Metal Recovery from Electronic Waste Generated in Bangladesh

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ABSTRACT

This generation can't be imagined without copper, the most used metal element in electrical and electronic appliances due to its efficient electric conductivity. That causes as the usual high yield of copper in the waste stream too. As energy resources are limited, alternative methods should be developed to recover those energy resources for keeping the ecosystems balanced. The printed circuit board is the main source of value metals like gold, silver, copper etc. To recover value metals, hydrometallurgical methods are mostly used due to their low emissions and high efficiencies. Dissolving printed circuit boards in strong acid media with oxidant and then depositing copper by electrolysis may yield 99% in the pure form. On the other hand, this era of electronics is creating an ambivalent situation for human civilizations. The waste stream coming through this pipeline causes hazardous environment and performing the role of secondary resources of value metals. The printed circuit board is the point of attraction as it acts as the brain of the whole system. Thus, it has to carry the elements that have good electrical and mechanical properties. However, to satisfy the requirement, the value and hazardous elements are used there at the same time. When Gold, Silver, Copper etc. are used mostly for their conductivity, Tin is mostly used as a soldering material. As energy sources are fixed for planet earth, resources should be taken care of. Recycling used appliances is a great option where value metal like Tin can be extracted and reused. Hydrometallurgical routes are found to be the most efficient to recover value metals.

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Chapter 1

INTRODUCTION

1.1 Motivation behind this work

In Bangladesh, there is a growing concern of generation of e-waste and its subsequent handling and disposal. E-waste and its reuse and recycling processes can cause significant environmental and health hazards. At present, there is a lack of awareness about the hazards of electronic waste in Bangladesh. The electronic waste is reused, broken down for parts or disposed of completely. The present informal practice of recycling is not carried out safely and it becomes a danger to human health and the surrounding environment. Information technology has rapidly advanced, and the volume of electronic devices has surged, as well as an increasing amount of obsolete electronic devices starting to pile up. These are called E-Waste. It describes electrical & electronic products nearing their end of life. It's unwanted and has no resale value or market. It can be anything of unwanted electronics like computers, TVs, monitors, cell phones, PDAs, VCRs, CD players, fax machines, printers, etc. The waste generated from these obsolete electronic devices contains precious metals like gold, copper, tin, cobalt, nickel and toxic substances including Lithium, lead, chromium, plastics etc.

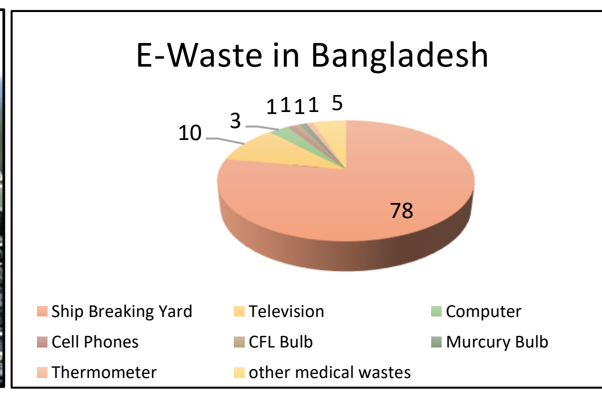


Figure 1: E-Waste ***Figure 2: E-Waste Scenario in Bangladesh [1]***

According to Bangladesh Electronic Machinery Marketing Association (BEMMA), Bangladesh consumes around 3.2 million tons of electronic products each year. Of this amount, only 20 to 30 percent is recycled and rest is dumped as obsolete or disposed of in open places, which is hazardous to health and environment. Presently, there is no specific law and ordinance for e-waste management and recycling, and no formal plant for recycling of e-waste in a hazard free manner. Most of these electronic products are recycled by the informal sector located mainly in Dhaka and Chittagong. According to a survey by ESDO, every year about 2.8 million metric tons of e-wastes is generated in Bangladesh. Among them 10,504 metric tons of toxics e-waste are generated from cell phones alone in the last 21 years. Every year around 296,302 TV sets are scrapped and generate approximately 0.17

million metric tons of e-waste. E-waste generated from ship breaking yards alone accounts for more than 2.5 million metric tons of toxics e-waste each year. In Bangladesh every year more than 15% of child workers die because of e-waste recycling and more than 83% are exposed by toxics substances and become sick and are forced to live with long term illness. Approximately fifty thousand children are involved in the informal e-waste collection and recycling process, amongst them about 40% are involved in ship breaking yards. [1]

Recycling of scrap and secondhand goods and products is one of the profitable businesses in developing countries like Bangladesh. It costs approx. $20 to recycle a PC in the U.S while it costs $2 in Bangladesh due to low cost of labor. The government already made a draft of National 3R (Reduce, Reuse & Recycle) Strategy and in that draft e-waste issues were addressed. So the concerns over e-waste recycling techniques are just booming.

1.2 Worldwide IT Industry

The world IT industry is growing day by day. The cell phone market is the most growing among them. Smartphone is the main reason of that. However, laptop computers are replacing desktop computers and tablet PCs are also very popular now-a-days. The IT sector is represented in the following table.

	US Sales (million unit)				**Global Sales (million unit)**			
Year	**2013**	**2014**	**2015**	**2016**	**2013**	**2014**	**2015**	**Future**
Computers	61.1	64.2	62.8		316	313.8	306.3	317
Televisions	36.6	39	39	27				400
Tablets	77.4	89.3		60	206.8	229.6	236.7	257.9
Cell phones	138	152	173	183	2.2 b	3.2b	3.5b	3.8b
Others		5.7		40				

Table 1: US & World IT Industry [2]

These equipment have an average lifetime of 3 years. After that time, they become obsolete producing hazardous E-Waste. They will affect human health as well as the environment. The consequences may be represented by the following table:

Source	Component	Hazard	Effect on Human
CRTs	Pb, Ba (heavy metals)	Toxic phosphor	Anemia, Insomnia, renal
Batteries, housing & medical equipment	Li/Hg	Active materials, air emissions	Muscle Tumors, mental retardation, cerebral palsy
Plastics	BPA, DBP, phthalates	Harmful chemicals from chlorinated objects	Heart problems, obesity
PVC & polymer, paints transformer & capacitors	PCBs	Extreme pollutions	Damage in liver, immune & nervous system

Table 2: Constituent & Effect of E-Waste

These e-waste sources have also some valuable metals which can be recovered in an economic way. Recovering valuable metals from e-waste is more economic than extracting metals from ore. So, e-waste should not be referred to as waste rather than it should be referred to as wealth.

Electronics have significant impact in metal demand –

		world mine-production*	by-product from	demand for electronics (EEE)*	demand related to mine production	metal price**	Main uses in electro/electronics
		t/a		t/a		€/kg	
silver	Ag	20.000	(Pb, Zn)	6.000	30%	350	contacts, switches, (leadfree) solders, conductors, MLCC, ...
gold	Au	2.500	(Cu)	250	10%	16.000	bonding wire, contacts, IC
palladium	Pd	215	PGM	32	15%	8.500	Multilayer capacitors (MLCC), connectors, PWB plating, ...
platinum	Pt	220	PGM	13	6%	29.000	hard disks, thermocouple wires, fuel cells
ruthenium	Ru	30	PGM	6	20%	18.000	hard disks, resistors, conductive pastes, plasma display panels
copper	Cu	16.000.000		4.500.000	28%	5	cables, contacts, conductors, transformer, e-motors
tin	Sn	275.000		90.000	33%	10	(leadfree) solders (incl. other solder uses)
antimony	Sb	130.000		*65.000*	50%	4	flame retardants, CRT glass
cobalt	Co	58.000	Ni, Cu	11.000	19%	40	rechargable batteries
bismuth	Bi	5.600	Pb,W,Zn	900	16%	16	leadfree solders, capacitors, heat sinks, electrostatic screening, ...
selenium	Se	1.400	Cu	240	17%	37	electrooptic, copiers, solar cells, ...
indium	In	480	Zn, (Pb)	380	79%	520	LCD glass, leadfree solders, semiconductors/LED, ...
* rounded, source: USGS Mineral commodity summaries 2007							** rounded, as of 03/2007

Table 3: demand of valuable metals & mine production

Plastics & steel dominate weight mainly. Precious metals mostly dominate economic & ecological value. E-waste from different sources contains various types of valuable metals. Majority of these metals which dominate in weight are given below –

weight-%	plastics	Fe	Al	Cu	Ag [ppm]	Au [ppm]	Pd [ppm]
TV-board	28%	28%	10%	10%	280	20	10
PC-board	23%	7%	5%	20%	1000	250	110
mobile phone	56%	5%	2%	13%	3500	340	130
portable audio	47%	23%	1%	21%	150	10	4
DVD-player	24%	62%	2%	5%	115	15	4
calculator	61%	4%	5%	3%	260	50	5

value-share	Fe	Al	Cu	Ag	Au	Pd	sum PM
TV-board	4%	10%	50%	7%	22%	7%	36%
PC-board	0%	1%	18%	5%	61%	15%	81%
mobile phone	0%	0%	9%	13%	64%	14%	91%
portable audio	2%	0%	82%	3%	10%	2%	15%
DVD-player	13%	3%	42%	5%	32%	5%	42%
calculator	0%	5%	14%	7%	69%	4%	80%

<1%	1-10%	10-20%	20-50%	50-70%	>70%

Table 4: value metal content in e-waste

From all this e-waste we selected mobile phone PCB board to recover precious metals. We also selected metal powder obtained from local sellers to recover metal.

1.3 Cell Phone Market of Bangladesh

The cell phone market has boomed by the innovation of smartphones. And Bangladesh is one of the most cell phone importing countries worldwide. In recent years, the

Smartphone imports through legal channels increased 39% to 56.27 lakh pieces in 2015 from a year earlier, mostly led by low-cost devices. Although smartphone imports and sales are increasing fast, the market is still dominated by the feature phones accounting for 50 percent of the market in 2015, according to Bangladesh Mobile Phone Importers Association (BMPIA). For 2016, BMPIA has set the target of importing 90 lakh pieces of smartphones. The total import target for mobile phones is about three crores.

Around 30 percent of the 8.92 crore active handsets in Bangladesh were brought in through illegal channels. To improve the situation, importers have moved to curb the inflow of unregistered and smuggled handsets into Bangladesh. At present, handsets worth about Tk. 9,000 crore are sold a year and the amount is expected to reach Tk. 25,000 crore by 2020, according to the importers' association.

The mobile phone industry got a boost in 2012 and 2013, especially in the smartphone segment, mainly because of the initiation of 3G services and a rise in the number of mobile users. In 2012, only 3 percent of the total mobile imports were smartphones, which climbed to 7.88 percent in 2013; 19.7 percent in 2014 and 21 percent in 2015, according to BMPIA. [3]

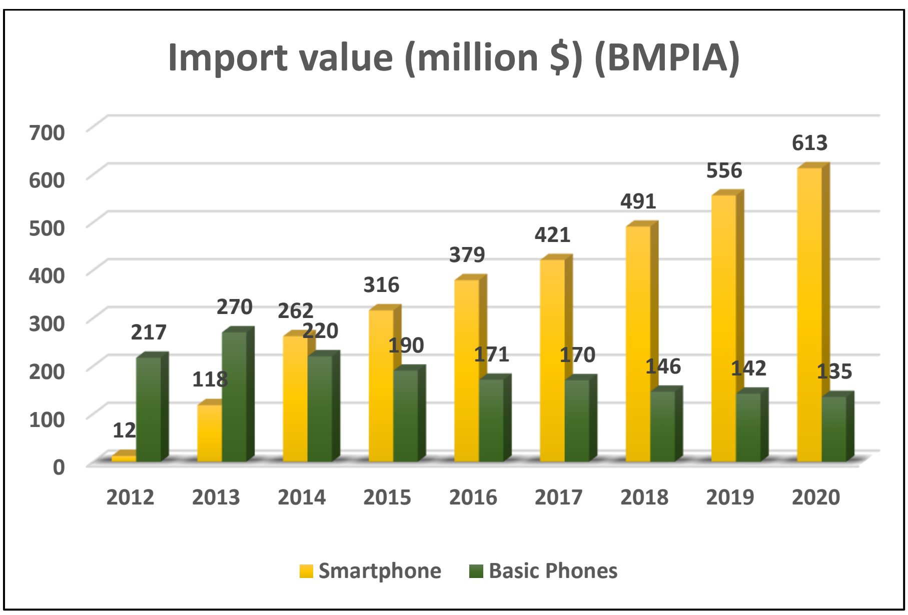


Figure 3: The expenses to import cell phone yearly

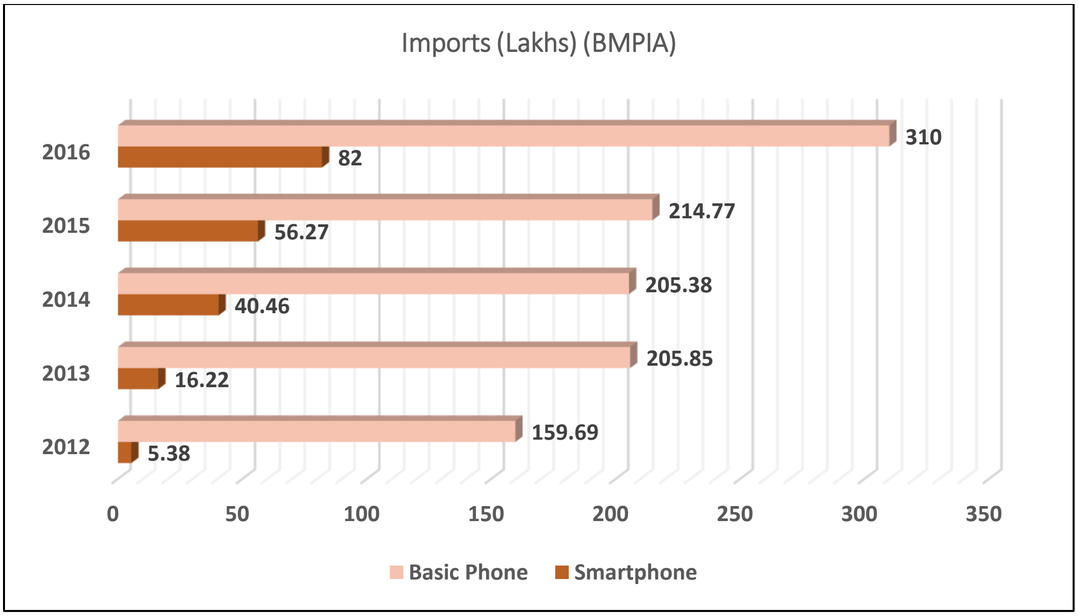


Figure 4: The amount of cell phone imported

1.4 Mobile PCB board

Printed Circuit Boards have commonly existed in computers, laptops and mobile phones. Since it contains a variety of metals and semiconductors, it is difficult to recover the materials in PCB. Among other electronics and electrical equipment, mobile phones and computers have the most rapid development in technology. Since the introduction of the first mobile phone by Motorola in 1985,

the mobile phone technology has evolved to flip phones in 1989, 2G GSM network in 1991, introduction of SMS in 1992, vibrating phones in 1996, mobile web and first Blackberry mobile in 1999, internal antenna in 2000, camera embedded phones and 3G network in 2001 to the introduction

of 4G in 2009. The size and weight of mobile phones also decreases with time, from 794 grams to around 100 grams nowadays. With an estimation of over 4 billion phones worldwide and the advancement of technology, the amount of waste produced from used mobile phones is expected to grow rapidly. Based on a survey conducted in a university in Indonesia on student's mobile phone consumption, most students only use their mobile phones for one year. This result is in conformity with EPA reports cited in [4] and annual mobile phone collection report by Australian Mobile Telecommunication Association, which reported that Australians upgrade or exchange their mobile phones every 18 to 24 months. This consumption pattern led to 106 tons of collected mobile phones in Australia during July 2010 to June 2011 or an estimated of 140 million mobile phones worldwide. [5]

Meanwhile, the development of computers dated back to 4000 B.C. and had evolved in the early years of the 20th century as the development of microchips were established. Modern computing had transformed the world since the late 1940s up until now. Now, new technology is rapidly developing to enhance the use of computers. Computers become inseparable to human life. This rapid development, although beneficial to human life, also produces a major problem in terms of electronic waste generation. In 2008, U.S. Environmental Protection Agency reported an estimation of 29.9 million desktops and 12 million laptops were discarded in 2007. Both of these electronics products have a similarity [6]. Both contain printed circuit boards (PCB). PCB is a thin board made of epoxy resin or fiberglass, which is coated with layers of thin copper films. PCB consists of various valuable metals such as Au, Pd, Ag, and Cu. However, it may also contains hazardous materials such Gallium Arsenide, Antimony, Berylliums, Brominated flame retardants and many more. Much research has been conducted to recover the precious metals and to remove the harmful elements in PCB. However, most of these methods require high tech equipment and large investments.

1.5 Metal Powder

The demand for electrical and electronic equipment (EEE) has increased dramatically with the advancement in technology. Drastic innovations on the electrical and electronic technologies further shortened the life and thus enhanced the generation of waste from electrical and electronic equipment (WEEE) or electronic waste (e-waste). The global production of e-waste/WEEE is increasing rapidly and is expected to accelerate in the near future. Currently, 20 to 25 million tons per year of e-waste are being generated globally with a major share of Europe, USA and Australasia. However, China, Eastern Europe and Latin America are expected to become significant e-waste producers in the next decade. In Europe, it is expected that the production of e-waste will increase by 45% between 1995 and 2020. Therefore, a three pillars strategy of waste prevention, recycling and reuse has been suggested to minimize the environmental impact and promote the efficient utilization of wasted resources.

E-waste is classified as hazardous material therefore should be managed properly. However, the presence of precious metals (PMs) in e-waste such as gold (Au), copper (Cu), tin (Sn), silver (Ag), platinum (Pt), Gallium (Ga), palladium (Pd), tantalum (Ta), tellurium (Te), germanium (Ge) and selenium (Se) makes it attractive for recycling.[7]

Many recycling companies operate to separate metals from PCB boards. Plastics are then removed and only metal is obtained. These metals are ground into smaller particles like powder. We collected metal powder from local suppliers. It's more effective to separate valuable metals from metal powder and as well as economic.

Figure 5 : phone PCB imported & recycling

1.6 Outline of this thesis

The primary aim of this work is to determine the quantity and the nature of metallic values in PCB & metal powder and to determine the optimum conditions for the extraction of metal values from these two sources. The successful completion of the work will help to reduce our dependence on imported important metals like copper, tin and as well as it will help to reduce environmental pollution.

The academic interest of the work includes the study of the mechanism of the various steps (leaching, chemical precipitation, etc.) involved in the process of recovery of metal values from Chines mobile PCB and metal powder. The outline of this work is discussed below:

- Mobile PCB boards and metal powder were collected from local scrap dealers and other sources. Different types of PCBs were collected and sorted.
- The PCBs were dismantled for the physical identification and separation of the different component parts. The weight proportions were also determined.
- The metals in PCBs and metal powder were identified by x-ray fluorescence analysis.
- Leaching was carried out in hydrochloric acid, sulphuric acid for copper. Leaching was carried out in nitric acid for tin. Hydrogen per oxide was used in acid as a reducing agent.
- Copper is separated from the leachate solution of cupric chloride using two extraction process of carrying electrolysis and using aluminum.
- Tin is recovered through filtration, heating, leaching, cementation and then electrodeposition.

Chapter 2

LITERATURE REVIEW

2.1 What is E-waste?

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. In fact, whole categories of old electronic items contribute to e-waste such as VCRs being replaced by DVD players, and DVD players being replaced by Blu-ray players. E-waste is created from anything electronic: computers, TVs, monitors, cell phones, PDAs, VCRs, CD players, fax machines, printers, etc.

