase in the current density the amount of copper deposition was increased. (Ref SEM AND EDX analysis fig)

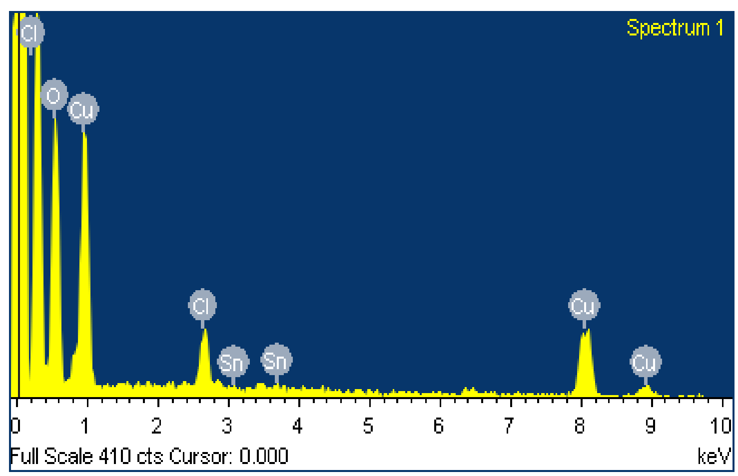
But as the current density increases, the adhesion of metal to the plate decreases. Hence, a balance should be struck between the deposition time and the current density.

Chapter 4 Results And Discussion

Element	Weight%	Atomic%
O K	39.72	71.25
Cl K	5.84	4.73
Cu L	51.74	23.37
Sn L	2.70	0.65
Totals	100.00	



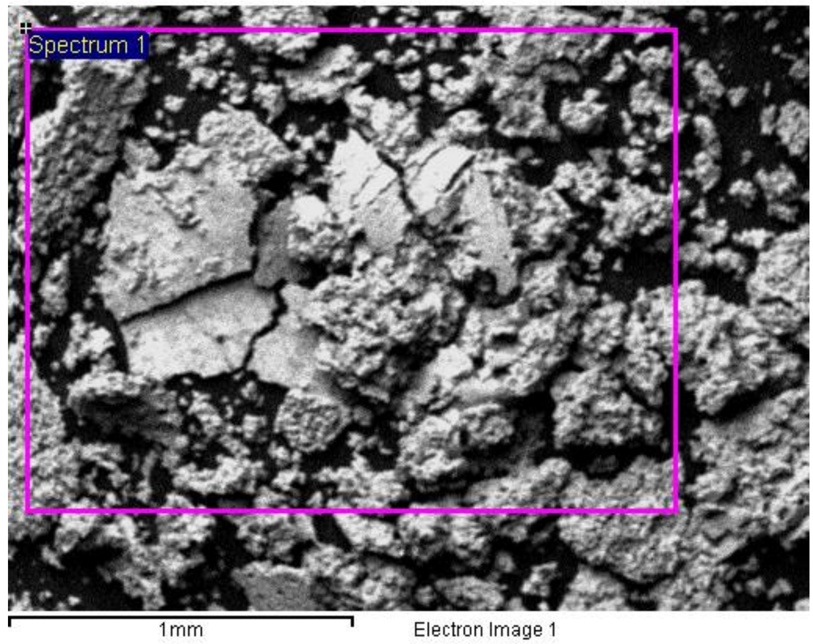
SEM image of Sample 1



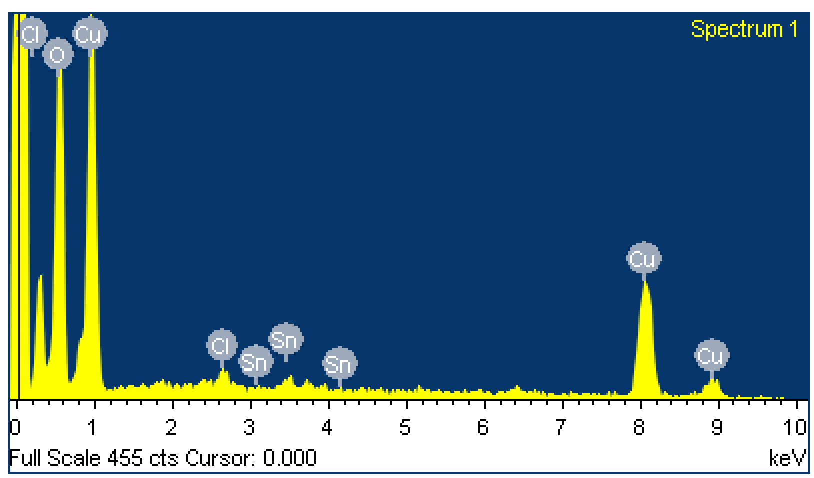
EDAX Analysis Of Sample 1

Chapter 4 Results And Discussion

Element	Weight %	Atomic %
O K	38.34	71.26
Cl K	1.28	1.08
Cu L	57.64	26.98
Sn L	2.74	0.69
Totals	100.00	



