

RECOVERY OF COPPER NANOPARTICLES FROM WASTE PRINTED CIRCUIT BOARD AND ITS CHARACTERIZATION

by

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MASTER OF SCIENCE IN MATERIALS AND METALLURGICAL ENGINEERING



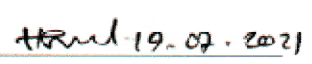
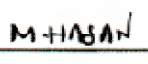
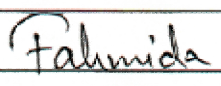
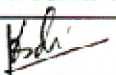
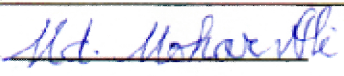
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ABSTRACT

Waste PCBs were collected and shredded by a shredder in the current work. Shredded PCBs were treated by NaOH solution to remove or loosen up the polymer coating painted on the PCB. As copper was the target element in this experiment two step leaching process was adopted. In the first step, low concentration HNO_3 treatment was done to leach the solders and other metals except copper and second step leaching was done by H_2O_2 added HCl solution for copper leaching. Copper was reclaimed as nanoparticles by electrowinning process using this copper pregnant leach liquor as the electrolyte. Concentration of various elements in the leach liquors of two step leaching process was determined by Atomic absorption spectrometry (AAS). Different characterization techniques such as particle size analysis, SEM with EDX, XRD and Rietveld refinement were applied to characterize copper nanoparticles. Final Cu rich solution found the concentration of Cu 29,437.5 ppm with the presence of few other elements. Reclaimed copper particles were in the range of around 30 to 200 nm revealed by SEM images while having the average crystallite size of 76 nm determined by Rietveld refinement. Presence of metastable cuprous oxide phase was found from the XRD analysis and elemental Cu phase percentage was 65. Macro scale EDX analysis confirmed that vacuum drying of the Cu particles dropped the O contamination from 30% to 6%.

Table of Contents

CANDIDATE’S DECLEARATION	Error! Bookmark not defined.
ACKNOWLEDGEMENTS.....	iii
ABSTRACT	v
1 INTRODUCTION	2
1.1 Objectives of the Current Work:.....	4
2 Literature Review.....	7
2.1 Printed Circuit Board	7
2.2 Why is PCB a concern?.....	8
2.3 Geopolitical impacts of PCB recycling.....	9
2.4 Economic Impacts of PCB Recycling.....	13
2.5 Environmental Impacts of PCB Recycling	17
2.6 Social Impacts of PCB Recycling:.....	19
2.7 Legislation of PCB Recycling:	20
2.8 Types of PCB:.....	21
2.8.1 Single-layer PCB:	22
2.8.2 Double-layer PCB:.....	22
2.8.3 Multi-layer PCB:	23
2.9 Structure of PCB:.....	24
2.9.1 Copper Foil:.....	25
2.9.2 Prepreg:	25
2.9.3 Inner-Layer Core:	26
2.10 Mobile Phone PCB:	26
2.11 Recycling of PCBs.....	29
2.12 Pretreatment of waste PCB for recycling.....	31

2.12.1	Dismantling/Disassembly.....	31
2.12.2	Size Reduction.....	33
2.13	Traditional processes for waste PCB recycling.....	35
2.13.1	Uncontrolled Incineration	35
2.13.2	Mechanical Separation.....	35
2.14	Advanced Methods for WPCB Recycling.....	37
2.14.1	Pyrometallurgy	37
2.14.2	Hydrometallurgy.....	39
2.15	Recovery of Metals	43
2.15.1	Chemical Precipitation.....	44
2.15.2	Cementation.....	45
2.15.3	Electrowinning (EW)	45
2.15.4	Solvent Extraction (SX)	46
2.15.5	Ion Exchange (IX)	47
2.16	Scope of the work	47
3	Experimental.....	49
3.1	Introduction	49
3.2	Materials and Equipments	50
3.2.1	Materials:.....	50
3.2.2	Instrumentation.....	50
3.3	Methods.....	51
3.3.1	Manual dismantling:	51
3.3.2	Size Reduction:.....	52
3.3.3	Removal of polymer coating:	54
3.3.4	Solder Removal:	55
3.3.5	Magnetic Separation:	56