Obsolete electronic devices are rapidly filling the landfills of the globe. In the US alone, more than 100 million computers are thrown away with less than 20% being recycled properly. The EPA estimates as much as 60 million metric tons enter landfills every year. Most electronics that are thrown away contain some form of harmful materials such as beryllium, cadmium, mercury and lead. These materials might be trace elements, but when added up in volume, the threat to the environment is significant. Besides adding harmful elements to the environment, improper disposal of e-waste is a recycling opportunity lost. Almost all electronic waste contains some form of recyclable material, including plastic, glass and metals. [8]

Figure 6 : Dumped E-Waste

E-waste is one of the fastest growing solid waste streams around today. According to a study conducted by European Union, e-waste is growing at a rate of 3.0 – 5.0% per annum or approximately three times faster than other individual waste streams in the solid waste sector (Schwarzer et al. 2005). Rapid uptake of information technology around the world coupled with the advent of new design and technology at regular intervals in the electronics sector is causing the early obsolescence of many electronic items used around the world today. According to the EU's revised directive on WEEE, e-waste can be categorized.[8]

E-Waste Category	Some examples of Product
Large Household Appliances	Refrigerator, Freezer, Washing machine, Cooking appliances etc.
Information and Communication Technology Equipment	Computers, Laptops, Mobiles, Computer Accessories, Printers, Copying Equipments.
Consumer Electronics	Toaster, coffee machines, clock, watches, hair dryers, TV, Radio, Video Camera, Amplifiers, Shavers etc.
Small Household Appliances	Vacuum cleaner, Watch, Grinders, Hair Dryers etc.
Electrical and Electronic Tools	Drills, Saws, Sewing Machines etc.
Lighting Equipments	CFL, Sodium Vapor lamp, Fan, Switches, Wires etc.
Toys, Leisure and Sports Equipments	Computers, Phones, Video games, Electric trains etc.
Medical Devices	Radiotherapy, Cardiology, Neurology, Dialysis equipment etc.
Monitoring and Controlling Equipment and Automatic Dispenser	Smoke Detector, Thermostat, ATM, Coffee vendors etc.

Table 5: Categories of E-Waste

2.2 Composition of E-Waste

Electrical and electronic equipment contain various fractions of valuable materials. Most of the valuable substances are found in printed circuit boards, which occur in relevant quantities mainly in the categories Office, Information and Communication Equipment as well as Entertainment and Consumer Electronics. Besides well-known precious metals such as gold, silver, platinum and palladium also scarce materials like indium and gallium start to play an important role, due to their application in new technologies (e.g flat screens, photovoltaics).[9]

The following table presents the composition of a desktop computer plus a CRT screen in 1996. More than 80% of the weight consists of silica (glass), plastics, iron and aluminum. Precious and scarce materials account for only a small percentage of the total weight. Nevertheless, the concentration of such metals, e.g. gold, is higher in a desktop computer than found in naturally occurring mineral ore.

Material name	Content (% of total weight)	Weight of material in computer (kg)	Use	Location
Plastics	22.9907	6.26	Insulation	Cable, Housing
Lead	6.2988	1.72	Metal joining	Funnel glass in CRTs, PWB
Aluminum	14.1723	3.86	Structural, Conductivity	Housing, CRT, PWB, connectors
Germanium	0.0016	< 0.1	Semiconductor	PWBs
Gallium	0.0013	< 0.1	Semiconductor	PWBs
Iron	20.4712	5.58	Structural, Magnetivity	Housing,CRTs, PWBs
Tin	1.0078	0.27	Metal joining	PWBs, CRTs
Copper	6.9287	1.91	Conductivity	CRTs, PWBs, connectors
Barium	0.0315	< 0.1	Â	Panel glass in CRTs
Nickel	0.8503	0.23	Structural, Magnetivity	Housing, CRT, PWB
Zinc	2.2046	0.6	Battery, Phosphor emitter	PWB, CRT
Tantalum	0.0157	< 0.1	Capacitor	Capacitors/PWB, power supply
Indium	0.0016	< 0.1	Transistor, rectifier	PWB
Vanadium	0.0002	< 0.1	Red Phosphor emitter	CRT
Terbium	0	0	Green phosphor activator, dopant	CRT, PWB
Beryllium	0.0157	< 0.1	Thermal Conductivity	PWB, connectors
Gold	0.0016	< 0.1	Connectivity, Conductivity	Connectivity, conductivity/PWB, connectors
Europium	0.0002	< 0.1	Phosphor activator	PWB
Titanium	0.0157	< 0.1	Pigment, alloying agent	Housing
Ruthenium	0.0016	< 0.1	Resistive circuit	PWB
Cobalt	0.0157	< 0.1	Structural, Magnetivity	Housing, CRT, PWB
Palladium	0.0003	< 0.1	Connectivity, Conductivity	PWB, connectors
Manganese	0.0315	< 0.1	Structural, Magnetivity	Housing, CRT, PWB
Silver	0.0189	< 0.1	Conductivity	Conductivity/PWB, connectors
Antinomy	0.0094	< 0.1	Diodes	Housing, PWB, CRT
Bismuth	0.0063	< 0.1	Wetting agent in thick film	PWB
Chromium	0.0063	< 0.1	Decorative, Hardner	Housing
Cadmium	0.0094	< 0.1	Battery, blue-green Phosphor emitter	Housing, PWB, CRT

Table 6 : Composition of a Desktop Personal Computer Based on a typical desktop computer, weighing ~27 kg

Category	Compounds
Precious metals	Gold (Au), Silver (Ag), Palladium (Pd), and to a lesser extent Platinum (Pt)
Base metals	Copper (Cu), Aluminum (Al), Nickel (Ni), Tin (Sn), Zinc (Zn), Iron (Fe)
Metals (toxic) of concern	Mercury (Hg), Beryllium (Be), Indium (In), Lead (Pb), Cadmium (Cd), Arsenic (As), Antimony (Sb
Halogens	Bromine (Br), Fluorine (F), Chlorine (Cl)
Combustibles	Plastic and organic fluids

Table 7 : **Main compounds commonly found in E-Waste (Hagelüken 2006)**

Regardless of the particular type of electronic component concerned, all e-waste can be broken down to a bunch of specific metals, polymers and glass.[10]

Toxic substances and other harmful substances are usually concentrated in printed circuit boards (PCB) and Cathode Ray Tube (CRT). The metal flows split into ferrous metals (the second largest group of the whole system), Al, Cu and mixed and precious metals. It has been found from a study (Suvesh, 2007), that a computer with an average wt. of 31.5 kg contains a number of toxic elements.

Metal extraction from e-waste is more efficient than from ore. Ore is not homogeneous in their precious metal content, and very few ores can be classified as high grade. Extraction from these ores is achieved in a multitude of steps, with material losses occurring in each successive step. Ore processing is also very toxic for the environment. In contrast, metal extraction from e-waste is simpler and requires very few steps as most of the precious metals exist in elemental forms. Table 8 provides a comparison of metal extraction efficiency from discarded electronics and typical ores. Because of the presence of a number of value metals, e -waste is often called urban mine.

	Item	Copper (%wt.)	Silver (ppm)	Gold (ppm)	Palladium (ppm)
EEE	Television board	10	280	20	10
	PC board	20	1000	250	110
	Mobile phone	13	3500	340	130
	Portable audio scrap	21	150	10	4
	DVD Player scrap	5	115	15	4
	Avg. electronics	13.8	1009	127	51.6
Ore/mine		0.6	215.5	1.01	2.7

Table 8: Metal concentration in electronics and ore (Desjardins, 2014; Investing News Network, 2016; McLeod, 2014; Namias, 2013; Vincic, 2015)[10]

It has been reported in several studies that 1 tonne of phone handsets contains 3.5kg of Ag, 340 g Au, 140g of Pd and 130 kg of Cu. Gold content of total e-waste generated in 2014 is roughly 300 tonnes, which represents 11% of the global gold production from mines in 2013.1 tonne of e-waste from personal computers contains more gold that can be recovered from 17 t of gold ore (Khaliq et al., 2014).

2.3 E-waste Generation

2.3.1 E-Waste Generation Around the World

In 2016 the world generated e-waste -- everything from end-of-life refrigerators and television sets to solar panels, mobile phones and computers -- equal in weight to almost nine Great Pyramids of Giza, 4,500 Eiffel Towers, or 1.23 million fully loaded 18-wheel 40-ton trucks, enough to form a line from New York to Bangkok and back.

Experts foresee a further 17% increase -- to 52.2 million metric tons of e-waste by 2021, -- the fastest growing part of the world's domestic waste stream. The Global E-waste Monitor 2017, l is a collaborative effort of the United Nations University (UNU), represented through its Sustainable Cycles (SCYCLE) Program hosted by UNU's Vice-Rectorate in Europe, the International Telecommunication Union (ITU), and the International Solid Waste Association (ISWA).[11]

Only 20% of 2016's e-waste is documented to have been collected and recycled despite rich deposits of gold, silver, copper, platinum, palladium and other high value recoverable materials. The conservatively estimated value of recoverable materials in last year's e-waste was US $55 billion, which is more than the 2016 Gross Domestic Product of most countries in the world. About 4% of 2016's e-waste is known to have been thrown into landfills; 76% or 34.1 Mt likely ended up incinerated, in landfills, recycled in informal (backyard) operations or remained stored in our households. On a per capita basis, the report shows a rising trend as well. Falling prices now make electronic and electrical devices affordable for most people worldwide while encouraging early equipment replacement or new acquisitions in wealthier countries. As a result, the average worldwide per capita e-waste generated was 6.1 kilograms in 2016, up 5% from 5.8 kg in 2014.[11] The highest per capita e-waste generators (at 17.3 kilograms per inhabitant) were Australia, New Zealand and the other the nations of Oceania, with only 6% formally collected and recycled. Europe (including Russia) is the second largest generator of e-waste per inhabitant with an average of 16.6 kg per inhabitant. However, Europe has the highest collection rate (35%). The Americas generates 11.6 kg per inhabitant and collects only 17%, comparable to the collection rate in Asia (15%). However, at 4.2 kg per inhabitant, Asia generates only about one third of America's e-waste per capita. Africa, meanwhile, generates 1.9 kg per inhabitant, with little information available on its collection rate.

The 3 EEE categories that contribute the most to e-waste are also growing fastest. It is expected that the following three EEE categories, which already constitute 75% of global e-waste by weight (33.6 Mt of 44.7 Mt), will also see the fastest growth.

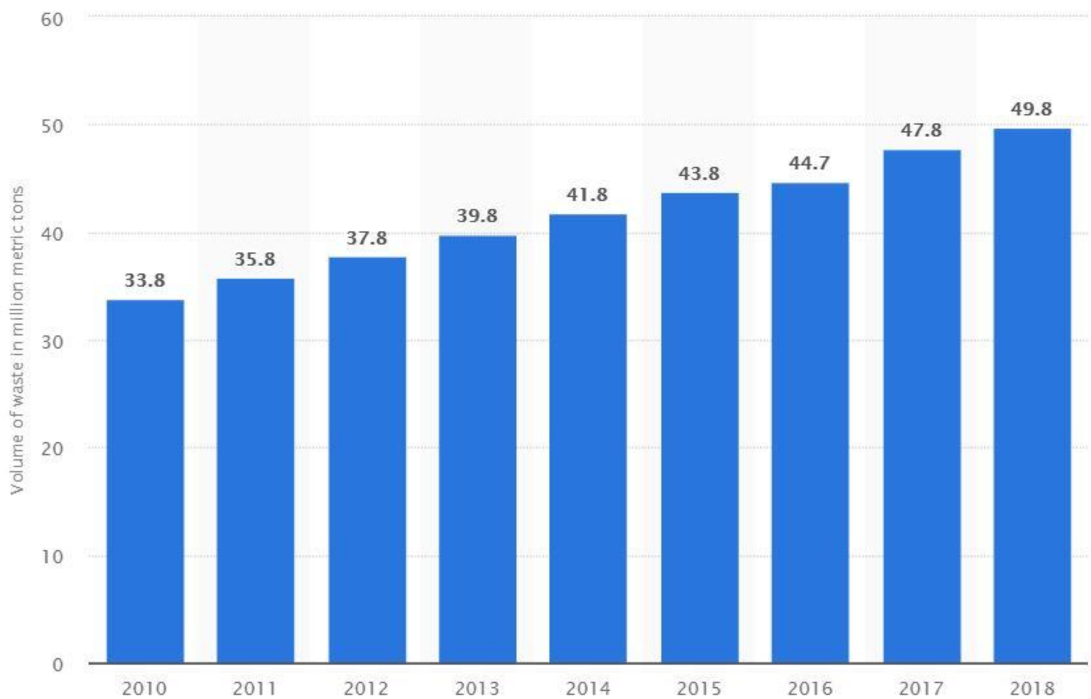


Figure 7 : Global generation of e-waste [11]

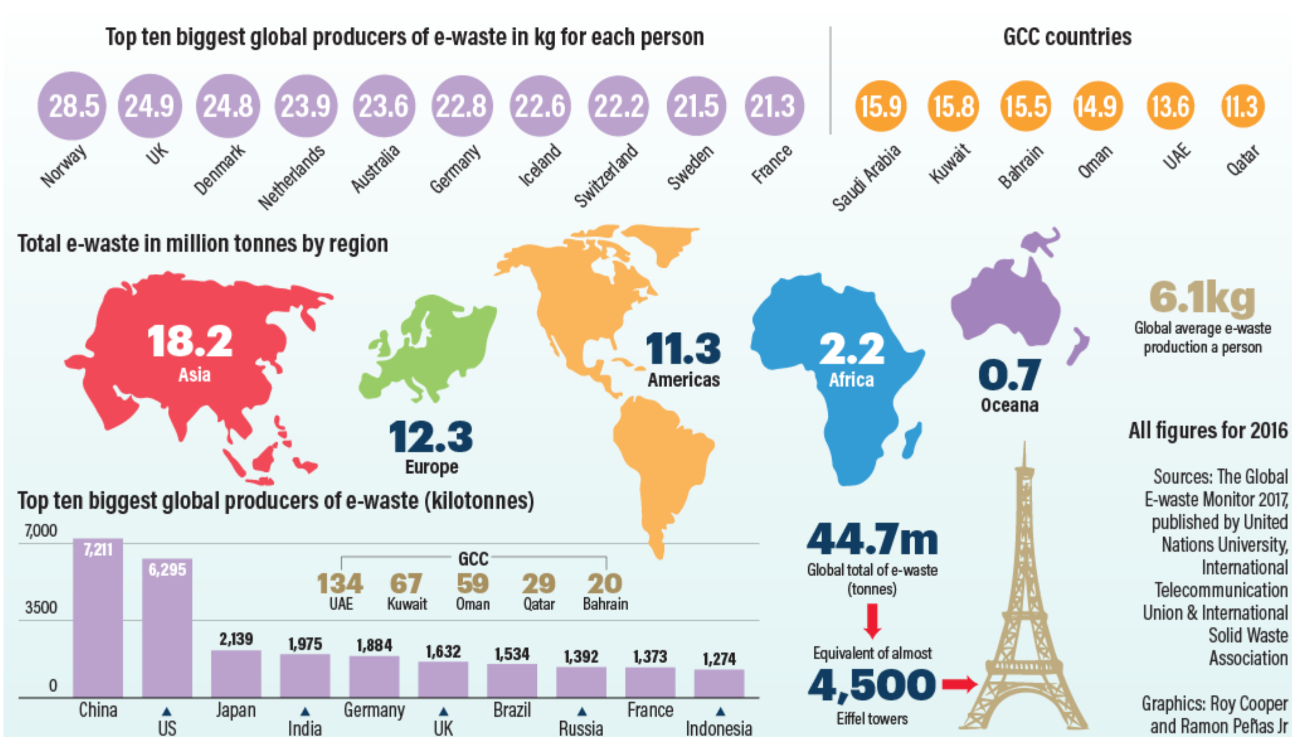


Figure 8 : generation of e-waste in some particular countries

2.3.2 E-Waste Generation in Bangladesh

Bangladesh is developing with the increasing of technology usage. Sustainable and safe use of technology is a big challenge for Bangladesh. The wastes from electronic goods come to Bangladesh as curse. People consume and dump useless products without any consideration of environmental damage and sustainability. Moreover, every year significant number of scrap ships is imported to Bangladesh by importer legally and/illegally. These ships are broken in ship breaking yard located mainly in southern part of Bangladesh. During ship breaking, many heavy metals and toxic pollutants emit to the environment and oil spills to land and water bodies. As Bangladesh has binding to import scrap ships, thus illegal import and trade off of e-waste is happening by importer to make profit and hence, e-waste vulnerability of Bangladesh is increasing. The scrap ships carry large volume of toxics products and electrical & electronic waste, includes: antiques, barometers, clothes irons, electronics, lamps/light bulbs, light switches, paint (Latex), pesticides, television sets, thermometers, mirrors, washing machines, calculators, desktop liquid crystal display. (LCD) monitors, laptop, LCD monitor etc.

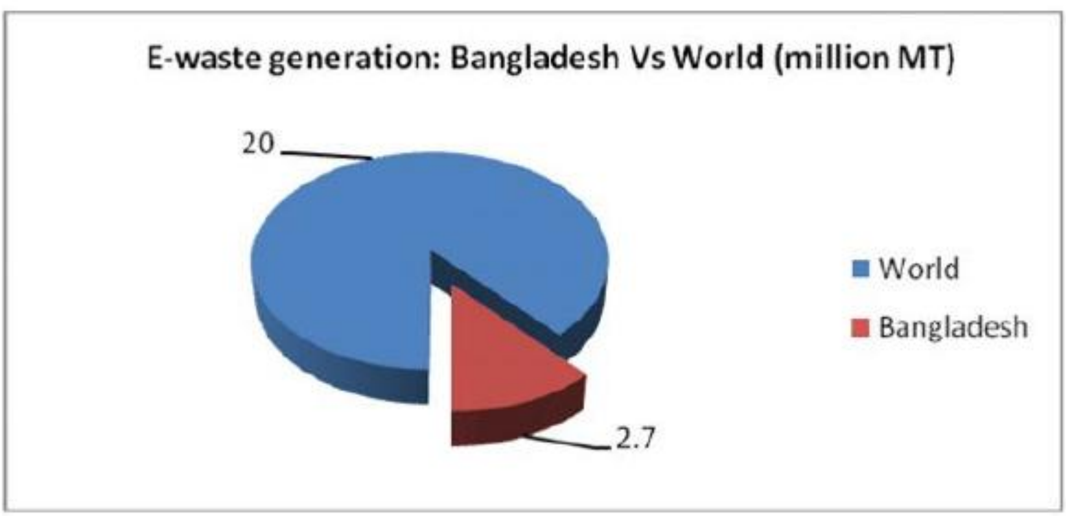


Figure 9 : E-Waste generation in Bangladesh Vs World (ESDO, 2010)[12]

In Bangladesh almost 2.7 million metric tons of e-waste generated per year. According to yearly generation figures, it is clear that ship breaking yard occupied the highest (2.5 million metric tons) position. Waste from television sets have taken the second highest (0.182 million metric tons) position with an exponentially increasing rate. Bangladesh is one of the highly e-waste generating countries in the world. In Bangladesh about 2.7 million metric tons of e-waste has generated per year, in contrast, it is stated in the report —From e-waste to Resource that in the world volume of e-waste generated per year is 20 million metric tons. However, according to UNEP projections, an estimated 20-50 million tons of e-Waste is being generated annually in the world. No inventory has been made to assess the extent of e-waste problem in Bangladesh.[12]

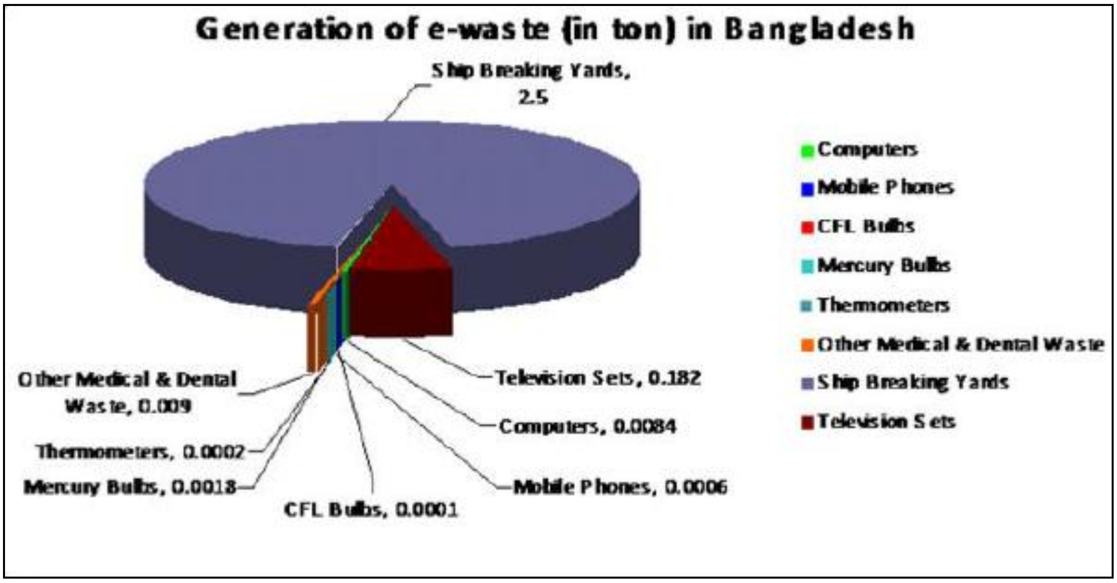


Figure 10 : E-Waste generation in Bangladesh (ESDO, 2010)

The goods bellow generates e-wastes in Bangladesh;[12]

- Total number of PCs, TVs and Refrigerators in the year 2006 was 600,000, 1,252,000 and 2,200,000.
- The total number of TV sets users is roughly 10.3 million at the end of the year 2008.
- Every year around 59, 85,000 TV sets become scrape and generated 88,357.14 metric tons of e-waste.
- The total number of mobile phone active subscribers in Bangladesh was 58.36million at the end of May 2010.
- Each year more than 2.8 million tons of electronic waste (it includes e-waste from ship breaking yard) generated in Bangladesh.
- E-waste generated from ship breaking yards about 2.5 million metric tons in a year.
- POPs: from ship breaking sites, PCB, Dioxin, Furan
- 10,504 metric tons of toxic e-waste by cell phone sets within last 21years.
- Within the last 10 years IT sector generated 35,000 metric tons of e-waste in Bangladesh.