SEM Image Of Sample2



EDAX Analysis Of Sample 2

Chapter 4 Results And Discussion

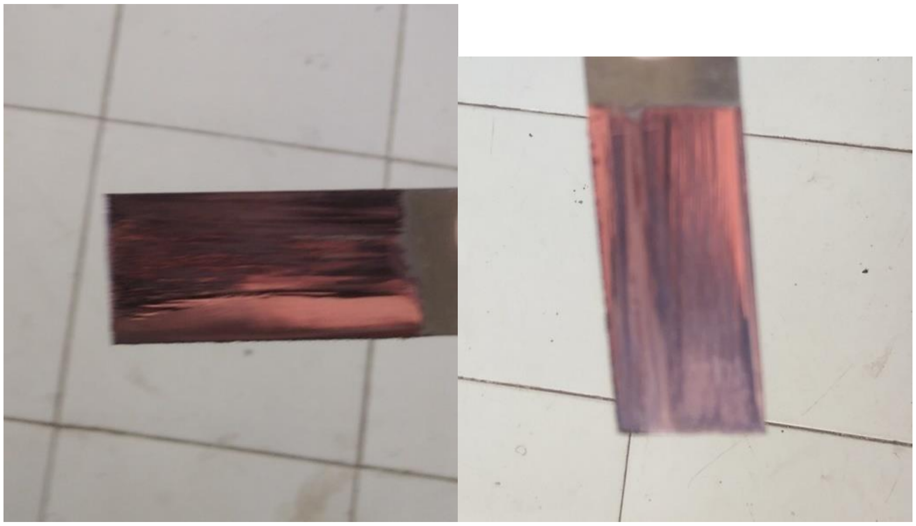


Figure 10- Copper deposition on stainless steel plate after electro deposition

After electrolysis, it was found that only copper gets deposited on cathode using Nitric acid as electrolyte as shown in the fig-10.

1.2) Results of electrodeposited metals from Hydrochloric acid

Table7- Chemical analysis of electrodeposited metals from Hydrochloric acid

LEACHING SOLUTION (500ML)	LEACHING TIME (IN MINS)	CURRENT (IN AMPERES)	VOLTAGE (IN VOLTS)	DEPOSITION TIME (IN MINS)	% WEIGHT CONTENT		
					COPPER (CU)	TIN (SN)	LEAD (Pb)
HCL Sample3	25	1.3 -1.5	2.1-2.3	15	19.49	48.38	6.95

Chapter 4 Results And Discussion

Results of chemical analysis of electrodeposited metals from Hydrochloric acid obtained shows Tin is mainly element was present while some amount of copper & lead also get deposited.(Ref SEM And EDAX analysis)

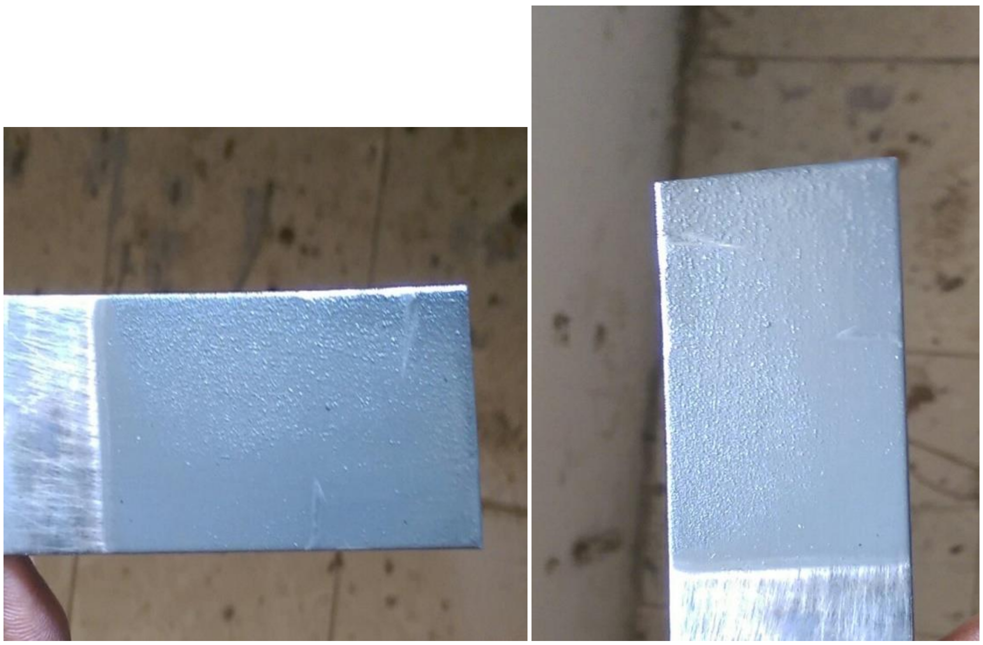


Figure 11- Solder metal (tin & lead) deposition on stainless steel plate after electro deposition