3.3.6	Leaching of Copper:	57
3.3.7	Recovery of Copper:	58
3.4	Summary:	62
4	RESULTS AND DISCUSSION	64
4.1	Dismantling and Shredding	64
4.2	AAS of Leaching Solution	64
4.3	Selectivity Ratio	65
4.4	Recovery of Copper element	67
4.5	Particle Size Analysis	68
4.6	SEM Micrographs	70
4.7	EDX Analysis	73
4.8	XRD Analysis	74
4.9	Rietveld Refinement	76
4.10	Comparison with Literature Data	77
5	CONCLUSIONS	80
5.1	Future Work	81
	REFERENCES	82

LIST OF TABLES

Table 2.1: Value of Copper in a typical computer PCB.....	9
Table 2.2: Consumption of metals present in PCB.....	10
Table 2.3: Copper production from mines in several countries.....	12
Table 2.4: Value of PCB market [28]	14
Table 2.5: Percentage of materials in the printed circuit boards (PCB's) of cellphones [29].	15
Table 2.6: Element and ion concentration during the steps of PCB recycling [34]	18
Table 2.7: Levels of toxic emission from EEE production and e-waste recycling.....	19
Table 2.8: Metal concentration (wt%) of PCBs as reported in different studies.....	28
Table 2.9: Mean concentrations of metals in the PCBs of mobile phone samples.....	29
Table 2.10: Characteristics of connection types related to their specific degree and nonrandomness of liberation behavior after shredding with different connection complexities.....	32
Table 2.11: Comparison of most commonly used two mineral acids, AR and ionic liquids, used in base metal leaching [31].....	39
Table 3.1: Overview of the experimental path	49
Table 4.1: AAS data of Leach Liquor	65
Table 4.2: Selectivity Ratio data for final leach liquor	66
Table 4.3: Composition of sample-1 and sample-2 summarized from EDX analysis.....	73
Table 4.4: Summary of crystallite parameters found from the Rietveld Refinement.....	77
Table 4.5: Comparison with literature data	78

LIST OF FIGURES

Figure 1.1: Global E-Waste Generated [3].....	3
Figure 2.1: A printed circuit board integrates components and conductors [8]	7
Figure 2.2: Snapshots of Typical PCBs	8
Figure 2.3: Use of metals versus GDP: copper and lead [16]	11
Figure 2.4: Simplified World Mining Map [17].....	12
Figure 2.5: Value of shipments printed circuit assembly manufacture in US [27]	14
Figure 2.6: Relative value of cellphone PCB materials processed through formal channels in Mexico [29]	16
Figure 2.7: Recycled material energy savings over virgin materials [32]	16
Figure 2.8: States with Electronic Waste Recycling Programs [38].....	20
Figure 2.9: Functionality of collected WEEE [39]	21
Figure 2.10: Single-layer PCB [40]	22
Figure 2.11: Double-layer PCB [40].....	23
Figure 2.12: Multi-layer PCB [40].....	24
Figure 2.13: Laminated Panels [41].....	26
Figure 2.14: Mobile Phone PCB Boards [43].....	27
Figure 2.15: E-waste recycling chain and end-of-life WEEE/WPCB treatment options [31]	30
Figure 2.16: Imperfect liberation leads to imperfect separation [31]	34
Figure 2.17: Comparative extraction efficiencies of different metals from WPCBs using HCl and H ₂ SO ₄ lixivants, 50 g/L pulp density, 25 °C, 300 rpm, and 12 h [66].	41
Figure 2.18: Metal recovery techniques [31].....	44
Figure 2.19: Solvent extraction process feeds and products [31]	46
Figure 3.1: Locally purchased MPCBs showing different small parts mounted.....	51
Figure 3.2: Surfaces of MPCBs after removing the tiny parts	52
Figure 3.3: Shredder used for size reduction.....	53
Figure 3.4: Shredded PCB.....	53
Figure 3.5: NaOH treatment of whole PCB	54
Figure 3.6: HNO ₃ solution filtering (a) and HNO ₃ treated air dried PCB sample	56
Figure 3.7: Visualization of HCl+H ₂ O ₂ solution filtering (a) and HCl+H ₂ O ₂ treated air dried PCB sample	58