According to an estimate, more than 500 thousand computers were in use in 2004 and this number has been growing at 11.4 per cent annually. Even if the figure of 500 thousand were taken as the baseline, that many PCs would contain approximately 15.323 tons of waste *(%* 27.2 kg/PC for 5 year obsolescence) in 2010 containing deadly plastics, lead, mercury etc. The quantity of e-waste (PC and Cell phone) to be generated has been estimated by following two methods. The first method, Market Supply Method A. (MA) assumes that the average lifetime of an electronic product is approximately five years and after that these are discarded and come to the waste stream. The second method, Market Supply Method B (MB), assumes that all the products are not disposed of at the same time; rather they are disposed of in varying quantities over successive years. Here a weighted average method is used to show the product disposal trend. For PCs the growth rate is considered to be 11.4 per cent and for cell phones a 100% growth rate is considered annually.

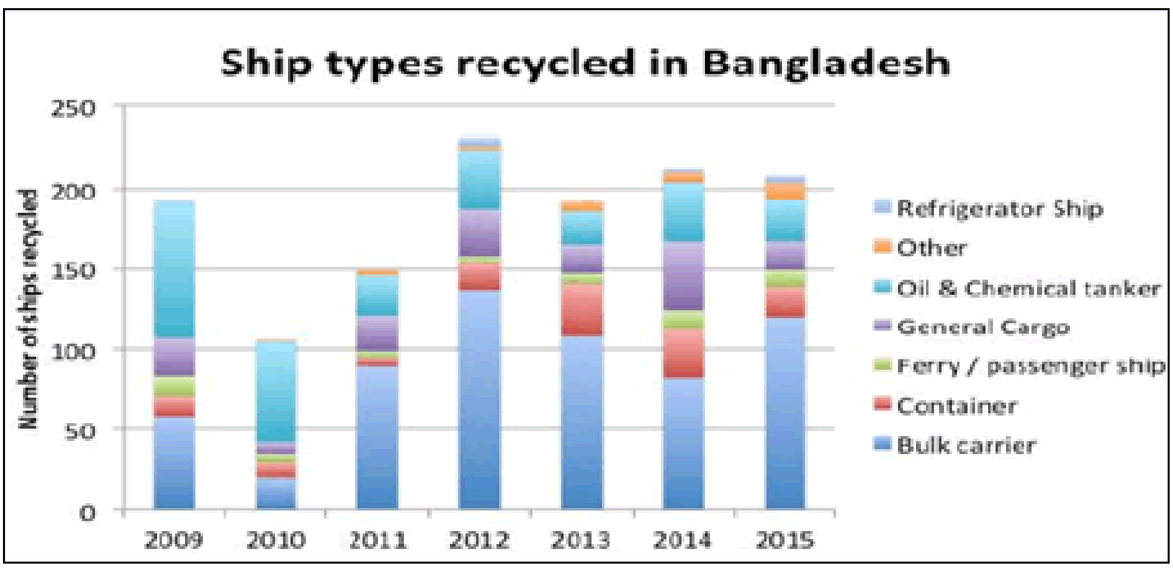


Figure 11 : Total number of ships recycled in Bangladesh by type/category between the years 2009 to 2015 (Sujauddin et al., 2014)[13]

2.3.3 E-Waste from Cell Phone Market

Smart phone penetration in the Bangladeshi market has increased exponentially. According to GSMA (2018), almost half of the population of the country were unique subscribers of telecom services by the end of 2016.

	Unique Subscriber Penetration	Mobile Internet Penetration	Proportion of 3G Connections	Proportions of 4G Connections
Bangladesh	53%	33%	20%	0%
India	48%	35%	18%	1.7%
Southern Asia	50%	34%	21%	1.9%
World	65%	48%	32%	23%

Table 9: Mobile market in Bangladesh (GSMA, 2018)[14]

According to Bangladesh Mobile Phone Importers Association (BMPIA), smart phone imports have increased exponentially in the last few years. From Figure 12, it is evident that a considerable number of cell phones will become as e-wastes at the end of their life span.

Figure 12 : Value of Smartphone imports in Bangladesh (Islam, 2016)[14]

2.4 Environment, Health and Human Right Concern of E-waste

Several scholars across geo-cultural divides have argued that linking human rights with environmental issues creates a rights-based platform to environmental protection that places the people harmed by environmental degradation or pollution at its center. The articulation of the rights of human beings thus creates the opportunity to secure those rights through juridical bodies in the international and domestic fora. This has particular implications for those human groups that are most vulnerable to environmental harm and least able to access political remedies within their own meager means. The connectivity between human rights and the environment reveals that human rights abuse often lead to environmental harm, just as environmental degradation or pollution often causes egregious human rights violations. With more than one hundred national constitutions recognizing and protecting the right to a safe, clean and healthy environment, and virtually all international and regional human rights treaty monitoring bodies also recognizing the direct linkage between environmental harm and human rights norms, it is safe to posit that interjecting the electronic waste discourse from a rights-based perspective at this juncture is neither out of place nor abstract.[15] In her seminal work produced on behalf of the World Health Organization in 2002, Shelton had proffered sweeping validation for the inclusion of a rights-based approach to every discourse on environmental health in following-

First, the emphasis on rights of information, participation, and access to justice encourages an integration of democratic values and promotion of the rule of law in broad-based structures of governance. Experience shows better environmental decision-making and implementation when those affected are informed and participate in the process: the legitimacy of the decisions exercises a pull towards compliance with the measures adopted. Another benefit of a rights-based approach is the existence of international petition procedures that allow those harmed to bring international pressure to bear when governments lack the will to prevent or halt severe pollution that threatens human health and well-being. In many instances, petitioners have been afforded redress and governments have taken measures to remedy the violation. In other instances, however, the problem appears to be the result of a combination of governmental lack of capacity and lack of political will. The pollution may be caused by powerful enterprises whose business and investment are important to the state, or the state may have inadequate monitoring systems to ensure air or water quality. Even in these instances, however, petition procedures can help to identify problems and encourage a dialogue to resolve them, including by the provision of technical assistance.

The non-functioning computers that arrive at most developing countries i.e. Bangladesh are sold as scrap, smashed up and discarded, a common practice within electronic wastes receiving countries that often lack capacity in the handling and recycling of the hazardous materials within the electronic wastes. Instead, manual dismantling, open burning to recover materials, and open dumping of residual fractions occurs. In Bangladesh, this is predominantly carried out by some disorganized informal and very few formal electronic wastes recycling sector. Consequently, relatively more hazardous material is introduced into informal electronic wastes burning and dumping grounds across many developing countries like Bangladesh, with higher implications for the environment and human health. {15]

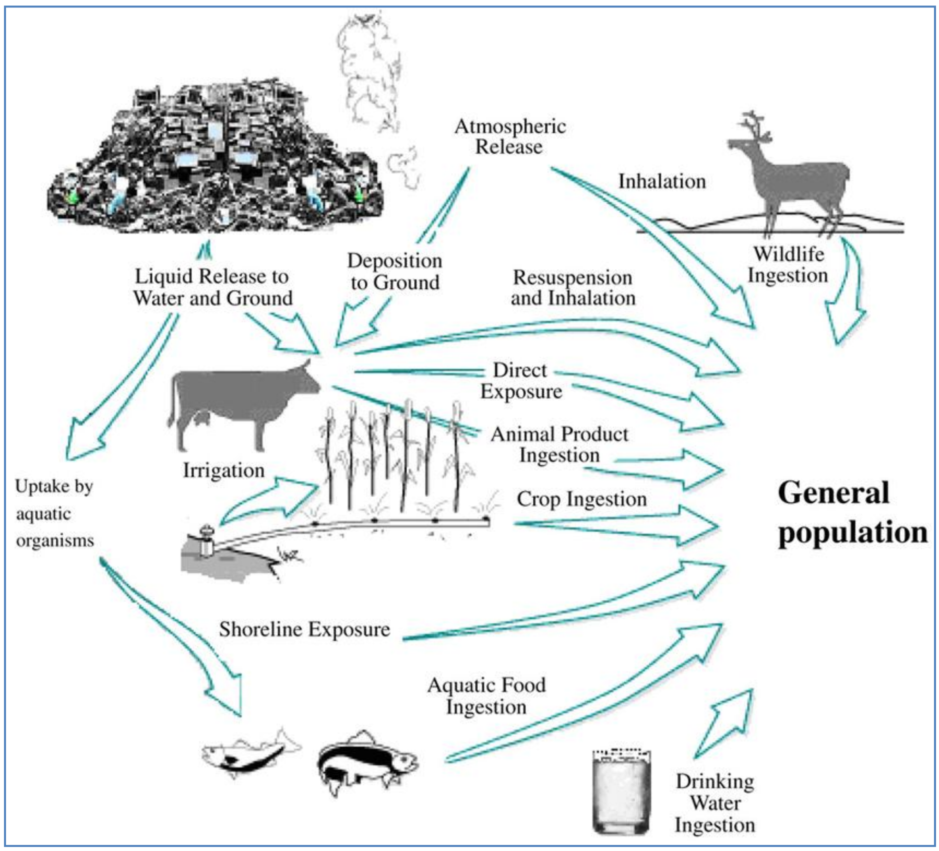


Figure 13 : Exposure routes and fate of e-waste in environment and food chain (Frazzoli et al., 2010) [16]

Electronic waste presents severe environmental and health challenges for the country saddled with the task of processing them, by reason of both the quantity and inherent dangers of toxicity. Electronic waste can contain more than a thousand assorted substances, many of which are lethal. These may be in form heavy metals or chemicals such as mercury, lead, cadmium, chromium, magnetic properties and antimony (flame retardants), including polybrominated biphenyls, polyvinyl chloride, polychlorinated biphenyls, and polybrominated diphenyl ethers. Perhaps the most hazardous components of electronic waste are the mercury-containing components, batteries, printed circuit boards, CRTs, and the plastics which contain the brominated flame retardants. Accidental leakages and evaporation of these substances occur at the electronic wastes dumping sites, and results in the contamination of surrounding natural resources including soil, crops, water, livestock and fish. Empirical studies at shipyard of Chittagong, Bangladesh revealed lead, mercury, cadmium, arsenic, antimony trioxide, polybrominated flame retardants, selenium, chromium, and cobalt contents in soil samples at rates far higher than average. Of course, when the electronic waste is burnt, further toxic substances can be inadvertently generated. Beyond the environmental degradation concerns, the hazardous materials found in electronic waste pose a significant risk to human health. After all, empirical research has established that people who break electronic wastes open often suffer radiation, nausea, headaches, respiratory failure among other health problems. However, it is not only the people working directly with electronic waste who are susceptible to their harmful effects but also people living in the ambience of the waste dumps, and those indirectly affected through resulting contamination of the food chain, soils and rivers.

These people are exposed to hazardous substances through dermal exposure, dietary intake, dust inhalation or particle intake, with the latter two sources found to be particularly significant. Other expert studies state that exposure to chemicals from e-waste – including lead, cadmium, mercury, chromium and polybrominated biphennyls – could injure the human brain and nervous system, distress the kidneys and liver, and lead to birth defects. The Minamata disease in Japan between 1954 and 1965; the Love Canal incident, near Niagara Falls in the US; the Koko incident of 1988 in Nigeria; the Thor Chemicals diseases of the early 1990s in South Africa; the disastrous Trafigura dumping of hazardous wastes incident in Ivory Coast, in 2006, are among the numerous pointers to the grave consequences that unscrupulous waste dumping could have on human beings, jeopardizing their livelihood, liberty and very existence. The essence of the above is to demonstrate that the totality of human rights guarantees and particularly the right to life, the right to development, and the entire gamut of economic, social and cultural rights cannot be realized in the absence of the right to a healthy environment.[15]

2.5 E-waste Management System

It is estimated that 75% of electronic items are stored due to uncertainty about how to manage it. This electronic junk lies unattended in houses, offices, warehouses etc. and normally mixed with household waste, which is finally disposed of at landfills. This necessitates implementable management measures. [15,17]

In industries management of e-waste should begin at the point of generation. This can be done by waste minimization techniques and by sustainable product design. Waste minimization in industries involves adopting:

- inventory management,
- production-process modification,
- volume reduction,
- recovery and reuse.

Inventory management

Proper control over the materials used in the manufacturing process is an important way to reduce waste generation (Freeman, 1989). By reducing both the quantity of hazardous materials used in the process and the amount of excess raw materials in stock, the quantity of waste generated can be reduced. This can be done in two ways, i.e. establishing material-purchase review and control procedures and inventory tracking system.

Developing review procedures for all material purchased is the first step in establishing an inventory management program. Procedures should require that all materials be approved prior to purchase. In the approval process all production materials are evaluated to examine if they contain hazardous constituents and whether alternative non-hazardous materials are available.

Another inventory management procedure for waste reduction is to ensure that only the needed quantity of a material is ordered. This will require the establishment of a strict inventory tracking system. Purchase procedures must be implemented which ensure that materials are ordered only on an as-needed basis and that only the amount needed for a specific period of time is ordered.

Production-process modification

Changes can be made in the production process, which will reduce waste generation. This reduction can be accomplished by changing the materials used to make the product or by the more efficient use of input materials in the production process or both. Potential waste minimization techniques can be broken down into three categories:

i) Improved operating and maintenance procedures,

ii) Material change and

iii)Process-equipment modification.

Improvements in the operation and maintenance of process equipment can result in significant waste reduction. This can be accomplished by reviewing current operational procedures or lack of procedures and examination of the production process for ways to improve its efficiency. Instituting standard operation procedures can optimize the use of raw materials in the production process and reduce the potential for materials to be lost through leaks and spills. A strict maintenance program, which stresses corrective maintenance, can reduce waste generation caused by equipment failure. An employee-training program is a key element of any waste reduction program. Training should include correct operating and handling procedures, proper equipment uses, recommended maintenance and inspection schedules, correct process control specifications and proper management of waste materials.

Hazardous materials used in either a product formulation or a production process may be replaced with less hazardous or non-hazardous material. This is a very widely used technique and is applicable to most manufacturing processes. Implementation of this waste reduction technique may require only some minor process adjustments, or it may require extensive new process equipment. For example, a circuit board manufacturer can replace solvent-based products with water-based flux and simultaneously replace solvent vapor degreaser with detergent parts washer.

Installing more efficient process equipment or modifying existing equipment to take advantage of better production techniques can significantly reduce waste generation. New or updated equipment can use process materials more efficiently producing less waste. Additionally, such efficiency reduces the number of rejected or off-specification products, thereby reducing the amount of material which has to be reworked or disposed of. Modifying existing process equipment can be a very cost-effective method of reducing waste generation. In many cases the modification can just be relatively simple changes in the way the materials are handled within the process to ensure that they are not wasted. For example, in many electronic manufacturing operations, which involve coating a product, such as electroplating or painting, chemicals are used to strip off coating from rejected products so that they can be recoated. These chemicals, which can include acids, caustics, cyanides etc are often a hazardous waste and must be properly managed. By reducing the number of parts that have to be reworked, the quantity of waste can be significantly reduced. [15,17]

Volume reduction

Volume reduction includes those techniques that remove the hazardous portion of a waste from a non-hazardous portion. These techniques are usually to reduce the volume, and thus the cost of disposing of waste material. The techniques that can be used to reduce waste-stream volume can be divided into 2 general categories: source segregation and waste concentration. Segregation of wastes is in many cases a simple and economical technique for waste reduction. Wastes containing different types of metals can be treated separately so that the metal value in the sludge can be recovered. Concentration of a waste stream may increase the likelihood that the material can be recycled or reused. Methods include gravity and vacuum filtration, ultra filtration, reverse osmosis, freeze vaporization etc.

For example, an electronic component manufacturer can use compaction equipment to reduce volume of waste cathode ray-tube.

Recovery and reuse

This technique could eliminate waste disposal costs, reduce raw material costs and provide income from scalable waste. Waste can be recovered on-site, or at an off-site recovery facility, or through inter-industry exchange. A number of physical and chemical techniques are available to reclaim waste material such as reverse osmosis, electrolysis, condensation, electrolytic recovery, filtration, centrifugation etc. For example, a printed-circuit board manufacturer can use electrolytic recovery to reclaim metals from copper and tin-lead plating bath.

However, recycling hazardous products has little environmental benefit if it simply moves the hazards into secondary products that eventually have to be disposed of. Unless the goal is to redesign the product to use nonhazardous materials, such recycling is a false solution. [15,17]

2.5.1 E-waste Management System in Bangladesh

In Bangladesh, there exists no systematic arrangement for e-waste management. The collection, dismantling, recovery and recycling of e-waste is mainly done by informal sectors following manual and crude procedure. Since there is no law or rule regarding e-waste management and due to the unawareness of consumer, most of the e -waste remain uncollected and they end up in the landfill site along with other solid wastes. According to a study conducted by ESDO (2016) showed that for fully damaged electronic devices, 50% of waste is disposed of and for partially damaged equipment, about 90% get repaired in Bangladesh.[15,17]

Figure 14 : recycling of old computer in Dhaka city informal sector

The e-waste management system exist in Bangladesh is presented in Figure 14. E-waste Importers also source the materials from abroad at a cheap price and sell them in the local market. Refurbishers use working components from these waste electronics to restore out-of-service local e-waste to service conditions. Products which cannot be refurbished are dismantled, scavenged for value metals and dumped in landfills (Lepawsky, 2011). The E-waste industry of Bangladesh is concentrated in a few locations in Dhaka: dismantling activities take place in Elephant Road, Gulistan, Kotwali and Motijheel. Metals, plastics and glass are moved to Lalbagh and Kotwali for reconfiguration into household goods like plastic containers and cutlery. Kotwali is the recipient of precious metals such as gold, which are sold wholesale to the jewelry sector for production. Open burning, dumping of e-waste in landfills and manual desoldering of circuit boards are common techniques used by informal recyclers to extract value metals such as copper from the circuit boards (Karim et al., 2014). Burning is highly inappropriate as it releases lots of toxic heavy metals and unburnable, insoluble plastics into the environment (Berkhout, 2004).