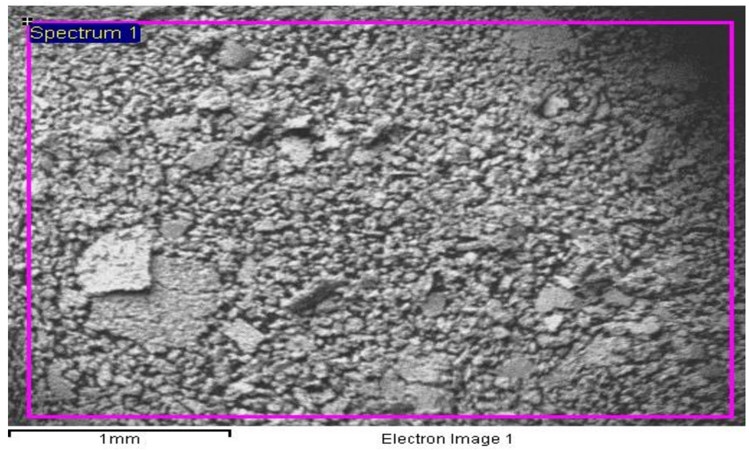
After electrolysis, it was found that mainly tin&lead metals get deposited oncathode using Hydrochloric acid as anelectrolyte shown in the figure-11.

Copper is less reactive than hydrogen in the reactivity series of metals and thus copper cannot displace the hydrogen ions in Hydrochloric Acid.

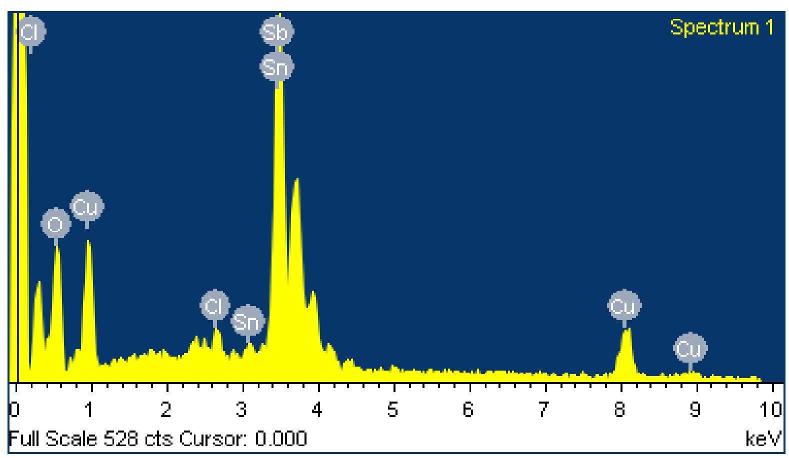
Therefore, Copper will be effectively recovered from oxidizing acids like Sulphuric and Nitric Acid, whilst Tin and Lead will be recovered more effectively from, reducing acids like Hydrochloric Acid.

Chapter 4 Results And Discussion

Element	Weight%	Atomic %
O K	23.98	65.05
Cl K	1.20	1.47
Cu L	19.49	13.31
Sn L	48.38	17.69
Sb L	6.95	2.48
Totals	100.00	



SEM Image Of Sample 3



EDAX Analysis Of Sample3

Conclusion

Conclusion

- The recycling of e-waste is important for resource and waste management as the presence of PMs in e-waste makes recycling an attractive and viable option both in terms of environment and economics.
- Metallic values can recovered by both hydrometallurgy & pyro-metallurgy.
- Pyrometallurgical routes are economical and eco-efficient for the recovery of PMs but however, hazardous emissions should be controlled to minimize environmental pollution.
- Hydrometallurgical routes for recovery of precious metals from PCBs are not preferred due to the very low content of PMs in them but Solder materials like Tin and Lead and also some base metals like Copper, Aluminum, Nickel can be effectively recovered .
- The solder materials mainly lead and tin can be effectively recovered by using hydrochloric acid as a leachant.
- The solder materials mainly lead and tin along with copper can be effectively recovered by using nitric acid as a leached solution.
- The amount of copper deposition increases with increasing current density using nitric acid as a leachant.

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