Figure 3.8: Graphite layer issue while using pencil battery graphite rod (a) and electrowinning using locally purchased graphite electrode (b).....	59
Figure 3.9: Visualization of various steps during centrifugation.....	60
Figure 4.1: Representation of Effectiveness of Selectivity Ratio	66
Figure 4.2: Image of reclaimed copper (a) with stirring and temperature effect (b) without stirring and temperature effect.....	67
Figure 4.3: Particle size analysis of copper (sample-1) without temperature and stirring.....	68
Figure 4.4: Particle size analysis of copper (sample-2) with temperature and stirring.....	69
Figure 4.5: SEM Micrographs of Copper particles without stirring and temperature conditions (Sample-1) (a) 35,000 magnification (b) 50,000 magnification (c) 100,000 magnification	70
Figure 4.6: SEM Micrographs of Copper particles with stirring and temperature conditions (Sample-2) (a) 30,000 magnification (b) 50,000 magnification (c) 100,000 magnification	71
Figure 4.7: Macro Scale EDX of (a) Sample-1 and (b) Sample-2.....	73
Figure 4.8: XRD analysis of sample-1	74
Figure 4.9: XRD analysis of sample-2	75
Figure 4.10 Presentation of achieved accuracy during rietveld refinement: a & b for sample-1 and c & d for sample-2.....	76

CHAPTER 1

INTRODUCTION

1 INTRODUCTION

Natural resources should be managed through the way where goods are manufactured, repaired, re-used, and then recycled. Our design should be allowed to green growth and part of resource-efficient, circular economy so that nothing is considered as waste. United Nations Environment Program (UNEP) set initiatives for Green and Circular Economy (GCE). This approach provides a guideline for economy which can lead world community for human well-being and social equity, on the other hand considerably reducing environmental and ecological risks. World business hub of Electrical and Electronic Equipment (EEE) is in a growing trend. Development of these industries is associated with increased demand of metals, especially of precious metals (PM) and rare earth element which leads to huge amount of Waste Electrical and Electronic Equipment (WEEE). On the other hand, rapid innovations in technological fields very often comes with new models and new features which further shorten the life of products. Thus rate of WEEE increment is following a nature which is like an exponential feature. Researcher has found that half of the WEEE is generating from electrical appliances and the rest from electronic goods[1]. Sources of these wastes can be generally classified in ten categories: (1) Large household appliances; (2) Small household appliances; (3) IT and telecommunications equipment; (4) Consumer equipment; (5) Lighting equipment; (6) Electrical and electronic tools (with the exception of large-scale stationary industrial tools); (7) Toys, leisure, and sports equipment; (8) Medical devices (with the exception of all implanted and infected products); (9) Monitoring and control instruments; and (10) Automatic dispensers.

E-waste generating from these EEEs in total can contain up to 1000 toxic substances, including lead, chromium, and plastic additives. In 2007 UNEP[2] projections revealed that, around 20-50 million tons of E-Waste are being generated per year in the world. United Nations University[3] (UNU) has reported that in 2016 generation of E-waste has grown to 44.7 million metric tonnes annually which is equivalent to almost 4,500 Eiffel Towers. This report also depicts that all the countries in the world combined generated a staggering 44.7 million metric tonnes (Mt), or an equivalent of 6.1 kilogram per inhabitant (kg/inh), of e-waste annually in 2016, compared to the 5.8 kg/inh generated in 2014. On the other hand, extrapolation of the study depicts that the amount of e-waste is expected to increase to 52.2

million metric tonnes, or 6.8 kg/inh, by 2021. Though it is very tough to control the use of EEE, the statistics of E-waste generation is alarming in every aspects of the world fig. 1.1.