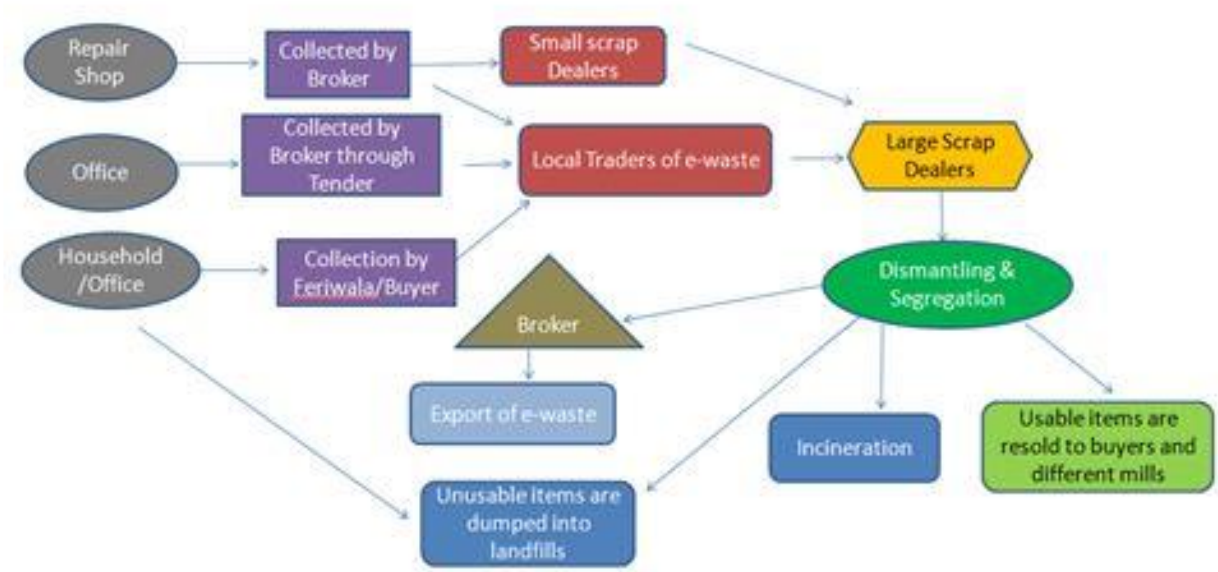


Figure 15 : E-Waste Flow Diagram in Bangladesh

The value addition occurs to the e-waste stream by means of repairing, remanufacturing and dismantling. Hence, it could be said that e-waste in Bangladesh is not necessarily treated as "waste" but as products with enough remaining utility to constitute an entire industry. Formalization of this highly potential industry will ensure worker safety, create more jobs, add revenue to the state coffers and contribute to sustainable development practices in the country. The success of any e-waste recycling initiative depends on the awareness of the consumers. Consumers are an integral part of the recycling process, either in paying an Advanced Recycling Fee at the time of purchase of electronic devices or disposing the e-waste at designated sites. Ahmed (2011) comments that while the awareness level about e-waste situation is very low in Dhaka households, there is a surprisingly high willingness to pay for e-waste disposal arrangements. A survey was conducted among 185 households across 90 wards in Dhaka.

2.5.1 E-waste Management System in Developed Countries

Currently developed countries are giving top priorities in managing e-waste, realizing its fast generation and threat to environment and human health. As a result, they have been developing policies and systems to confront the problem, some of which are becoming ever more sophisticated.

European countries, in particular, have developed e-waste systems that rely heavily on the principle of Extended Producer Responsibility (EPR). EPR stipulates that the manufacturer of an electrical or electronic device bears responsibility for that product beyond the initial sale. This is a core principle of the European Union's Waste Electronic and Electrical Equipment (WEEE) Directive, which outlines the producer's responsibility to manage the collection and recycling of these products. Crucially, this principle requires the producer to assume the cost of the recycling. Thus, producers of electrical and electronic devices in Europe have a financial interest in the life cycle of these products and thereby they are emphasizing the recycle and recovery options. The e-waste system being developed in Europe, in particular, involves not only national governments, producers and recyclers, but also consumers, retailers and municipalities.[18]

For example, in France, manufacturers can choose to dispose the end-of-life products by themselves or financially contribute to eco-organizations to do that on their behalf. The latter is the more popular option. There are 3 such eco-organizations – *Ecosystems*, *Eco-logic* and *ERP* (European Recycling Platform). [18]

There are two different approaches to collecting these wastes: the first has individuals deliver e-waste to collection points inside cities. There are more than 22,900 collection points in France, which are main players in collection process. Eco-Logic, Eco-Systems and

Figure 16 : E-Waste Management in France (Vadoudi, 2015)

ERP manage these points and deliver waste to recovery centers. The second approach involves producers or individuals using out-of-town recovery centers. There are more than 4500 centers in France for the second approach (Agence de l'Environnement et de la Maîtrise de l'Énergie, 2014). The material and financial flow are illustrated in Figure 17.

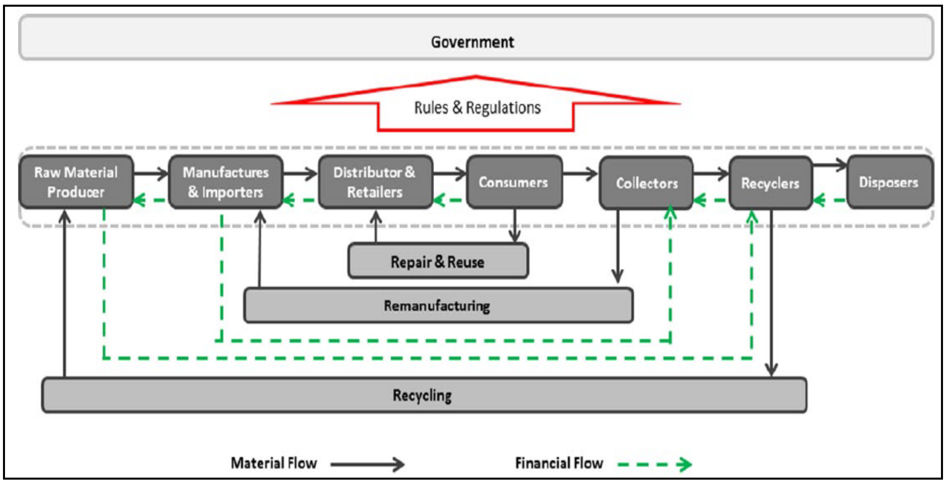


Figure 17 : Material and Financial flow of e-waste management in France (Vadoudi, 2015)

Required finance for day-to-day functioning of the system (for collection, transport and recycling/disposal) is generated from different taxes, which have been applied since November 2006 (CNRS, 2015). Producers pay a fee for each product they supply onto the French market to their nominated E-waste. The fees vary according to the products and E-waste. A standard percentage increase and decrease is applied to the product fee for six specific products based on specific design for dismantling, recovery and reuse criteria. Developing these criteria were based on three fundamental principles: life cycle and durability criteria, hazardous material content and recycled content. The smooth functioning of the system is ensured by DREAL (directions régionales de l'Environnement, de l'aménagement et du logement) (Ministry of Sustainable Development, 2015), a unified regional level of the Ministry of Sustainable Development that was established in December 2007. These government agencies like DREAL, which handle environmental affairs, are typically given additional responsibilities associated with supervising system operations. These responsibilities might include collection fees, reimbursing collectors and processors, setting and enforcing treatment standards, enforcing sales bans on original equipment manufacturers who do not comply with take-back system laws and approving processors and collectors to take part in the system. Government entities may be tasked with supervising a single take-back system for an entire region or multiple systems within a region. [17,18]

Australia's e-waste management is guided by the National Waste plan and has at its core the Product Stewardship Act. Like the EU's WEEE directive, producers and importers of electrical and electronic devices in Australia bear a financial responsibility for the life cycle of their products. But coverage under Australia's e-waste system, outside of voluntary schemes, is limited to personal computers, computer accessories and televisions, whereas the EU directive applies to a much broader range of electrical and electronic equipment.

2.6 Value Metal Recovery from Electronic Waste

Country like Japan adopts a different approach, for example, places the majority of the cost on the consumer, who pays a fee when recycling. Some countries, including Japan and Finland, are also making a special effort to encourage the collection and recycling of smaller devices to recover value metal.

2.7 Value metal source

2.7.1 Electronic waste as a secondary source of metals

In addition to all the hazards originating from WEEE, manufacturing of mobile phones and personal computers consumes considerable fractions of the gold (Au), silver (Ag) and palladium (Pd) mined annually worldwide (Hadi et al., 2015). The electronics industry is the third largest consumer of gold, accounting for 12% of the total gold demand (about 282 tons) in 2014 (Schipper and Haan, 2015). Worldwide, more than one million people in 26 countries across Africa, Asia and South America work in gold mining, mostly in unregistered substandard conditions (Mccann and Wittmann, 2015), driven by the demand of this precious metal for electronics.

An illustrative explanation of the role of landfill mining, recycling and urban mining is given in Figure 6. The reintegration of waste and by-products back in the economy strongly relies on the concept of waste as a secondary raw material (Jones et al., 2013). In urban mining of end-of-life (EOL) devices, WEEE is a primary target owing to its high content of valuable critical metals. In addition to being a hazardous waste, WEEE is an important secondary source of metals in the transition to a circular economy. The complexity of WEEE increased with the development of technology as the production of electronic devices relies on a great number of elements. Modern devices consist of up to 60 elements in various mixtures of metals (Bloodworth, 2014). From the recyclers point of view, highly complex alloys pose a challenge to develop efficient metal recovery technologies from WEEE.[19]

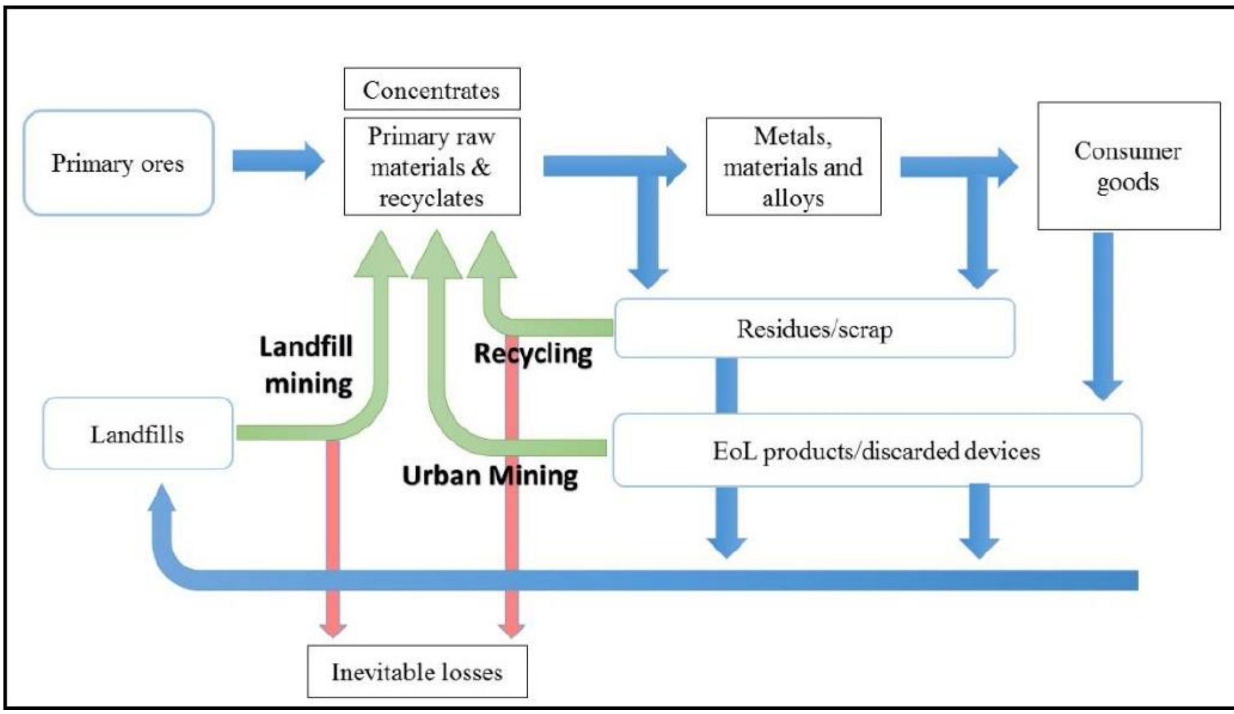


Fig 18 : Loop of Material Flow in a Circular Economy (Jones et al., 2013)

2.7.2 Energy and Resource Conservation

Recycling e-waste for metal recovery is also important from the perspective of saving energy. The U.S Environmental Protection Agency (Office of Solid Waste, 2008) 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. The energy savings for a number of common metals and materials are summarized in Table 10.

Table 10: Recycled materials energy savings over extraction from ores (ISRI, 2003)

Materials	**Energy Efficiency (%)**

Aluminum	95
Copper	85
Iron and Steel	74
Lead	65
Zinc	60
Paper	64
Plastics	>80

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 Precious Metals from electronic scrap, in limited cases are easier than their primary ores (Rankin, 2011) [19]. If Precious Metals and Scarce Elements are unrecovered, it will be a significant loss of precious resource.

2.7.3 Economic Value of Targeted Precious Metals

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%.). 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, Sn, Pb and Zn) from e-waste is a major economic drive due to their associated value.

Weights%	Fe (wt%)	Al (wt%)	Cu (wt%)	Plastics (wt%)	Ag (ppm)	Au (ppm)	Pd (ppm)
TV-board	28%	10%	10%	28%	280	20	10
PCBs	7%	5%	20%	23%	1000	250	110
Mobile phone	5%	1%	13%	56%	1380	350	210
Portable audio	23%	1%	21%	47%	150	10	4
DVD-player	62%	2%	5%	24%	115	15	4
Calculator	4%	5%	3%	61%	260	50	5
Value-share	**Fe**	**Al**	**Cu**	**Sum PMs**	**Ag**	**Au**	**Pd**
TV-board	4%	11%	42%	43%	8%	27%	8%
PCBs	0%	1%	14%	85%	5%	65%	15%
Mobile phone	0%	0%	7%	93%	5%	67%	21%
Portable audio	3%	1%	77%	19%	4%	13%	2%
DVD-player	13%	4%	36%	47%	5%	37%	5%
Calculator	0%	5%	11%	84%	7%	73%	4%

Table 11 : Weight vs. Value Distribution in WEEE (Hagelüken, 2006).

2.7.4 Metal recovery from Printed Circuit Boards

Most of the electronic equipment is installed with printed circuit boards as the main component. As a result, the number of wastes of electric and electronic equipment (WEEE) containing 3% of printed circuit boards is dramatically increasing. The typical composition of PCB is non-metals (plastics, thermosets, glass fiber, ceramics) >70%, copper ~16%, solder ~4%, iron, tin, ferrite ~3%, nickel ~2%, silver 0.05%, gold 0.03%, palladium 0.01%, others (bismuth, antimony, tantalum, etc.) <0.01%. Significant quantities of nonmetallic materials in PCBs (up to 70 wt.%) present an especially difficult challenge for recycling. The nonmetallic materials of PCBs mainly consist of thermosetting plastics (TS), thermoplastics (TP), glass fibers and ceramic fractions. Thermosets cannot be remelted or reformed because of their cross-linked polymeric structure. Incineration is not the best method for treating non-metallic materials because of the presence of inorganic fillers such as glass fiber, which significantly reduces fuel efficiency. Disposal in landfills is the main method for treating non-metallic materials of PCBs, but it may cause secondary pollution and resource-wasting. Since the metallic elements are covered with or encapsulated by various plastic or ceramic materials on printed circuit boards, a mechanical pre-treatment process allowing their liberation and separation is first needed in order to facilitate their efficient extraction with acid or alkali by hydrometallurgical methods. Electronic scrap from printed circuit board can be processed by mechanical methods like stamp, hammer or cutting mill. The value of metals contained in PCB scrap is economic incentives for the recyclers.[19]

The printed circuit board of a typical mobile phone weighs 15-43% by weight. The weight percentage of precious metals in PCB is less than 1% but its momentary value among PCB material is 80%. The presence of metals in printed circuit boards has been studied by various authors with different methodologies. The metals in mobile phones may be categorized as precious metals (Au, Ag), platinum group metals (Pd, Pt, Rh, Ir and Ru), base metals (Cu, Al,Ni, Sn, Zn and Fe), hazardous metals (Hg, Be, In, Pb, Cd, As and Sb), scarce or trace metals (Te, Ga, Se, Ta and Ge) as pointed out in Khaliq et al. (2014). The typical medium grade PCB in 2002 contained gold (0.025%), Palladium (0.010%), silver (0.100%), Copper (16%), Tin (3%), Lead (2%), Nickel (1%), Aluminum (5%), Iron (5%) and Zinc (1%) respectively (Chatterjee, 2012). One study reveals the PCB feed by weight percentage as gold (0.039%), silver (0.156%), Palladium (0.009%), Copper (18.448%), other metals (9.35%) and non-metals (70%) (Chehade et al.,2012). The composition of PCB varies from model to model of each brand. Many studies focus on recoverable metals in mobile PCBs. It is revealed that the concentration of precious metals in one-ton mobile phone is 3573 g silver, 368 g gold and 287 g palladium respectively (Chancerel et al., 2009). A study found that 1000 million units of cell phones contain 250 tons silver, 24 tons gold, 9 tons Palladium and 9000 tons Copper (Hageluken, 2008). Another study revealed that 1000 kg of PCBs contain recoverable metals such as gold (279.93 g), precious metals – Pt, Pd, In (93.31 g), Copper (190.512 kg), Aluminium (145.152 kg), Lead and tin (30.844 kg) and silver (450 g) (Kumar and Shah, 2014). It is also predicted that 6000 mobile sets weighing one ton approximately would contain 130 kg Copper (United Nations University, 2009). Hence, the metals of interest for recovery in mobile phone are copper, gold, silver, palladium and ferrous metals.

2.7.5 Metal Recovery through metallurgical processes

There are three main technologies for recovering metals from WEEE – pyrometallurgy, hydrometallurgy, biohydrometallurgy. The vast majority of the industrial metal recovery processes for WEEE use physical pretreatment and pyrometallurgical processes, and to a smaller extent hydrometallurgical processes (Cui and Zhang, 2008). Physical separation is a common technique to process all types of WEEE. However, the one size-fits-all approach proves inefficient for such a complex type of waste. Moreover, high energy consumption, relatively low efficiency, as well as loss and contamination by metals are important obstacles in physical processing of WEEE for metal recovery (Chancere et al., 2009; Zhang et al., 2015). [19,20] Thermodynamic limitations necessitate novel liberation and separation strategies, particularly for the metals embedded in the non-metal components (Ueberschaar and Rotter, 2015). Pyrometallurgical processes, encompassing smelting and pyrolysis, require the heating of WEEE at very high temperatures (up to 1500°C) to separate materials. Hydrometallurgical treatments comprise the use of leaching agents in aqueous solutions, such as strong acids (e.g. sulfuric acid, nitric acid, hydrochloric acid) and/or bases (e.g. sodium hydroxide and sodium hypochlorite) often applied together with oxidants (e.g. hydrogen peroxide and ferric iron) and complexing agents (e.g. cyanide and thiosulfate). Biohydrometallurgy is based on similar principles where lixiviants are biologically produced. The leaching rates of hydrometallurgical processes are relatively faster than those of bio hydrometallurgical processes, whereas biological processes are more environmentally friendly and cost-effective (Ilyas and Lee, 2015). Microbes that can adapt to toxic conditions, e.g. eventually increase their metal tolerance, are used in bio hydrometallurgical processes (Navarro et al., 2013).[20]

The three main techniques are discussed briefly as follows and a comparison is made in the Table later. Mechanical pre-treatment serves to prepare and optimize the e-waste feed for subsequent metallurgical treatment.

2.7.5.1 Pyrometallurgy

Smelting: Smelting is currently the industrial best available technology (BAT) and a few full-scale WEEE processing plants are already in operation. At Boliden Rönnskär smelters (Skelleftehamn, Sweden), discarded PCB are directly fed into a copper converter to recover Cu, Ag, Au, Pd, Ni, Se and Zn (Ghosh et al., 2015). At Umicore's integrated metal smelter and refinery in Hoboken (Belgium), PCB are first treated in an IsaSmelt furnace to recover precious metals. It is further refined with hydrometallurgical processes and electrowinning (Zhang and Xu, 2016). In the Ausmelt TSL reactor of Outotec (Espoo, Finland), WEEE is processed in copper/lead/zinc smelters in a combined process to recover Zn, Cu, Au, Ag, In, Pb, Cd, and Ge (Ebin and Isik, 2016).

Disadvantages of Smelting: (i) high energy consumption (ii) low selectivity towards desired metals (iii) emission of SO_2 and liberation of toxic heavy metals (Cappuyns et al., 2006; X. Zhang et al., 2012). (iv) emission of dioxins due to presence of flame retardants (Mäkinen et al., 2015) (v) unsuitable for a large range of WEEE due to low calorific value (Sun et al., 2015)

Pyrolysis: Pyrolysis of discarded PCB, carried out at elevated temperatures up to 900°C in the presence of inert gases, generates 23% oil, 5% gases and 70% metal-rich residue (Hall and Williams, 2007). As such, discarded LCD panels are subjected to pyrolysis in ceramic ovens at 700°C, and the organic-rich polarizing film is converted into pyrolysis oil and gas, whereas the liquid crystal is eliminated through deformation and detoxification of the hazardous substances under high temperature conditions (Ma and Xu, 2013).

Disadvantages of Pyrolysis: (i) high energy and reagent consumption (ii) formation of toxic compounds at high temperatures [20].All in all, even though pyrometallurgical techniques are highly economical, they have some glaring disadvantages which have slowly driven them out of use. These are as follows: -

- Recovery of plastics is not possible because plastics replace coke as a source of energy.
- Iron and aluminum recovery are 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 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 processing and the thermodynamics of possible reactions will be difficult.

2.7.5.2 Hydrometallurgy

Hydrometallurgical metal recovery processes involve an oxidative leaching for the extraction of metals, followed by separation and purification procedures (Schlesinger et al., 2011). It has advantages over pyrometallurgy such as lower toxic residues and emissions, and higher energy efficiency. However, these processes still pose a threat due to the use of large amounts of toxic, corrosive and flammable reagents and the generation of high volumes of effluents and other solid wastes (Tuncuk et al., 2012).[23,24]

Oxidative Acid Leaching : Acid leaching of metals from WEEE has been investigated using various acids and oxidants, or mixtures thereof. It is an essential process when extracting valuable metals from PCB (Ghosh et al., 2015), indium from ITO glass (Zhang et al., 2015) and neodymium from HDD (Li et al., 2009). In oxidative acid leaching, the important parameters are temperature, concentration and contact time with the former being the most important. The leaching of metals in various oxidative acidic media has been investigated for their effectiveness in metal recovery from waste PCB, including hydrochloric acid (Jha et al., 2012), sulfuric acid (Kumar et al., 2012), nitric acid (Joda and Rashchi, 2012), sodium hypochlorite (Akcil et al., 2015), thiosulfate (Ha et al., 2010), thiourea (Jing-ying et al., 2012) and halides (Syed, 2012).[21,22]

Cyanide leaching of copper: The feasibility of using alkaline cyanide solutions for leaching copper, gold, and silver from Cu/Au/Ag ores is analyzed and compared with acid leaching. A key operation in the cyanide leaching circuit proposed is a SART process (Sulphidization, Acidification, Recycling and Thickening), which is being used presently at many gold plants to recover cyanide and to remove and recover CN-soluble copper contained in the ore, thus reducing cyanide consumption. Additionally, operational evidence exists in gold cyanidation plants showing that very low-grade copper can be dissolved, which supports the thesis that under certain conditions the cyanide process might be able to dissolve lower copper contents, achieving lowers residual copper in tails than in the acid leaching process. A technical and economical trade-off analysis of the cyanide and acid leaching processes is presented in order to establish under what conditions cyanide copper leaching is a competitive alternative against copper acid leaching.[21]

Thiosulfate leaching of copper: Thiosulfate (S2O32−) is a non-toxic alternative to cyanidation for primary (Grosse et al., 2003) and secondary (Akcil et al., 2015) ores. S2O32− leaching attracted interest as an alternative valuable metal leaching agent owing to its environmental advantages (Zhang, 2008). Thiosulfate leaching can be considered as a non-toxic process, and the copper dissolution rates can be faster than conventional cyanidation (Ayumore and Muir, 2001). In alkaline or near neutral solutions of thiosulfate, Cu dissolves in the presence of a mild oxidant. Sodium thiosulphate with hydrogen peroxide can do the job of extracting Cu by producing copper sulphate solution. Moreover, the process could become more cost-effective than cyanidation (Abbruzzese et al., 1995; Ayumore and Muir, 2001). Several studies investigated the leaching of precious metals from waste PCB, such as the effect of the $S_2O_3^{2-}$concentration, alkalinity agent (e.g. NH4OH) and catalyzing agent (e.g. Cu2+ions) (Ficeriová et al., 2011; Ha et al., 2010; Petter et al., 2014). Similar to cyanide, dissolved copper may adversely affect the leaching process due to the decomposition of $S_2O_3^{2-}$.The reaction then becomes relatively inefficient and slow at ambient temperatures. High consumption of the leaching agent, its chemical instability and low cost-effectiveness are the main bottlenecks of this process to be applied to WEEE (Akcil et al., 2015).[23]

Metal Chloride leaching of copper: With the metal chloride family of echants, the first and most famous member is Ferric Chloride. Chemistry works by oxidizing the copper-to-copper chloride while the ferric chloride is reduced to ferrous chloride. A great advantage is it does not decay in storage and an unused echant can last indefinitely in an airtight container. Recycling is possible but requires extra chemicals and a lot of effort. It might be more straightforward to dispose of it. [24,25]

Galvanic sludge: Galvanic sludge belongs to hazardous waste because of various heavy metals like Cu, Zn, Cd, Cr and other substances like cyanides, fluorides etc. Economic treatment is very difficult because of chemical heterogeneity of galvanic sludge. The focus of this investigation was the hydrometallurgical treatment of complex galvanic sludge containing Cu, Zn, Cr, Cd, Ni, Fe, Si, Ca and other elements. The aim of experiments was to verify the leaching behavior of copper, zinc and chromium in sulphuric acid solution of concentration range of 0.01-1M H2SO4. Based on experimental results it was confirmed that maximum copper and zinc extraction 90 % and 85 % could be reached after 5 minutes at room temperature by using of acid concentration of 0.25 M and solid to liquid ratio 1:40. The extraction of chromium did not exceed value of 25 % regardless of leaching conditions. It was also shown that copper and other metals extraction decreased when S:L ratio increased. The highest extraction of Cu 95 % by using of 0.5 M HSO4 was achieved. The second part was focused on recovery of copper from leaching solution by selected separation process- cementation on an iron plate. The cementation process proved at given conditions as a possible way of how to selectively obtain copper from the complex polymetallic leaching solutions. The product with minimum copper content of 96 % and cementation efficiency more than 84 % at the temperature of 20 °C after 24 hours without stirring was achieved.[22]

There are also some other hydrometallurgical processes of copper recovery like – Ammonical Pressure Leach Process, Arbiter Ammoniacal Leach, R-L-E Process, Lime R-L-E Process, Cymet Process.

Tin-Bearing Alloys and Tin Anode Slime: Global tinned steel sheet consumption is more than 18 MT's, in which the average tin content is approximately 0.5–2 wt. %. Although the service life of tinned steel is approximately 20–50 years, the recycling of tin from used tinplating and tin- bearing alloy wastes has become the focus of many researchers. [26-33] Electro-alkali dissolution and alkali detinning are often used for recovering tin from these wastes.

Before electro-alkali dissolution, the recyclable tin-plated steel sheet is first cleaned and then used as the anode, whereas sheet iron is used as the cathode. Both sheets are placed in a Na_2SnO_3 solution, and then a direct current is passed through the electrolyte at room temperature. [26-29] The anodic reactions can be expressed as Eqs. 1 and 2 in Table.

Tin exists in the form of $Sn(OH)_6^{2-}$ in the alkaline solution, in which tin exists in +4 oxidation state. The evolution reaction at the cathode is expressed as Eq. 3 in Table, and sponge tin is obtained at the cathode with a purity of more than 95 wt.%.

An alkali detinning method has been proposed to separate tin from Fe-Sn alloys because metallic tin reacts with NaOH, whereas metallic iron does not. During this process, a hot NaOH solution (40–100°C) is used for leaching, and O_2, H_2O_2, or $NaNO_3$ is used as an oxidizing agent (as Eqs. 4 to 6 in Table)[30-33]. Finally, a high-purity Na2SnO3 solution is obtained after separation and purification processes and can be used as an electroplate or electrolyte solution.

A vacuum evaporation process is used to address complex tin-bearing alloys containing volatile metals such as Bi, In, Pb, and As. It is a physical process that separates different metals with various evaporation temperatures. Yang et al. [34] have reported that a vacuum distillation was conducted for Sn–Pb alloys and Sn-Zn alloys at a distillation temperature of 900–1100°C and a chamber pressure of 20–50 Pa. The recovery of tin was higher than 99 wt.%, and the content of impurities in the metallic tin was no more than 0.05 wt.%. [34,43,44]

Tin anode slime is a by-product of the electrolytic refining process of crude tin. The standard electrode potentials of Sb, Bi, Cu, Ag, and Au are substantially higher than that of Sn; these metals are in the form of insoluble phases and finally precipitate during the electro-refining process.[45,46] The metals Cu, Bi, Sb, Ag, and Au have great economic value, so an oxidation roasting process in air at 600–900°C is always conducted first to convert metallic tin to acid-insoluble SnO_2, and then Pb, Ag, and Cu can be leached and recovered from the oxidized products.[47,48] SnO_2 is finally enriched in the leaching residue and collected for the smelting process.

Han et al. [69] have used an alkaline pressure oxidative leaching technique to pretreat Sb-rich tin anode slime. Under the optimal conditions of a concentration of 2.5 M NaOH, a temperature of 130°C, and an oxygen partial pressure of 1 MPa, the extraction ratio of tin reached 92%. Meanwhile, antimony, bismuth, and silver hardly dissolved into the NaOH solution and were enriched in the residue. [49]

Electric-Wastes: Approximately 50 MT's of wasted electrical and electronic equipment (WEEE) including printed circuit boards (PCBs) are generated yearly. [35-37] Waste PCBs mainly consist of approximately 28% metallic, 23% plastic, and 49% ceramic materials. The multi-metal fractions contain Cu, Sn, Pb, Sb, and precious metals (Au, Ag, Pt, etc.). [37,38]

A pyrolysis process is conducted in air or the absence of oxygen to avoid the formation of highly toxic dioxins and furans. Unsaturated hydrocarbons are then obtained during the multilevel-cleavage reactions. [35-37]. Afterward, the concentrated residue with multi-metals is subjected to acid leaching using a sulfuric, hydrochloric, or nitric acid solution, which aims to recover copper and tin first. An oxidizing agent of O_2, $FeCl_3$, H_2O_2, or $SnCl_4$ is also used to accelerate the leaching process, and the main reactions are expressed as Eqs. 8 to 11 in Table. [35-38]. The precious metals are insoluble and are enriched in the leaching residue, and only Sn^{2+}, Cu^{2+}, Pb^{2+}, and Sn^{4+} exist in the leaching solution. In addition, both Cu^{2+} and Pb^{2+} can be removed as sediments by adding metallic tin and Na_2S to the solution, and the reactions are depicted as Eqs. 12 to 14. Finally, the tin-bearing solution is prepared for use as an electrolyte (a Na_2SnO_3 solution), or SnO_2 is precipitated out for the smelting process (as Eqs. 15 to 18 in Table).

Tin-Bearing Slag and Tin Middling: Volatilization processes are the most efficient methods to recover tin from middle-grade tin materials (tin mine middling, tin slag, and low-tin-grade hardhead).[33–35] Sulfide and chloride volatilization processes have been successfully applied on an industrial scale. SnO_2 is reduced to SnO by a solid or gaseous reductant, and then it reacts with a sulfurizing reagent (pyrite or sulfur) or a chlorination reagent ($CaCl_2$, HCl, Cl_2, etc.) to form SnS or $SnCl_2$. The stannous sulfide or chloride can be volatilized easily at a higher roasting temperature (1000–1200°C) in a rotary kiln or fluidized bed furnace. Later, the dust is re-oxidized, and SnO_2 is collected from the dust according to Eqs. 21 to 22 in Table . The tin recovery can reach as high as 99 wt. %, and the tin content in the final slag is less than 0.1 wt. %. Nevertheless, the iron oxides are easily reduced to FeO and then react with acid gangue at a higher roasting temperature, which is impossible to recover from the slag.

Types of resources	State of tin	Method	Conditions	Products	Reaction equations
Tin-bearing alloys and tin anode slime	Metallic tin or tin alloys	Electro-alkali dissolution[a]	Electrolysis in NaOH, Na_2SnO_3 or Na_2CO_3 solution	Sponge tin	$Sn + 3OH^- = HSnO_2^- + H_2O + 2e^-$ (1) $HSnO_2^- + 3OH^- + H_2O = Sn(OH)_6^{2-} + 2e^-$ (2) $Sn(OH)_6^{2-} + 4e^- = Sn + 6OH^-$ (3)
		Alkali detinning[a]	Leaching in NaOH solutions at 25–100°C	Na_2SnO_3 solutions	$Sn + 2NaOH + O_2 = Na_2SnO_3 + H_2O$ (4) $4Sn + 6NaOH + 2NaNO_3 = 4Na_2SnO_3 + 2NH_3$ (5) $Sn + 2NaOH + 2H_2O_2 = Na_2SnO_3 + 3H_2O$ (6)
		Vacuum evaporation[a]	Vacuum distillation at 900–1100°C, 20–50 Pa	Crude tin	$Sn_{(l)} = Sn_{(g)}$ (7)
Electric-wastes	Metallic tin	Selective leaching[a]	Leaching by $FeCl_3$ or $SnCl_4$ solutions	Preparation electrolyte or SnO_2	$Sn + 2H^+ = Sn^{2+} + H_{2(g)}$ (8) $Sn + 2H_2O_2 + 4H^+ = Sn^{4+} + 4H_2O$ (9) $Sn + 4Fe^{3+} = Sn^{4+} + 4Fe^{2+}$ (10) $Sn + Sn^{4+} = 2Sn^{2+}$ (11) $Sn + Cu^{2+} = Sn^{2+} + Cu$ (12) $Cu^{2+} + S^{2-} = CuS_{(s)}$ (13) $Pb^{2+} + S^{2-} = PbS_{(s)}$ (14) $Sn^{2+} + 2OH^- = Sn(OH)_2$ (15) $Sn^{4+} + 4OH^- = Sn(OH)_4$ (16) $2Sn(OH)_2 + O_2 = 2SnO_2 + 2H_2O$ (17) $Sn(OH)_4 = SnO_2 + 2H_2O$ (18)
Tin-bearing slag Tin middlings Tin-bearing iron concentrates	SnO and Sn SnO_2 SnO_2 and lattice Sn^{4+} in magnetite	Sulphide and chloride volatilization[a]	Roasted with sulfurizing or chlorination reagents at 1000–1200°C	Smoke dust (SnO_2) for smelting	$SnO_2 + CO + CaCl_2 = SnCl_2 + CO_2 + CaO$ (19) $3SnO_2 + 4FeS = 3SnS + 4FeO + SO_2$ (20) $2SnCl_2 + 2H_2O + O_2 = 2SnO_2 + 4HCl$ (21) $SnS + 2O_2 = SO_2 + SnO_2$ (22)
		Reduction sintering[c] Reduction volatilization[b]	Sintering with 10–15 wt.% coke Roasted under weak CO-CO_2 atmosphere at 950–1050°C	Smoke dust (SnO) for smelting	$SnO_2 + CO = SnO + CO_2$ (23)
Tin-bearing tailings	SnO_2 and lattice Sn^{4+} in magnetite	Mineral processing[a]	Gravity concentration, flotation	Tin middlings	–
		Roasting-cohesion-magnetic separation[c]	Magnetizing roasting, magnetic separation, flotation	Tin middlings	–
		Calcified roasting[c]	Roasted with CaO under 5–10% CO at 825–875°C	Tin middlings	$SnO_2 + 2CaO = Ca_2SnO_4$ (24) $Fe_{3-x}Sn_xO_4 + 2xCaO + CO_2 = xCa_2SnO_4 + (3 - x)/x \cdot Fe_3O_4 + (2X/3) \cdot CO$ (25)

Summary of tin recovery methods from tin-bearing secondary resources

Table 12 : Summary of hydrometallurgical recovery of precious metals from WEEE

Investigators	Leaching agent	Process conditions	Recovered metals
Park and Fray [41]	Aqua regia	Ratio of metals to leachant = 1:20 g/mL	Au, Ag and Pd
Sheng and Estell [49]	HNO_3 (1st stage), epoxy resin (2nd stage), and aqua regia (3rd stage)	Extraction was carried out in the three stages (self agitation)	Au
Quinet *et al.* [50]	H_2SO_4, chloride, thiourea and cyanide leaching	Leaching & metals recovery by cementation, precipitation, ion exchange and carbon adsorption	Au, Ag, Pd and Cu
Chielewski *et al.* [51]	HNO_3 and aqua regia	Roasting of e-waste in the presence of carbon; leaching with HNO_3 and aqua regia; and solvent extraction with diethyle malonate	Au
Zhou *et al.* [52]	HCl, H_2SO_4 and $NaClO_3$	Combustion of e-waste at 400–500 °C followed by leaching	Ag, Au and Pd
Kogan [53]	HCl, $MgCl_2$, H_2SO_4 and H_2O_2	Dissolution of e-waste in different solvents and leaching conditions; and recovery of metals in stages	Al, Sn, Pb and Zn (1st stage), Cu and Ni (2nd stage), Au, Ag, Pd and Pt (last stage)
Veit *et al.* [11]	Aqua regia and H_2SO_4	Mechanical processing and then dissolution of e-waste in different solvents	Cu
Mecucci and Scott [54]	HNO_3	Electrochemical deposition of Cu at cathode from solution	Pb and Cu

Hydrometallurgical processes have the following disadvantages which have prevented their widespread adoption: -

- Slow and time-consuming
- 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 can contaminate nearby waterbodies, thus jeopardizing aquatic wildlife and human consumers
- Temperature control in galvanic sludges is very important. Otherwise, it will not be effective in leaching copper.

- The use of thiourea leachants 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 copper 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.

2.7.5.3 Biohydrometallurgy

Biohydrometallurgy, the use of microbes to process metals, is an efficient technology to produce metals from primary ores. In the context of metal processing, biohydrometallurgy is defined as a blend of biotechnology and metallurgy (Ilyas et al., 2015). It is an established technology to process many metals including copper (Cu), tin (Sn), gold (Au), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), molybdenum (Mo), cadmium (Cd), and uranium (U) (Watling, 2015). More than 15% of the total annual 15 Mtons of Cu, 2.35 ktons of 5% Au, along with a small fraction of Ni and Zn are produced using biohydrometallurgical routes (Johnson, 2014; Schlesinger et al., 2011). Biohydrometallurgy uses acidophilic bacteria, cyanogenic heterotrophs and/or acid-producing heterotrophs to selectively recover metals from waste streams. Full scale biomining applications compensate high initial capital investments with lower operating costs over a long period (Brierley and Brierley, 2013). Furthermore, biotechnology relies on natural material cycles in more environmentally friendly processes than conventional metal extraction techniques. Biotechnological approaches will play a significant role in the treatment of waste for metal recovery in the future (Lee and Pandey, 2012). Despite the relatively slower kinetics compared to conventional methods, bioleaching has matured into a well-developed technology operated in advanced engineered systems. Biomining of low-grade ores, and in particular Cu, made a useful case study for bioprocessing of metals, which is expected to be the future trend for non-sulfide metal-rich wastes such as WEEE (Orell et al., 2010).

Finally, Table 13 compares pyrometallurgy, biohydrometallurgy and hydrometallurgy in terms of different feasibility criteria.

Table 13: Overview of Pyrometallurgy, Hydrometallurgy and Biohydrometallurgy

Parameters	**Pyrometallurgy**	**Hydrometallurgy**	**Biohydrometallurgy**
Environmental Impact	High, due to gaseous emissions	Moderate, due to toxic chemicals	Low
Selectivity	Low, only a fraction of metals	High	High
Economics	Capital intensive, low job creation	Low capital, high operating cost	Low investment and operating costs
Social acceptance	Low	Medium, some toxic reagents and end products	High, cleaner processes and auto-pollution control
Energy	Very high	Low, ambient conditions	Low to none
Final residue	High	Low	Low to none
Process conditions	Harsh thermal treatment conditions	Harsh corrosive acids	Safe conditions, low to non-toxic chemicals
Level of advancement	High, established full-scale technology	Medium, many pilot scale demonstrations	Low TRL, no pilot scale study
Advancement requirement	Abatement of environmental impacts	Selectivity towards individual metals, scale-up studies	Fundamental research, scale-up studies
Feasible applications	Low, only high grade WEEE	High, all metals and their alloys	Medium, restrictions due to toxicity on bacteria

Chapter 3

EXPERIMENTAL PROCEDURE

3.1 PCB Collection and Separation

For our experiment of recovering precious metals from PCB, samples of PCB of mobile phones of different companies were collected from Puran Dhaka. They sell PCB of different mobile companies. They sell it by weight. A wide range of mobile brands lke Nokia, Samsung, Symphony, Alcatel, Tencent, Gionee, Tecno etc. were collected. The samples were divided into different batches according to their brands. Some PCB were too damaged to take it for further proceeding. They were separated from others and discarded. Most of them were made in China or Korea. They have an average weight of 11-12g, and they are 3-4 inches in length on average. We collected 1kg PCB from Bakhshibazar, Puran Dhaka.