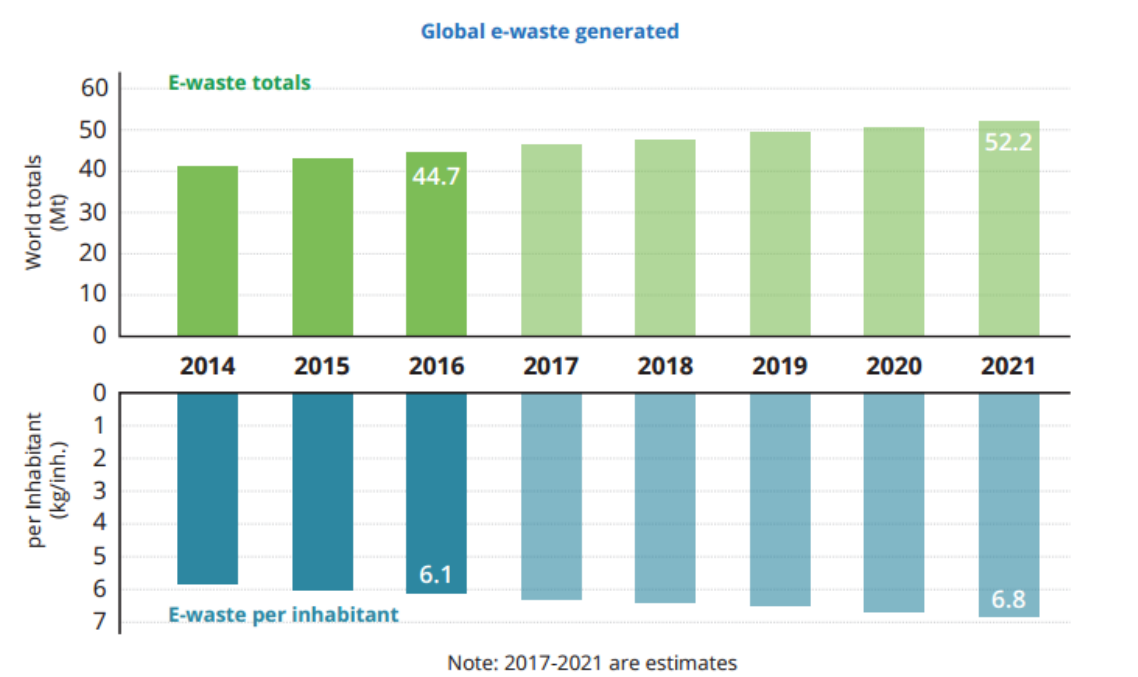


Figure 1.1: Global E-Waste Generated[3]

The consumption of EEE in general has also shown rapid growth over the period of 2000 to 2016. Keeping the pace with world, E-waste has become the fastest growing waste stream in this country.UNU report has shown that in 2016, Asia was the region that generated by far the largest amount of e-waste (18.2 Mt), followed by Europe (12.3 Mt), the Americas (11.3 Mt), Africa (2.2 Mt), and Oceania (0.7 Mt). Bangladesh has generated roughly 2.7 million (or according to BEMMA 3.2 million) metric tons of e-waste[4]. Theses wastes have also become an income source for poor people and unemployed laborers in Bangladesh, since these are rich in precious metals and other reusable materials such as plastics.

Not only developed countries generate e-waste; Asia discards an estimated 12 million tons each year[5].According to the UNEP study, the developed nations dump e-waste in “developing” Asian countries (India, Bangladesh, China and Pakistan) through legal/ illegal trade routes. Bangladesh dismantles nearly 60 per cent of the ships sent to scrap-yards across the globe. Unfortunately the scrap ships are carrying large volume of toxic products and

electrical & electronic waste. The ship breaking yards of the country alone produce 2.5 million metric tons of e-waste[4]. According to the Association of Plastics Manufacturers in Europe (APME), the material composition of EEE is 38% ferrous metal, 28% nonferrous metal, 19% plastics, 4% glass, 1% wood, and 10% others.

One of the major valuable parts of WEEE is the printed circuit board (PCB). Thus, the target e-waste material of this research work was the waste printed circuit boards (WPCBs). Polymers, ceramics, and metals are common components of discarded PCBs (Printed Circuit Boards). Due to the high presence of copper (about 20 wt. percent) and precious metals (0.1 wt. percent), waste PCBs are regarded an appealing secondary source of metals[6]. Copper is the second most common nonferrous metal (behind aluminum) and is utilized in a wide range of industries, including healthcare, construction, machinery, electronics, and telecommunications. In particular, the copper (Cu) concentration of waste PCBs is substantially higher than that of Cu ore[7]. Thus, this study focused to reclaim Cu nanoparticles as value added product. For this purpose, a Cu pregnant leach solution was prepared by hydrometallurgical route. This Cu rich solution was then used as electrolyte in electrowinning process for the recovery of Cu particles.

1.1 Objectives of the Current Work:

The principal objective involves establishing a process to synthesize Cu in the nanoparticle range from waste printed circuit board (PCB), and characterization of these particles. In line of this, the specific aims of the work include:

- i. Extraction of Cu from waste PCB through hydrometallurgical route
- ii. Synthesis of Cu in the nanoparticles range through electrometallurgical route and its characterizations

The Possible Outcomes are:

- i. A process outline for leaching Cu from waste PCB
- ii. Synthesis of Cu nanoparticles from this leach solution
- iii. Development of a process to produce value added product like Cu nanoparticles from wastes as well as pollution control
- iv. Reduction of pollution from hazardous electronic waste (PCB)

This thesis book will elaborately describe the past works in this study area in chapter two and then outline the scope of this work. Experimental processes adopted in this work will be described elaborately in chapter three which include the mechanical and hydrometallurgical steps for the preparation of Cu rich solution, and the details of electrowinning process that was adopted to reclaim Cu nanoparticles. Findings from the different characterization analysis such as AAS, particle size analysis, SEM, EDX, XRD and Rietveld refinement will be explained in chapter four which will reveal various features of the product. In chapter five conclusion of this study will be briefly delivered with the recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2 Literature Review

2.1 Printed Circuit Board

A printed circuit board (PCB) is an electrical circuit whose components and conductors are contained within a mechanical structure (Figure 2.1). Conductive features include copper traces, pads, heat sinks, or conductive planes. The printed circuit board is made up of layers of conductive copper sandwiched between layers of nonconductive insulation.