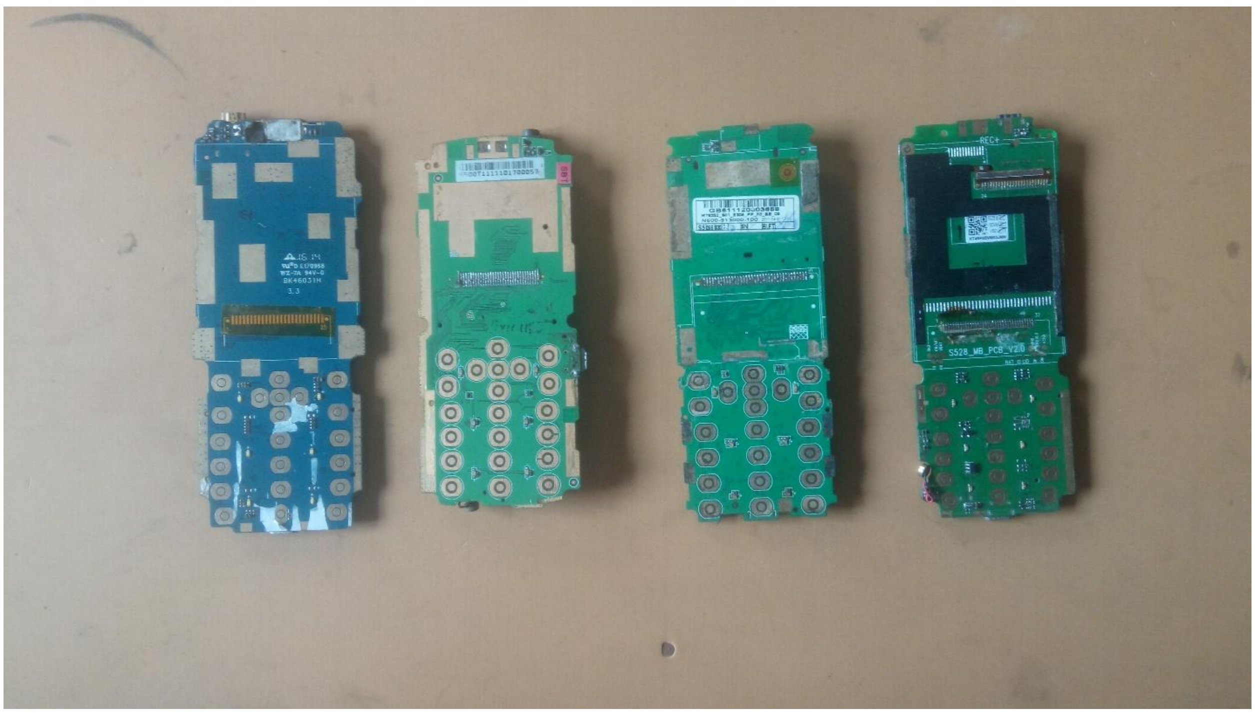


Figure 19 : collected PCB after seperation

3.2 Weight measurement of the spent

The collected PCBs were dismantled manually. The plastic cover of the batteries was removed by using a sharp cutting edge. The different component parts were carefully separated, and main PCB boards were taken. Then these were weighed carefully. The weight proportions of five PCB were taken. In some procedures, we broke each PCB board into two pieces for a better dissolution process.

3.3 Metal Powder Collection

For another process of recovering metals, instead of using PCB board we took metal powder. We collected metal powder from Azizu Trading Co. Azizu Trading Co., Bangladeshi's largest licensed & authorized electronic waste recycler started operations since 2008, is engaged in handling, recycling and reusing of Waste Electrical and Electronic Equipment (WEEE) in friendly way. They create an opportunity to transfer waste into socially and industrially beneficial raw materials like valuable metals, plastics and glass using simple, cost efficient, home grown, environmentally friendly technologies suitable to Indian Conditions. They collect PCB boards and separate metal from it and ground them into smaller particles like powder. We collected metal powder from them. To recover valuable metal from metal powder is easier than recovering metal from mobile's PCB board.

Figure 20 : collected metal powder

3.4 Weight measurement

From our collected metal powder, we took 12-15g powder for subsequent procedure.

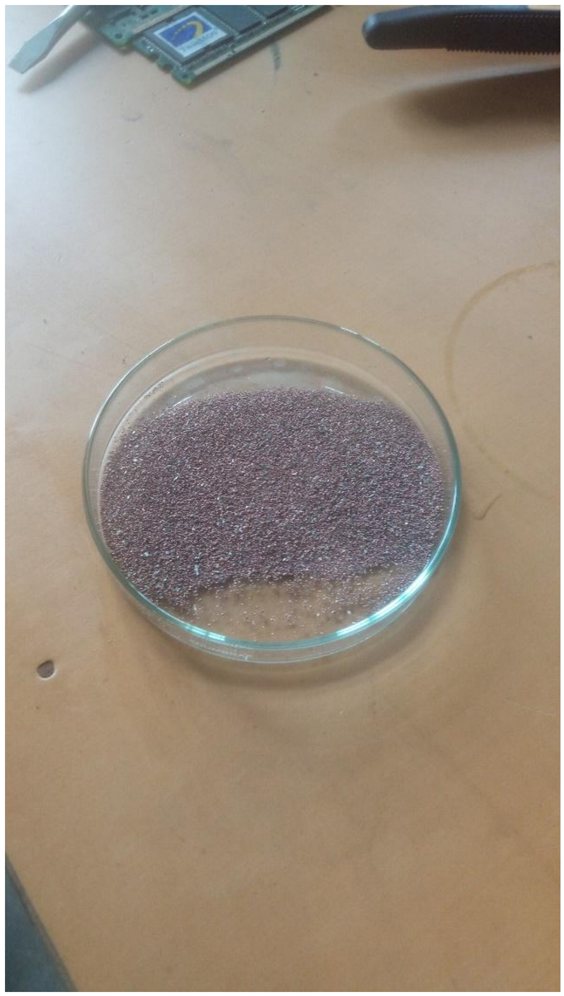


Figure 21 : weight measurement of collected powder

3.5 Procedure for AAS analysis

3.5.1 Preparation of aqua regia

For aqua regia preparation, we took hydrochloric acid fuming 37% and nitric acid 65%.

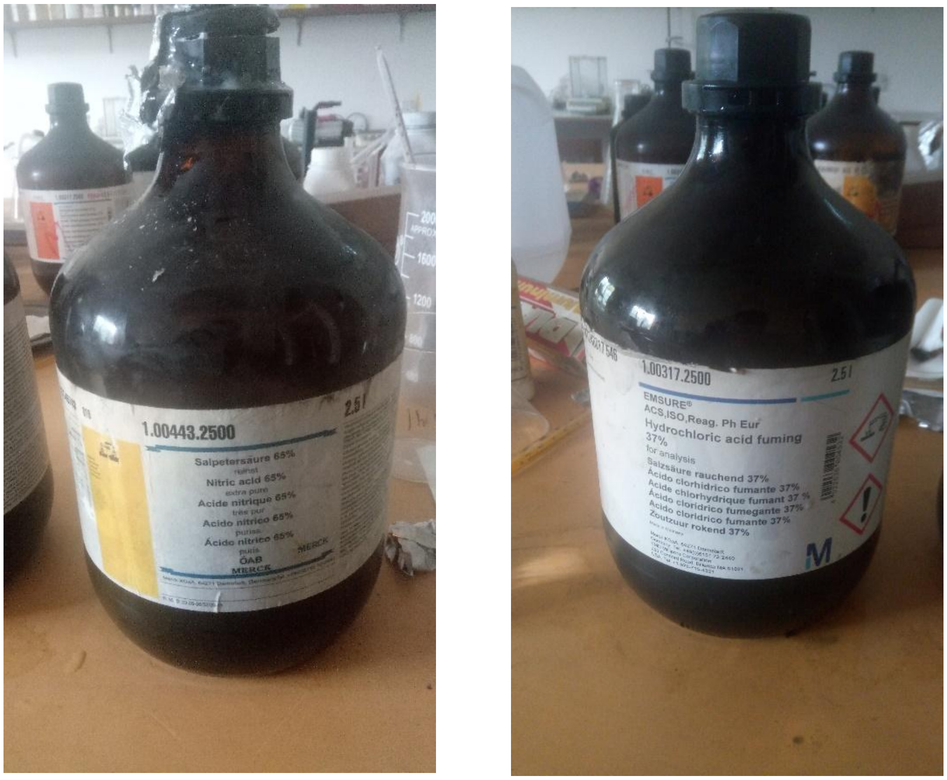


Figure 22 : nitric acid (65%), hydrochloric acid fuming (37%)

Then we prepared aqua regia following the ratio of 3 mol HCl and 1 mol HNO_3. The mixture then turned into orange producing so much fume. So, the reaction was done under exhaust fan.

Figure 23: aqua regia

Figure 24: reaction under exhaust fan

3.5.2 Dissolving PCB board into aqua regia

Before dissolving PCB boards into aqua regia, they cleaned by removing stickers on them and removing darts. Then each piece was dropped into the solution after 2-3 minutes as the reaction was vigorous. We took 10 Chinese mobile PCB boards for this process.

Figure 25: dissolving PCB into aqua regia solution

As it is a toxic process, precautions were taken. After dissolving PCB board, the solution was kept under exhaust fan for 6 hours. After that, the PCB boards were taken out from the solution. The solution was dark brownish green type color. And complete dissolution was achieved.

Figure 26: solution after complete dissolution

Figure 27: PCB taken out after dissolution

3.5.3 Filtering

The solution was then filtered using filter paper.

Figure 28: filtering the solution

3.5.3 Solution sent for AAS analysis

For AAS analysis, we needed a 10ml solution for each metal. A 150ml solution was taken and sent to BCSIR, Dhaka. From the AAS analysis, we found out which metals were present in the solution that means which metal were there in the Chinese mobile PCB board.

জীবনের জন্য বিজ্ঞান

শেখ হাসিনার দর্শন সব মানুষের উন্নয়ন

বাংলাদেশ বিজ্ঞান ও শিল্প গবেষণা পরিষদ (বিসিএসআইআর)

BANGLADESH COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH(BCSIR)

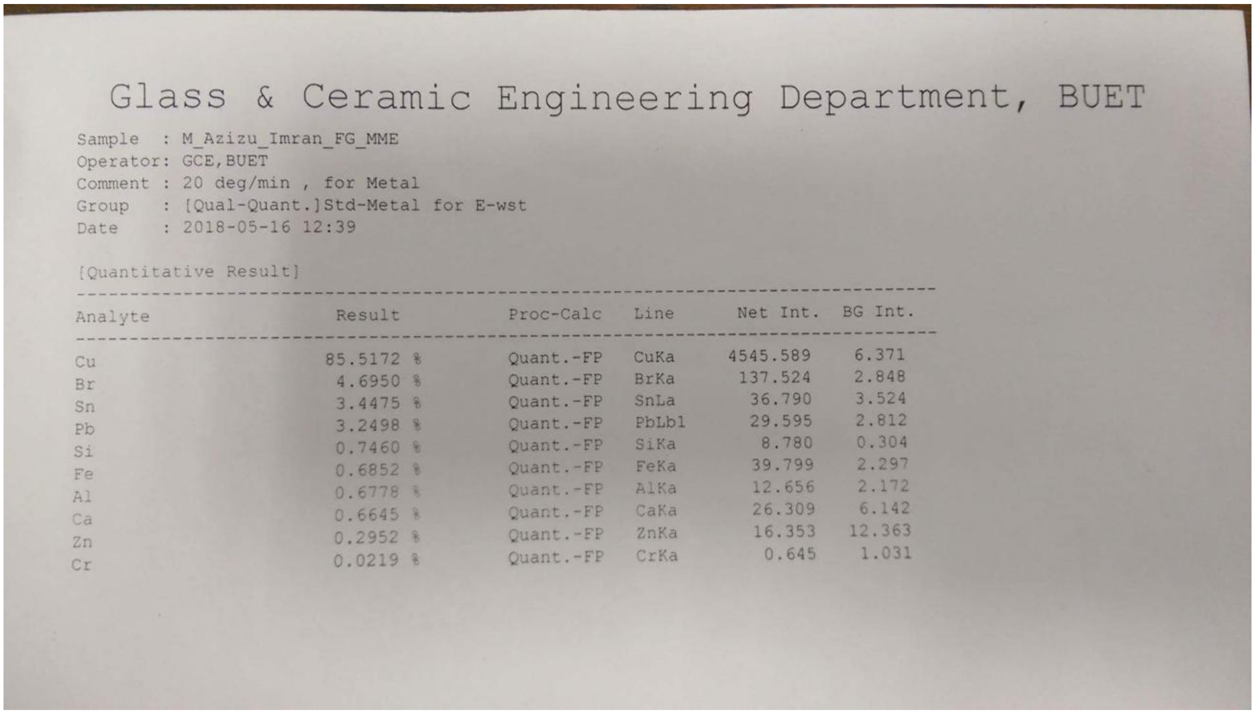
A-287	Sample (Chinese)	Aluminium (Al)	753 mg/L	3500.B
		Arsenic (As)	Less than 0.05 mg/L	3114.C
		Cadmium (Cd)	0.18 mg/L	3111.B
		Chromium (Cr)	278 mg/L	3113.B
		Cobolt (Co)	9.04 mg/L	3113.B
		Copper (Cu)	12825 mg/L	2340.C
		Calcium (Ca)	79.9 mg/L	3110.B
		Iron (Fe)	1528 mg/L	3111.B
		Lead (Pb)	193 mg/L	3111.B
		Manganese (Mn)	33.4 mg/L	3111.B
		Mercury (Hg)	1.67 mg/L	3112.B
		Nickel (Ni)	733 mg/L	3113.B
		Molybdenum (Mo)	3.59 mg/L	3113.B
		Silver (Ag)	33.3 mg/L	3111.B
		Tin (Sn)	1150 mg/L	3113.B

Figure 29: AAS analysis result of Chinese mobile PCB

From the AAS analysis, we selected Copper (Cu) and Tin (Sn) metals to recover from Chinese mobile PCB board.

3.6 XRF analysis of metal powder

For XRF analysis, we took metal powder about 5g obtained from Azizu Trading Co. and sent it to GCE department of BUET.



Glass & Ceramic Engineering Department, BUET

Sample : M_Azizu_Imran_FG_MME
Operator: GCE,BUET
Comment : 20 deg/min , for Metal
Group : [Qual-Quant.]Std-Metal for E-wst
Date : 2018-05-16 12:39

[Quantitative Result]

Analyte	Result	Proc-Calc	Line	Net Int.	BG Int.
Cu	85.5172 %	Quant.-FP	CuKa	4545.589	6.371
Br	4.6950 %	Quant.-FP	BrKa	137.524	2.848
Sn	3.4475 %	Quant.-FP	SnLa	36.790	3.524
Pb	3.2498 %	Quant.-FP	PbLb1	29.595	2.812
Si	0.7460 %	Quant.-FP	SiKa	8.780	0.304
Fe	0.6852 %	Quant.-FP	FeKa	39.799	2.297
Al	0.6778 %	Quant.-FP	AlKa	12.656	2.172
Ca	0.6645 %	Quant.-FP	CaKa	26.309	6.142
Zn	0.2952 %	Quant.-FP	ZnKa	16.353	12.363
Cr	0.0219 %	Quant.-FP	CrKa	0.645	1.031

Figure 30: XRF analysis result of metal powder

From the XRF analysis, it is seen that copper and tin are higher in value. So, we chose these two metals to be recovered from metal powder.

3.7 Recovery Process

3.7.1 Recovery of Copper

3.7.1.1 Recovery of Copper Using HCl & H_2O_2:

3.7.1.1.1 Preparing Leaching Solution

A mixture of 25 mL 37% fuming HCl, 25 mL 30% H_2O_2 and 50ml H_2O was prepared. This ratio was maintained to increase the volume of the leaching solution. We made 200ml of leaching solution to recover copper from PCB & metal powder. Since the mixing process is exothermic, the acid was slowly added to prevent overheating. The temperature of the mixture was stabilized at 20^0C by keeping the beaker in an oil bath. Two batches of solution were made for the two different sources.

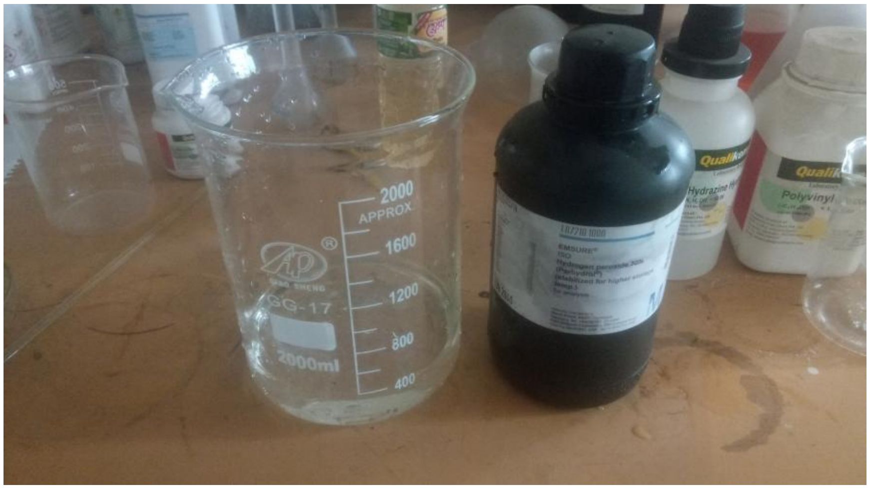


Figure 31 : Hydrogen Peroxide 30%

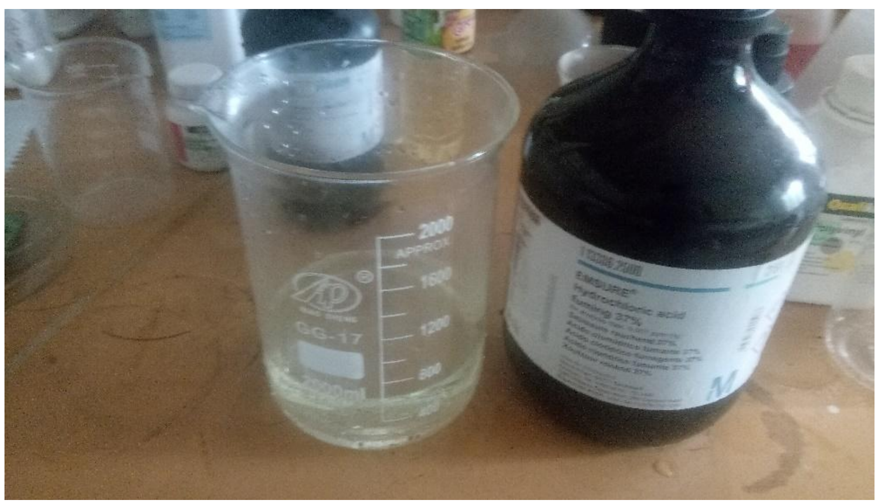


Figure 32: Hydrochloric acid 37% fuming

Figure 33: Leaching solution of HCl ,H_2O_2

3.7.1.1.2 Dissolving PCB and Metal Powder into Leaching Solution

For dissolving PCB board into leaching solution, they were broken into smaller pieces. Four PCB boards (almost 58g) were taken for dissolution. Metal powders were taken about 15g. As the reaction was vigorous, precautions were taken. As the PCB boards were broken into two pieces, they were added into the solution one by one after 30s – 1min interval. Reaction was more vigorous for metal powder. So, 1-2g powder was added at 3-4mins interval. The acid dissolves the solder joints and the welded components of the PCB, while the hydrogen peroxide dissolves the Copper in solution as its oxide. The seething beakers were kept under a fume hood for 2 – 3 hours for the reaction to complete.

$$H_2O_2 + 2HCl + Cu \rightarrow CuCl_2 + 2H_2O$$

After etching, we noticed the solution starting to aquire a light green tint. This was the copper that had dissolved into the solution. This green color grew deeper with each use. The dissolved copper created cupric chloride which can itself be used to etch metal.

Figure 34 : Vigorous reaction while dissolving

Figure 35: solution after completing leaching reaction (light green cupric chloride solution) & PCB after leaching

3.7.1.1.3 Filtering the Leachate Solution

Light green solutions of PCB & metal powder leachate were then filtered using filter paper.

Figure 36: filtering the leachate solutions

3.7.1.1.4 Recover Copper from Solution

Copper was recovered from cupric chloride green light solution using two process.

- By electrolysis

Electrolysis was done after filtering the solution. Graphite was used as both cathode and anode. 3A current was applied at 10V voltage. Electrolysis was carried out for 15-20 minutes. The recovery process is shown briefly in figure 39.

Figure 37: recovery of copper from PCB & metal powder by electrolysis

Cu deposited on the cathode as can be seen in figure 39. Deposited copper was separated and dried and weighed. Then the powder was characterized by X-Ray Fluorescence (Shimadzu Lab Center XRF-1800). Figure 40 summarizes the process flow for Cu extraction.