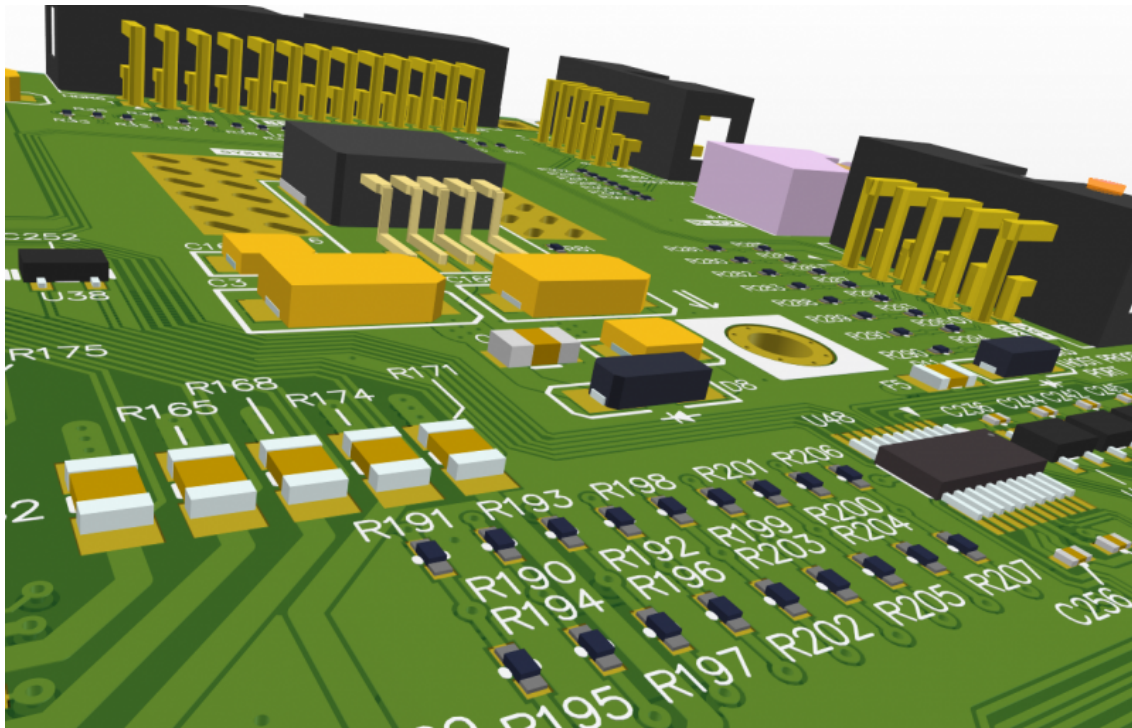
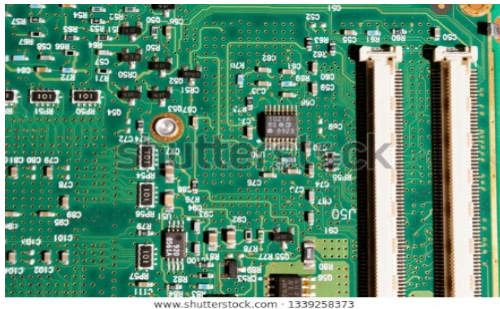


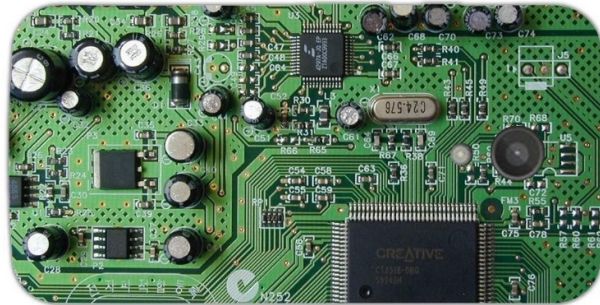
Figure 2.1: A printed circuit board integrates components and conductors[8]

The inner copper layers are engraved during the manufacturing process, leaving copper traces to bind circuit components. The copper layers are then laminated to the etched insulation content, and so on, until the printed circuit board is complete. After all of the layers have been etched and laminated together, electronic components are applied to the printed circuit board's outer layers. Through-hole parts are manually mounted while surface mount parts are applied by robots. Using reflow or wave soldering methods, all of the bits are then soldered onto the board. Following plating, the solder mask and final assembly are applied.

2.2 Why is PCB a concern?



Computer PCB



Mobile Phone PCB

Figure 2.2: Snapshots of Typical PCBs

E-waste possesses a lot of components among which PCBs are considered most valuable parts. If WEEE is considered to recycle then there is no way without processing PCBs it can be made beneficial. Figure 2.2 represents the typical outlook of a computer PCB and a mobile phone PCB. E-waste statistics are not only relevant in terms of the environmental impact; there is also an important economic component to the debate. The total value of all raw materials present in e-waste is estimated at approximately 55 Billion Euros in 2016, which is more than the 2016 Gross Domestic Product of most countries in the world. The value of secondary raw materials after waste management is just a fraction of the value of its components, mainly PCBs or the price of used appliances[3]. The United Nations presented an estimated total production of 12.7 Billion mobile phones, 94.4 million laptop computers, and 768.9 million digital cameras[9]. As per their functional modeling all of these products have at least one PCB. Once these products are discarded, equal number of PCBs are also discarded. The scenario of a developing country like Bangladesh is a little different. Along with the quality brand products there are abundant refurbished Chinese, local and other low endurance products in the appliance market. As a result such products are bought frequently, changed frequently and the volume of e-waste rises rapidly. Estimated 58,360,000[10] domestic mobile phone subscribers were present in mid-2010. It is safely assumed that at least two thirds of the owners are discarding their old phones by next year. This gives us an overwhelming 38,910,000 units of waste PCB for the year 2011 only. Approximately 10,504 metric tons of e-waste have been generated from just mobile phones within the last 21 years[4]; of which a massive portion is the PCBs.

Typically, a WPCB from PC can contain 7% Fe, 5% Al, 20% Cu, 1.5% Pb, 1% Ni, 3% Sn, and 25% organic compounds, together with 250 ppm (g/t) Au, 1000 ppm Ag, 110 ppm Pd, and trace amount of As, Sb, Ba, Br, and Bi. In common computer PCB, Cu and Au contents are, respectively, 20–40 times (Cu) and 25–250 times (Au) higher[11]. The weight of the disassembled PCBs from computers range from 200 to 315 grams[12]. It seems that a typical computer PCB may have 40 to 63 grams of copper only. Material value of a computer PCB only for copper is shown in the table below.

Table 2.1: Value of Copper in a typical computer PCB

Wt. of PCB	Cu contain	Cu Price	Cu price BDT	Value of Cu in a PCB
200-315 gm	40-63 gm	\$3 per pound	255 per 450 gm (appx)	23 – 36 BDT

Considering the only elemental Cu value of WPCB it is a hard to avoid the concern of these waste products while they also contain lot of precious metals like Au, Ag, Pd etc. Indonesia, as the fourth largest population in the world, is also having problems in managing its ewaste generation, especially from computers and mobile phones. In Jakarta, it is estimated that there are 10 tons of PCB waste that enters the waste stream every month. These wastes are managed without proper handling by informal sectors. Since these informal sectors cannot invest in high tech equipments and machineries, it is important to provide a more economical, yet environmentally friendly solution to this problem[13].

2.3 Geopolitical impacts of PCB recycling

To understand the impact of waste PCB, we must know the culture of countries in the context of producing PCB. Almost all the developed countries are involved with PCB industries, because this is the integral part of all kinds of electronics. There are few industries which only assemble for final product and these industries purchase from others. Thus the market of PCB is fact to be considered in the process of recycling and reusing of them. But before that, since the PCB is comprised of several metals we need to understand the global demand and supply of metals. World reserves of Copper, Aluminium and Silver are numbered as 470, 23000 and 270 million Kgs. On the other hand, value of Copper and Gold production in billion US dollars are 20.7 and 25.8 in 1993 while the number are 24.3 and 32 in the year

2003[14]. Nonrenewable resources became more available between 1870 and 1957, although the demand for mineral resources had exploded during the 20th century. In table 2.2[15], it is concluded that the metals consumption in 2050 will be almost doubled of 2003 which is much higher than the increment from 1984 to 2003. Al, Cu, Fe, Pb, Sn and Zn are the most available metals in PCB the demand of which are going to be increased very rapidly as shown in Table 2.2.