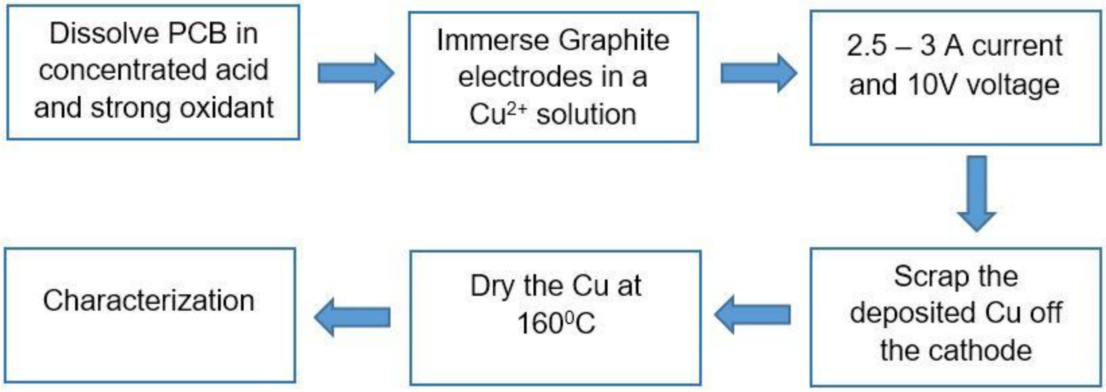


Figure 38: Flow chart of the Copper recovery process from cellphone PCBs (same goes for the metal powder)

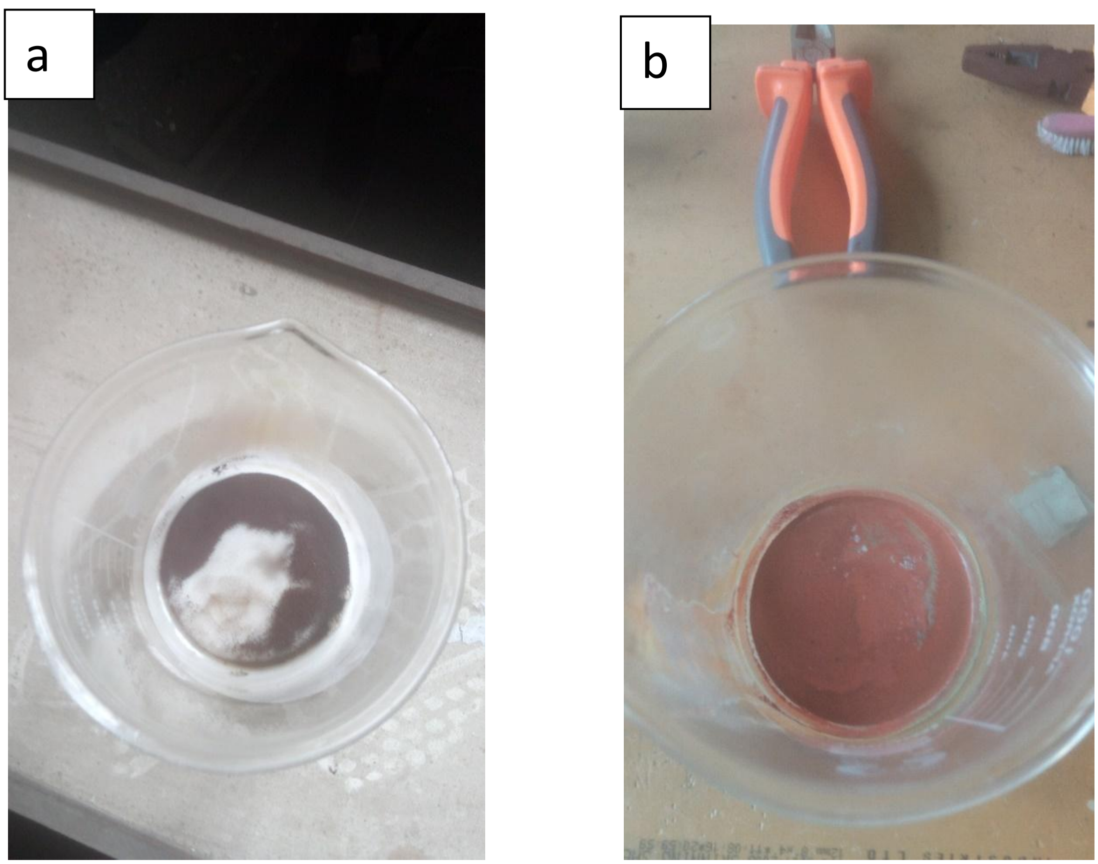


Figure 39: (a) copper powder recovered from PCB (b) copper powder recovered from metal powder using electrolysis process

- By using Aluminum foil or powder

Light green solution was taken & aluminum foil or powder were dropped into the solution on small amount. Aluminum reacts with cupric chloride to produce aluminum chloride and copper is precipitated.

Commonly, we would write the following

$2Al_{(s)} + 3CuCl_{2(aq)} \rightarrow 3Cu_{(s)} + 2AlCl_{3(aq)}$

Also, the aluminum ions in solution may be coordinated with four chloride ions:

$[AlCl_4]^{1-}$

But that isn't the whole story. Copper (II) ions will hydrolyze to produce an excess of hydrogen ions, making the copper (II) chloride solution slightly acidic.

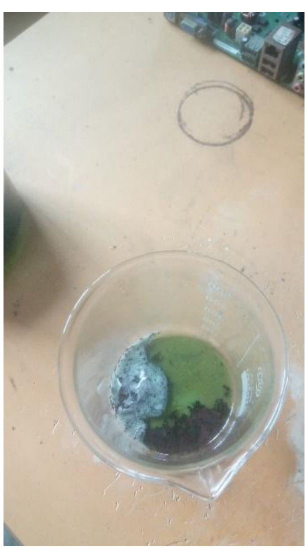
Aluminum metal is always covered in a thin, but protective layer of aluminum oxide, Al_2O_3. The chloride ion helps to separate aluminum from the oxygen so that the aluminum can react with the copper ions (and the water molecules).

$Cu^{2+} + HOH \rightarrow CuOH^{1+} + H^{1+}$

$Al_2O_3 + 4Cl^{1-} + H_2O + 2H^{1+} \rightarrow 2[Al(OH)_2Cl_2]^{1-}$

The reaction is also accompanied by the evolution of hydrogen gas

$2Al + 6H^{1+} \rightarrow 2Al^{3+} + 3H_2$



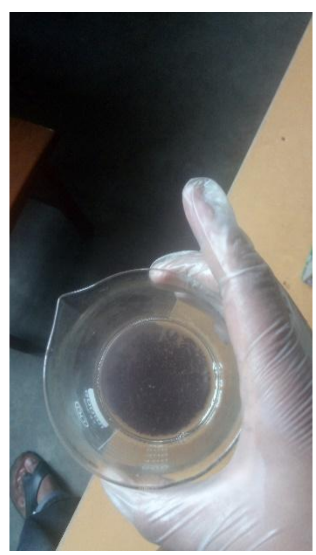


Figure 40 : precipitation of copper while using aluminum foil

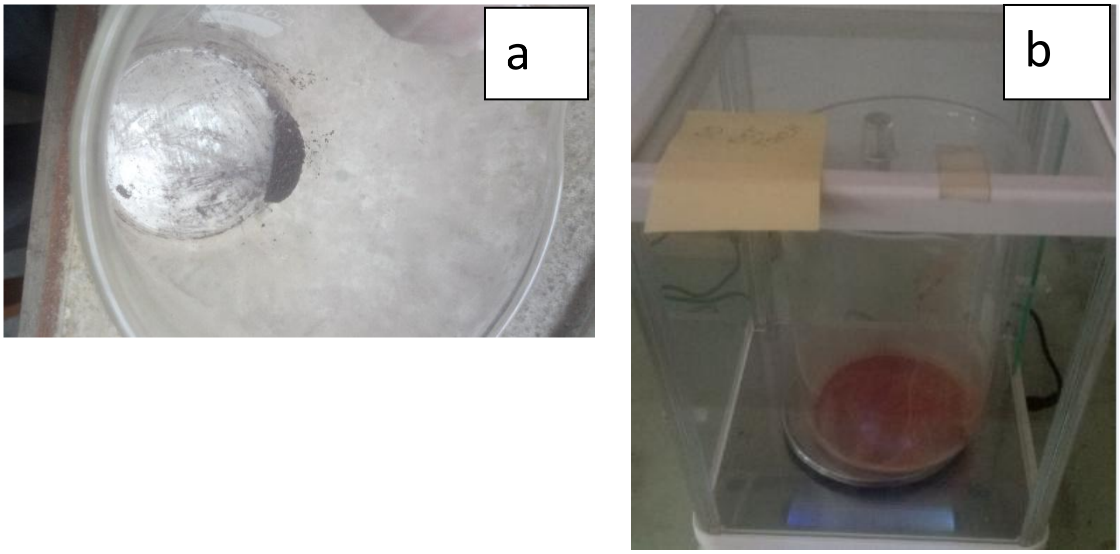


Figure 41 : (a) copper powder recovered from PCb (b) copper powder recovered from metal powder using aluminium

Copper powder obtained from the precipitation was washed and dried. Then it was sent for characterization by XRF.

3.7.1.2 Recovery of Copper Using H_2SO_4 & H_2O_2:

3.7.1.2.1 Preparing Leaching Solution

A mixture of 300 mL 98% H_2SO_4 and 100 mL 30% H_2O_2 was made. Since the mixing process is exothermic,

Figure 42 : sulphuric acid (98%), hydrogen peroxide (30%)

Figure 43: leaching solution of sulphuric acid & hydrogen peroxide

The acid was slowly added to prevent overheating. The temperature of the mixture was stabilized at 20^0C by keeping the beaker in an oil bath. Another batch of solutions was made using the same volumetric ratio for metal powder dissolution.

3.7.1.2.2 Dissolving PCB and Metal Powder into Leaching Solution

For dissolving PCB board into leaching solution, they were broken into smaller pieces. Four PCB boards (almost 60g) were taken for dissolution. Metal powders were taken about 12g this time. As the reaction was vigorous, precautions were taken. As the PCB boards were broken into two pieces, they were added into the solution one by one after 1min interval. Reaction was more vigorous for metal powder. So, 1.5-2g powder was added at 3-4mins interval. The acid dissolves the solder joints and the welded components of the PCB, while the hydrogen peroxide dissolves the Copper in solution as its oxide. The seething beakers were kept under a fume hood for 3 hours for the reaction to complete.

$$H_2O_2 + H_2SO_4 + Cu \rightarrow CuSO_4 + 2H_2O$$

Decomposition Reaction –

$$2H_2O_2 \rightarrow O_2 + 2H_2O$$

After etching, we noticed the solution starting to acquire a blue color for metal powder. This was the copper that had dissolved into the solution. This blue color grew deeper with each use. The dissolved copper created copper sulphate which can itself be used to etch metal.

Here we saw that the solution turned greenish while leaching PCB board using the leaching solution. Actually, copper sulfate changes color depending on how hydrated it is. $CuSO_4.5H_2O$ is blue, as we know, but copper sulfate with less water associated can be greenish, and completely anhydrous copper sulfate is a white powder, which slowly turns greenish blue as it absorbs water from the atmosphere.

Figure 44: blue leachate solution (metal powder), green leachate solution (PCB board)

3.7.1.2.3 Filtering the Leachate Solution

Light green solution of PCB and blue solution of metal powder were then filtered using the filter paper. Before filtering the PCB board leaching solution, the PCB boards dissolved into the solution were removed properly.

Figure 45: filtering the leachate solution

3.7.1.2.4 Recover Copper from Solution

Copper was recovered from copper sulphate green light solution and blue solution using electrolysis process.

Electrolysis was done after filtering the solution. But after filtering, the blue one had crystal type precipitate at the bottom of the beaker which was removed by heating the solution at about 50-60°C for 10 mins. Graphite was used as both cathode and anode. 3A current was applied at 10V voltage. Electrolysis was carried out for 15-20 minutes. . The recovery process is shown briefly in figure 48.

Figure 46 : recovery of copper from PCB & metal powder by electrolysis

Cu deposited on the cathode as can be seen in figure 48. Deposited copper was separated and dried and rinsed, then weighed. Then the powder was characterized by X-Ray Fluorescence (Shimadzu Lab Center XRF-1800). Figure 40 summarizes the process flow for Cu extraction that goes same for this process but the only difference is the leaching solution.

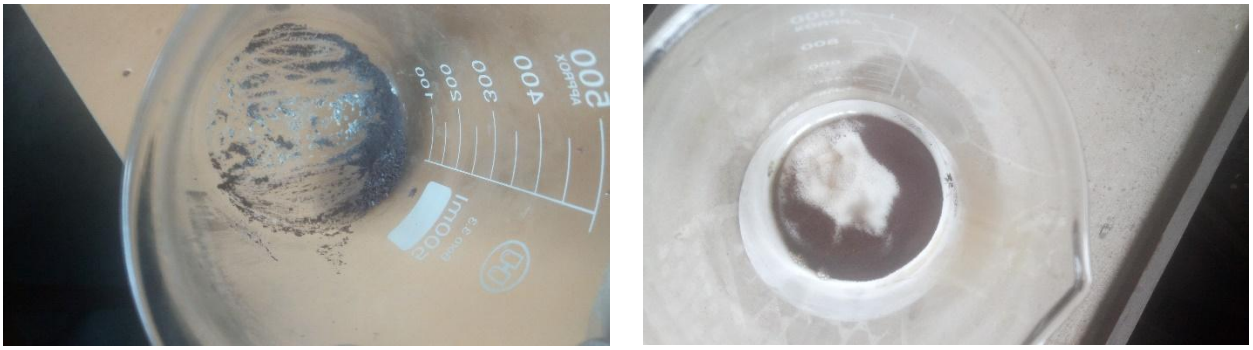


Figure 47: (a) copper powder from PCB, (b) copper powder from metal powder

3.7.1.3 Total Value Metal Amount

Copper powder recovered using two processes while using the two different sources, were weighted and put into small plastic box to prevent contamination.

3.7.2 Recovery of Tin

METHODOLOGY

The PCBs from Chinese mobiles used in the experiments were collected from local market. All chemicals used in the experiments were of analytical reagent grade; all glassware was made of borosilicate glass. The PCB powders from Chinese mobiles were prepared through dismantling and separating all non-metallic parts. The metallic parts were cut into small pieces and fed into a ball mill. A total of six samples were prepared for tin extraction.

Sample 1:

10 gm of waste mobile PCB powder was taken. At first, the sample was leached in 3N Nitric acid, 100 mL leach solution was heated to 60C for 120 minutes, after filtering Meta stannic Acid (H_2SnO_3) was found.

$$\mathbf{Sn + 4HNO_3 = H_2SnO_3 + 4NO_2 + H_2O}$$

The solid precipitation was preheated to 150C for 4 hrs. Then heated to 600C for removal of Pb and HCl was added for leaching.

$$\mathbf{H_2SnO_3 + 4HCl = SnCl_2 + Cl_2 + 3H_2O}$$

Sn was added then in leach liquor to cement tin and residual copper.

$$\mathbf{Sn + Sn^{4+} = 2Sn^{2+}}$$

$$\mathbf{Sn + Cu^{2+} = Sn^{2+} + Cu}$$

$BiCl_3$ and NaOH were added at 60C and heated for 0.5-hour, Sodium stannate was found $Na_2[Sn(OH)_6]$.

$$\mathbf{SnCl_2 + BiCl_3 + NaOH \xrightarrow{t°C} Bi + Na_2[Sn(OH)_6] + NaCl}$$

$$\mathbf{2Bi + 3CuCl_2 = 3Cu + 2BiCl_3}$$

Oplinger method was followed for electrodeposition of Sn. Sn deposited on the cathode. The deposited tin was separated and dried. Then the powder was characterized by X-Ray Fluorescence (Shimadzu Lab Center XRF-1800).

Electrodeposition Parameters:

Sodium stannate = 0.2375 mol/l
Sodium hydroxide = 1.0 mol/l
Hydrogen peroxide = 0.5 g/l
Anode = tin
Cathode = Graphite
Ratio of anode to cathode area = 3
Cathode current density = 30 A/f^2 or 322.9 A/m^2
E. M. F = 4.0 volts
Temperature of solution = 70 C

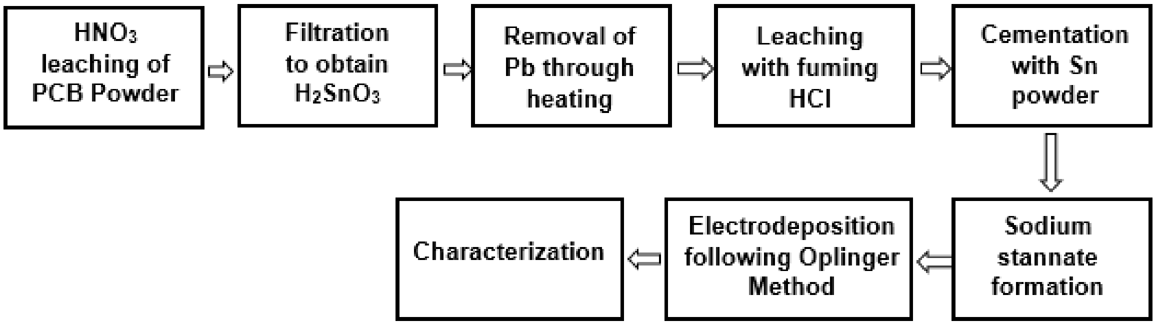


Figure 48: The process flow for Tin extraction of sample 1.

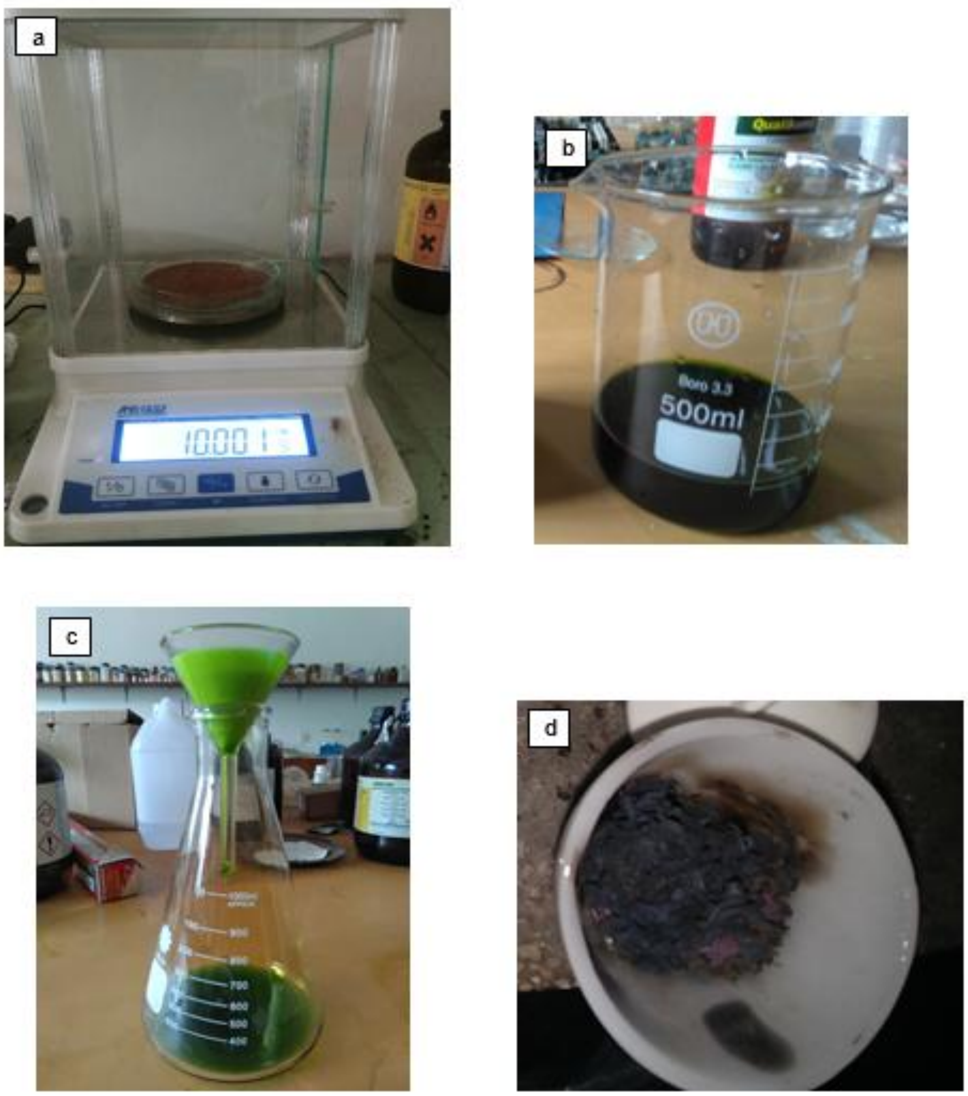


Figure 49 : . ***Different stages of Tin extraction: (a) Sample weighting (b) Acid Dissolving (c) S/L separating (d) Burning at 600C (e) Electrodeposition process***

Sample 2:

500 gm of waste mobile PCBs were collected, cut into identical sizes (3cm X 3cm), washed and dried. At first, the samples were leached in 25% Nitric acid, 1000 mL leach solution was stabilized for 24 hrs. After filtering Meta stannic Acid (H_2SnO_3) was found.

$$\mathbf{Sn + 4HNO_3 = H_2SnO_3 + 4NO_2 + H_2O}$$

The solid precipitation was preheated to 150C for 4 hrs. Then heated to 600C for removal of Pb and HCl was added for leaching.

$$\mathbf{H_2SnO_3 + 4HCl = SnCl_2 + Cl_2 + 3H_2O}$$

Zn was added then in leach liquor to cement tin and residual copper.

$$\mathbf{SnCl_2 + Zn \xrightarrow{t^\circ C} Sn + ZnCl_2}$$

Tin(II) chloride react with zinc to produce tin and zinc chloride. This reaction takes place at a temperature of 200-300°C.