Table 2.2: Consumption of metals present in PCB

	M tonnes, 1984	M tonnes, 2003	Increase Mt/year	Increase %/year	M tonnes, 2050
Aluminum	16	26	0.5	3.1	50
Copper	9.68	13.6	0.2	2	23
Iron (pig iron)	491	967	24	4.9	2100
Lead	5.4	6.8	0.07	1.3	10
Magnesium	0.34	0.49	0.0075	2.2	0.84
Manganese (ore)	23.8	24.3	0.025	0.1	25
Nickel	0.757	1.215	0.023	3	2.3
Tin	0.224	0.267	0.0022	0.9	0.37
Zinc	6.69	9.9	0.16	2.4	17

Another way to analysis the demand of metals is to look at the present growth of population and try to make some kind of estimate of the standard of living within certain regions at the desired year. Swedish economist Dan Nilsson reported in 2002 that there is a correlation between the per capita consumption of a metal and the gross domestic production in a country. In Figure 2.3 the per capita consumption per year for Cu and lead (Pb) from different countries is plotted against the gross domestic consumption.

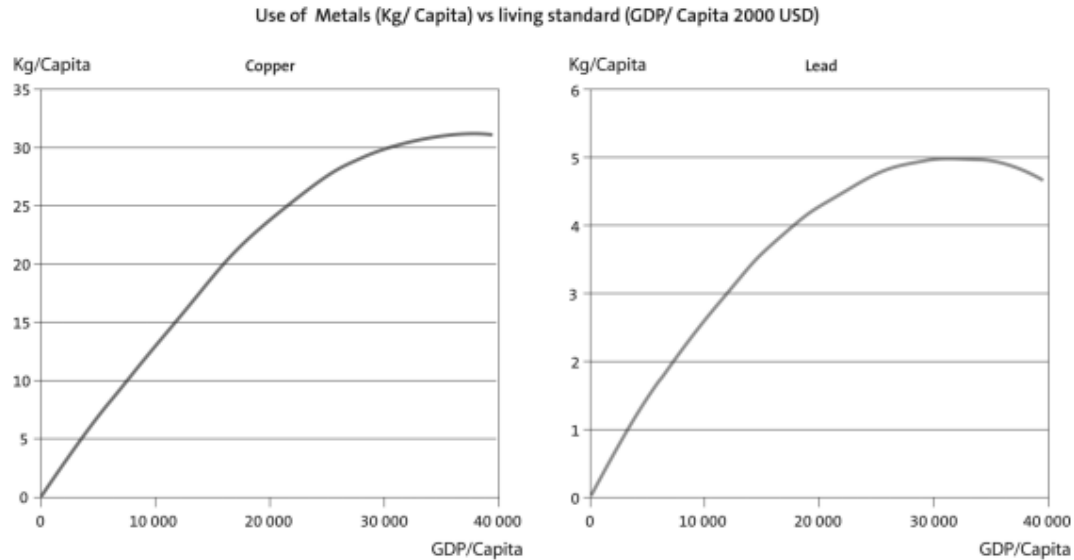


Figure 2.3: Use of metals versus GDP: copper and lead[16]

From Figure 2.3 we see that there is first a linear increase in yearly consumption of the metals, when the gross domestic production rises followed by a tendency for the curve to reach a peak and then slowly fall back. One of the key features of this study is that maximum Per capita consumption of Al, Cu, Pb and Zn are 32, 13, 5.2 and 8. With all kinds of accessories mounted on the PCB, it is a part of the electronics which possess a great value of at least in terms of the metals along with it. Now, before PCB is manufactured where these metals are supplied from is a question to answer.

PCBs are rich with some metals like copper, iron, tin, zinc and lead while these are also valuable for the presence of precious metals like gold, silver and palladium. Not all the countries and continents over the world are equally distributed in terms of metals mines. Some countries, especially the developed countries are the luckiest to have many of these mines which are very precious. Considering the mines for copper, Asia has the largest numbers of copper mines than any other continents. It seems that Europe, Africa and South America has almost same numbers of copper mines.