40 percent sodium hydroxide solution and 5 percent hydrogen peroxide (H_2O_2) were added at 60C and stirred for 1 hour, Sodium stannate was found $Na_2[Sn(OH)_6]$.[69]

$$\mathbf{Sn + 2NaOH + 4H_2O \xrightarrow{t^\circ C} Na_2[Sn(OH)_6] + 2H_2}$$

Oplinger method [70] was followed for electrodeposition of Sn. Sn deposited on the cathode. The deposited tin was separated and dried. Then the powder was characterized by X-Ray Fluorescence (Shimadzu Lab Center XRF-1800).

Electrodeposition Parameters:

Sodium stannate = 0.2375 mol/l
Sodium hydroxide = 1.0 mol/l
Hydrogen peroxide = 0.5 g/l
Anode = tin
Cathode = Graphite
Ratio of anode to cathode area = 3
Cathode current density = 30 A/f^2 or 322.9 A/m^2
E. M. F = 4.0 volts
Temperature of solution = 70 C

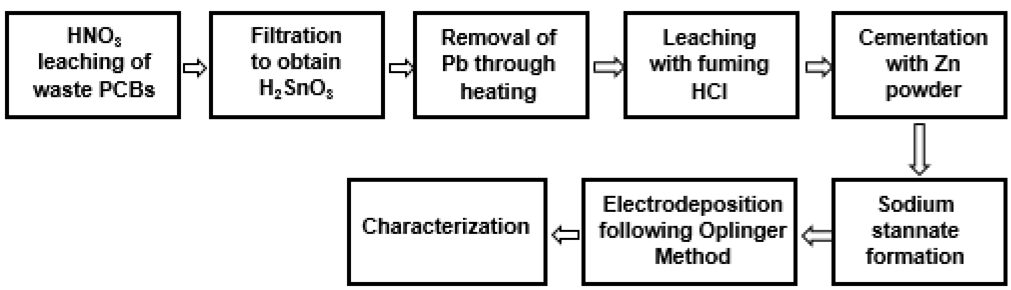


Figure 50: The process flow for Tin extraction of sample 2.

Total Value Metal Amount

Tin powder recovered using two processes while using the two different sources, were weighted and put into small plastic box to prevent contamination.

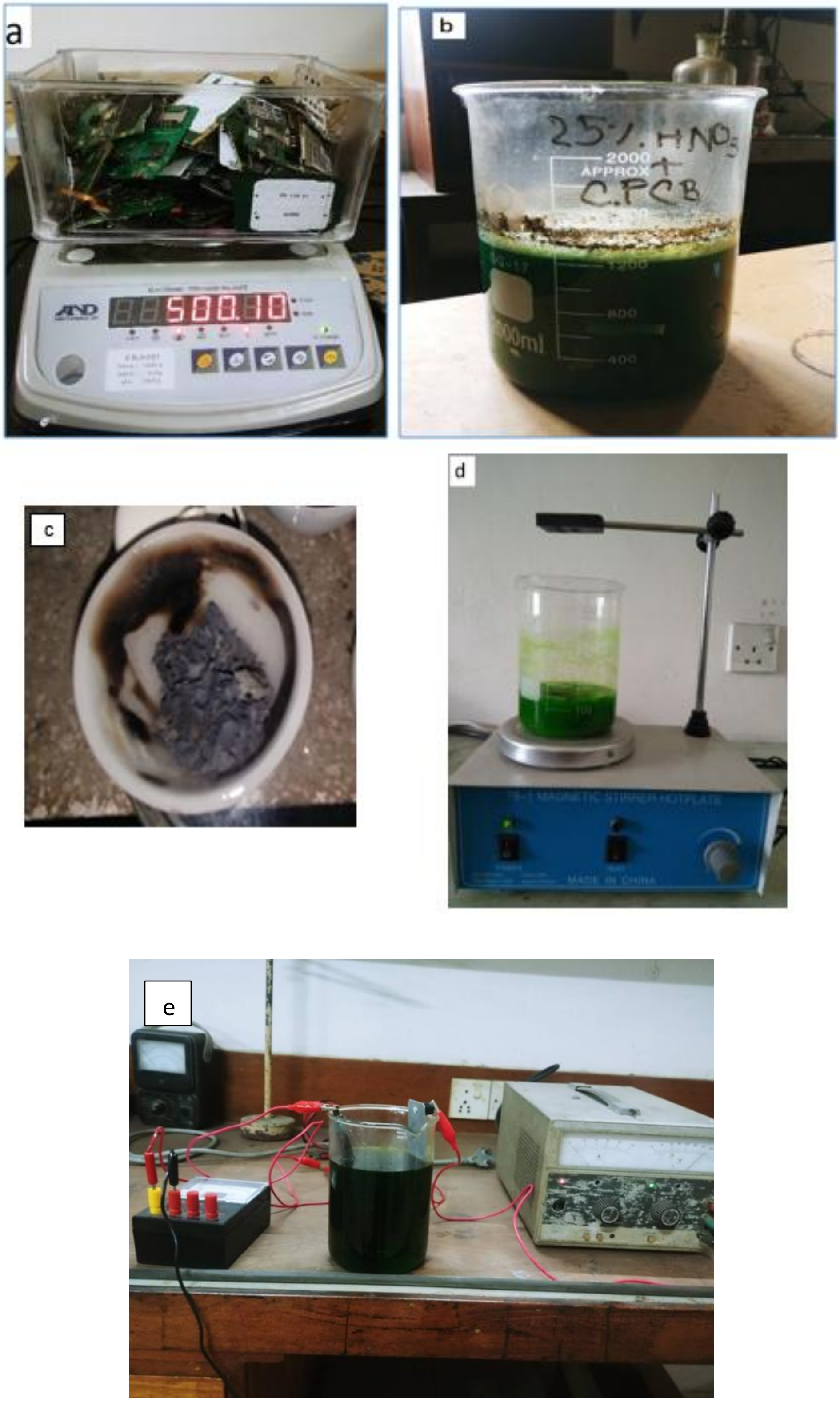


Figure 51: Figure 4. Different stages of Tin extraction: (a) Sample preparing (b) Acid Dissolving (c) Burning at 600C (d) Leach liquor stirring in HCl and Zn (e) Electrodeposition process

Chapter 4

Result Analysis & Discussion

4.1 AAS analysis of Chinese Mobile PCB Board

From the AAS analysis, we found 15 metals that were present in in the Chinese mobile PCB boards. From the AAS analysis we found that two metals copper & tin are higher in value. So we selected these two metals to extract from mobile PCB board.

LAB ID	Particulars of Supplied Sample	Parameters	Concentration (mg/L)	Test Method (APHA)
A-286	Sample (Chinese)	Al	753	3500.B
		As	0.05	3114.C
		Cd	0.18	3111.B
		Cr	278	3113.B
		Co	9.04	3113.B
		Cu	12825	2340.C
		Ca	79.9	3110.B
		Fe	1528	3111.B
		Pb	193	3111.B
		Mn	33.4	3111.B
		Hg	1.67	3112.B
		Ni	733	3113.B
		Mo	3.59	3113.B
		Ag	33.3	3111.B
		Sn	1150	3113.B

Table 14: AAS analysis of Chinese mobile PCB

4.2 XRF Analysis of Metal Powder

Metal powder obtained from Azizu Trading Co. was sent for XRF analysis. From the XRF analysis, it was certain that copper & tin are higher in portion in metal powder. So, our reason for selecting copper & tin metals to extract from powder was this x-ray fluorescence analysis report.

Qualitative Result:

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Cu	85.5172	Quant.-FP	CuKa	4545.589	6.371
Br	4.6950	Quant.-FP	BrKa	137.524	2.848
Sn	3.4475	Quant.-FP	SnLa	36.790	3.524
Pb	3.2498	Quant.-FP	PbLb1	29.595	2.812
Si	0.7460	Quant.-FP	SiKa	8.780	0.304
Fe	0.6852	Quant.-FP	FeKa	39.799	2.297
Al	0.6778	Quant.-FP	AlKa	12.656	2.172
Ca	0.6645	Quant.-FP	CaKa	26.309	6.142
Zn	0.2952	Quant.-FP	ZnKa	16.353	12.363
Cr	0.0219	Quant.-FP	CrKa	0.645	1.031

Table 15: XRF analysis of metal powder

4.3. XRF Analysis of Copper Powder

XRF analysis was carried over 15mm diameter copper tablet while pressing time was 1min & pressure was 40KN.

4.3.1. Metal Powder (leaching with HCl & H_2O_2, extracted by electrolysis)

From the XRF analysis, we have seen that Cu percentage was 99.7064%. So this process shows better efficiency.

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Cu	99.7064	Quant.-FP	CuKa	556.863	0.622
Si	0.1050	Quant.-FP	SiKa	0.117	0.021
Fe	0.0891	Quant.-FP	FeKa	0.677	0.202
Al	0.0565	Quant.-FP	AlKa	0.095	0.019
Cr	0.0431	Quant.-FP	CrKa	0.164	0.112

Table 16: XRF analysis of copper powder extracted from metal powder(electrolysis)

4.3.2 Chinese Mobile PCB (leaching with HCl & H_2O_2, extracted by electrolysis)

From the XRF analysis, we have seen that Cu percentage was 98.4112%. So this process shows better efficiency for PCB.

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Cu	98.4112	Quant.-FP	CuKa	509.904	0.602
S	0.7546	Quant.-FP	S Ka	1.426	0.091
Sn	0.5855	Quant.-FP	SnLa	0.629	0.434
Si	0.1026	Quant.-FP	SiKa	0.107	0.054
P	0.1006	Quant.-FP	P Ka	0.266	0.069
Fe	0.0456	Quant.-FP	FeKa	0.314	0.184

Table 17: XRF analysis of copper powder extracted from PCB (electrolysis)

4.3.3 Metal Powder (leaching with HCl & H_2O_2, extracted by aluminium)

From the XRF analysis, we have seen that Cu percentage was 95.3169%. So this process shows better efficiency even when extracted with aluminum.

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Cu	95.3169	Quant.-FP	CuKa	585.338	0.698
Sn	2.7898	Quant.-FP	SnLa	3.616	0.472
Pb	1.2897	Quant.-FP	PbLb1	1.250	0.153
Al	0.2459	Quant.-FP	AlKa	0.488	0.031
Si	0.1806	Quant.-FP	SiKa	0.237	0.024
P	0.0691	Quant.-FP	P Ka	0.229	0.054
Fe	0.0679	Quant.-FP	FeKa	0.511	0.219
Cr	0.0401	Quant.-FP	CrKa	0.152	0.127

Table 18: XRF analysis of copper powder extracted from metal powder (aluminum foil)

4.3.4 Chinese Mobile PCB (leaching with HCl & H_2O_2, extracted by aluminum)

From the XRF analysis, we have seen that Cu percentage was 92.2477%. So this process shows better efficiency even when extracted with aluminum.

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Cu	92.2477	Quant.-FP	CuKa	569.997	0.706
Sn	2.9629	Quant.-FP	SnLa	3.829	0.393
Si	2.3026	Quant.-FP	SiKa	3.059	0.028
P	0.6936	Quant.-FP	P Ka	2.279	0.090
S	0.6519	Quant.-FP	S Ka	1.518	0.082
K	0.5505	Quant.-FP	K Ka	2.584	0.381
Fe	0.2310	Quant.-FP	FeKa	1.734	0.236
Mg	0.1863	Quant.-FP	MgKa	0.068	0.024
Al	0.0873	Quant.-FP	AlKa	0.175	0.023
Ca	0.0862	Quant.-FP	CaKa	0.400	0.679

Table 19: XRF analysis of copper powder extracted from PCB (aluminium foil)

4.3.5 Metal Powder (leaching with H_2SO_4 & H_2O_2, extracted by electrolysis)

From the XRF analysis, we have seen that Cu percentage was 88.9275%. So, this process shows lower efficiency. So, it can be said that copper was not effectively recovered comparing to hydrochloric acid & hydrogen peroxide leaching solution.

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Cu	88.9275	Quant.-FP	CuKa	539.428	0.551
Sn	8.727	Quant.-FP	SnLa	24.549	0.542
Zn	1.1460	Quant.-FP	ZnKa	6.657	1.010
Fe	0.6257	Quant.-FP	FeKa	3.259	0.193
Pb	0.3893	Quant.-FP	PbLb1	0.448	0.160
Si	0.3294	Quant.-FP	SiKa	0.494	0.018
Al	0.1507	Quant.-FP	AlKa	0.338	0.028
P	0.0956	Quant.-FP	P Ka	0.361	0.057
Cr	0.0631	Quant.-FP	CrKa	0.167	0.068

Table 20: XRF analysis of copper powder extracted from metal powder (H_2SO_4 & H_2O_2, electrolysis)

4.3.6 Chinese Mobile PCB (leaching with H_2SO_4 & H_2O_2, extracted by electrolysis)

From the XRF analysis, we have seen that Cu percentage was 79.1275%. So, this process shows much less efficiency. So, it can be said that copper was not effectively recovered compared to hydrochloric acid & hydrogen peroxide leaching solution.

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Cu	79.1275	Quant.-FP	CuKa	424.317	0.624
Sn	6.3168	Quant.-FP	SnLa	6.917	0.383
Si	6.0099	Quant.-FP	SiKa	7.884	0.050
S	4.3687	Quant.-FP	S Ka	9.537	0.217
K	1.7689	Quant.-FP	K Ka	7.074	0.340
Pb	0.7408	Quant.-FP	PbLb1	0.734	0.223
Fe	0.6771	Quant.-FP	FeKa	3.743	0.216
Ca	0.5082	Quant.-FP	CaKa	1.955	0.640
P	0.3916	Quant.-FP	P Ka	1.213	0.077
Al	0.0905	Quant.-FP	AlKa	0.180	0.023

Table 21: XRF analysis of copper powder extracted from PCB (H_2SO_4 & H_2O_2, electrolysis)

Remarks:

- Each process is very toxic. So, precautions should be taken.
- As the reaction is exothermic, acid should be added slowly to prevent overheating.
- The reaction produces so much fume specially that with hydrochloric acid. So the reaction should be continued under exhaust fans.
- The temperature of the mixture should be stabilized at 20^0C by keeping the beaker in an oil bath.
- Adding metal powder or PCB into solution should be done at periodic time intervals.
- It will give a better result if aluminum powder is used instead of aluminum foil.
- Electrolysis should be done carefully by controlling current and voltage properly.
- Copper powder should be kept into an airtight plastic box to prevent contamination.
- Comparison,
  - metal powder yields better results than PCB which is obvious
  - leaching with hydrochloric acid gives better results than leaching with sulphuric acid.

- Yield can be low, due to

  -application on small scale

  -deception of the production company

- The increase of the volume of acid media can increase the leaching rate.

4.4 XRF Analysis of Tin Powder

XRF analysis was carried over 15mm dia. tin tablet while pressing time was 1min & pressure was 50 KN.

4.4.1 Metal Powder (leaching with HNO_3 & HCl, cemented by Sn, extracted by electrolysis)

From the XRF analysis, we have seen that Sn percentage was 99.7064%. So, this process shows better efficiency.

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Sn	97.7218 %	Quant .-FP	SnKa	507.713	0.603
Cu	0.9556 %	Quant .-FP	CuKa	1.124	0.091
Zn	0.5855 %	Quant .-FP	ZnKa	0.829	0.434
Si	0.2324 %	Quant .-FP	SiKa	0.268	0.054
Fe	0.1585 %	Quant .-FP	FeKa	0.107	0.069
Ru	0.1587 %	Quant .-FP	RuKa	0.104	0.184
Br	0.0549 %	Quant .-FP	BrKa	0.141	0.145
Cr	0.0555 %	Quant .-FP	CrKa	0.147	0.103
P	0.0771 %	Quant .-FP	P Ka	0.173	0.068

Table 22: XRF analysis of Metal Powder (leaching with HNO_3 & HCl, cemented by Sn, extracted by electrolysis)

4.4.2 Chinese Mobile PCB (leaching with HNO_3 & HCl, cemented by Zn, extracted by electrolysis)

From the XRF analysis, we have seen that Sn percentage was 86.5%. Some Copper is also present in the powder, which shows that not all Copper had been removed from the leach liquor. Moreover, Copper is a highly reactive metal and tends to readily precipitate in reducing environment, thus accounting for its residual presence in the sample.

Analyte	Result %	Proc-Calc	Line	Net Int.	BG Int.
Sn	86.5339 %	Quant .-FP	SnKa	453.681	0.771
Cu	10.6859 %	Quant .-FP	CuKa	68.389	0.472
Zn	1.4804 %	Quant .-FP	ZnKa	1.529	0.348
Si	0.7325 %	Quant .-FP	SiKa	0.753	0.030
Fe	0.2584 %	Quant .-FP	FeKa	1.672	0.168
Ru	0.1587 %	Quant .-FP	RuKa	0.319	0.678
Br	0.0649 %	Quant .-FP	BrKa	0.160	0.145
Cr	0.0456 %	Quant .-FP	CrKa	0.147	0.103
P	0.0398 %	Quant .-FP	P Ka	0.103	0.068

Table 23: XRF analysis of Chinese Mobile PCB (leaching with HNO_3 & HCl, cemented by Zn, extracted by electrolysis)

Remarks:

- Each process is very toxic. So, precautions should be taken.
- As the reaction is exothermic, acid should be added slowly to prevent overheating.
- The reaction produces so much fume, especially those in case of addition of hydrochloric acid and Zn. So, the reaction should be continued under exhaust fan.
- Adding metal powder or PCB into solution should be done at periodic time intervals.
- Zn should be added at a much larger beaker, as otherwise the fuming solution will over flow from the beaker

- Electrolysis should be done carefully by controlling current, voltage and temperature properly.
- Tin powder should be kept into airtight plastic box to prevent contamination.
- Comparison,

  - Metal Powder yields much better result also because of the use of Sn powder for cementation this result may seem much better.

  - Due to the use of Zn powder for cementation, the percentage of Zn is higher in sample 2 analysis, Zn powder should be avoided as the solution heats up and overflows, the yield can be low.
- The increase of the volume of acid media can increase the leaching rate.

The preparation of sodium stannate have to be controlled precisely, as the higher the amount of time the sample is kept under heat, the higher the formation of sodium zincate. This also is the reason to avoid Zn in this process.

Chapter 5
Conclusion

This work can be divided into several steps,

(i) Collection of e- waste & Characterization to find out the metals present

(ii) leaching of selected metals using hydrometallurgy process

(iii) recovery of copper & tin metals from leachate solutions

The characterization of copper & tin powder yielded the following results:

• Copper and tin content were subsequently 85.5 percent & 3.4 percent of the total weight of the metal powder, while 6.9 percent & 0.5 percent of the 58g weight of mobile PCB.

• Leaching with hydrochloric acid yields greater & efficient recovery of copper powder than leaching with sulphuric acid.

• Extraction of copper using electrolysis from leachate solution shows greater efficiency of copper recovery than using aluminum.

• Metal Powder yields much better result also because of the use of Sn powder for cementation.

• Due to the use of Zn powder for cementation, the percentage of Zn is higher in sample 2 analysis.

• As Zn has lower ability to cement Cu in the solution, the percentage of Cu was higher.

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