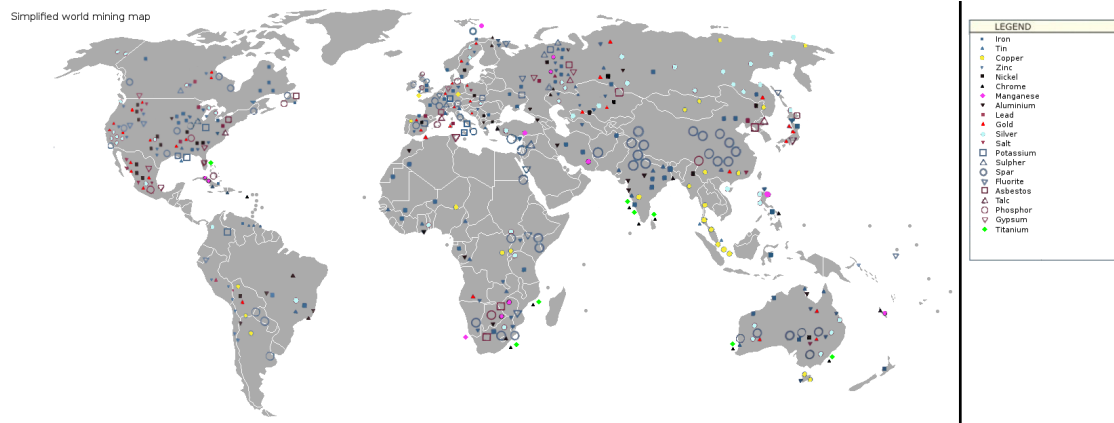


Figure 2.4: Simplified World Mining Map[17]

But if we consider the gold mines, North America and Europe are dominating continents for gold market compared to the Asia. From Figure2.4 it can be seen that South America and Africa have no hold on the global gold mining business.

A 2014 U.S. Geological Survey assessment of copper deposits indicated that identified resources contained about 2.1 billion tons of copper, and undiscovered resources contained an estimated 3.5 billion tons. Copper Reserves for multiple countries have been shown in the table below. The mining of copper across the world can be shown in a tabular format[18] as below.

Table 2.3: Copper production from mines in several countries

	Mine production		Reserves
	2018	2019	
United States	1220	1300	51,000
Australia	920	960	87,000
Chile	5,830	5,600	200,000
China	1,590	1,600	26,000
Congo (Kinshasa)	1,230	1,300	19,000
Indonesia	651	340	28,000
Kazakhstan	603	700	20,000
Mexico	751	770	53,000
Peru	2,440	2,400	87,000
Russia	751	750	61,000
Zambia	854	790	19,000
Other countries	3,540	3,800	220,000
World total (rounded)	20,400	20,000	870,000

PCB comprises maximum quantity of copper than any other metals present in it. Thus reclamation of Cu is mandatory to make the PCB recycling profitable. Producing copper from ore is increasing every year because of its demand in the global market. But it is not possible to meet all of our demands from mining, hence many countries are trying to make an alternative sources of metals by recycling various waste. In case of metals recovery from waste, electronic waste is always a good choice. On the other hand, when it comes to the point of recycling e-waste, PCB is a must source since all kinds of EEE contains at least one PCB.

2.4 Economic Impacts of PCB Recycling

Typically weight of copper content is one fourth of all the metals present in PCB. Thus recovery of copper is the prime target in the process of recycling PCB. But the focus is not limited to only this point since Printed circuit boards (PCBs) represent the most complex, hazardous, and valuable component of e-wastes. Some researchers have cited that certain PCB can hold more than 60 elements including heavy metals like Lead (Pb), Chromium (Cr), Cadmium (Cd), Mercury (Hg), Arsenic (As)) and toxic organic substances (such as brominated flame retardants, polycyclic aromatic hydrocarbons, dechlorane plus, etc.)[19][20]. Application of PCBs are being increased with the advancement of civilization. In the last decades, the use of PCB inside a car has been reached enormously and demand of these installation is because of all kinds of functional management of a car. Hence, this trend undoubtedly contributed in increasing volumes of PCBs produced and, so, to the overall amounts of WPCBs dismantled. In fact, the automotive sector, together with the mass electronics sector, is one of the most important sources of waste, both in volumes[21]–[24] and in materials content terms[25], [26].

By 2016, value of shipments of printed circuit assembly manufacture in the United States were projected to reach approximately 18.61 billion U.S. dollars (Figure 2.5). The statistics revealed that in 2008 to 2011 US had business over 20 million dollar which has been seen to fall near 2012 but followed almost a stable market of around 17-18 million dollar in later years of forecast. And it is clear that the amount of PCBs are created for applications will be waiting for being remanufactured or recycled in later days.

The economical features of PCB and its assembly market will be clear from the picture shown below (Figure 2.5).

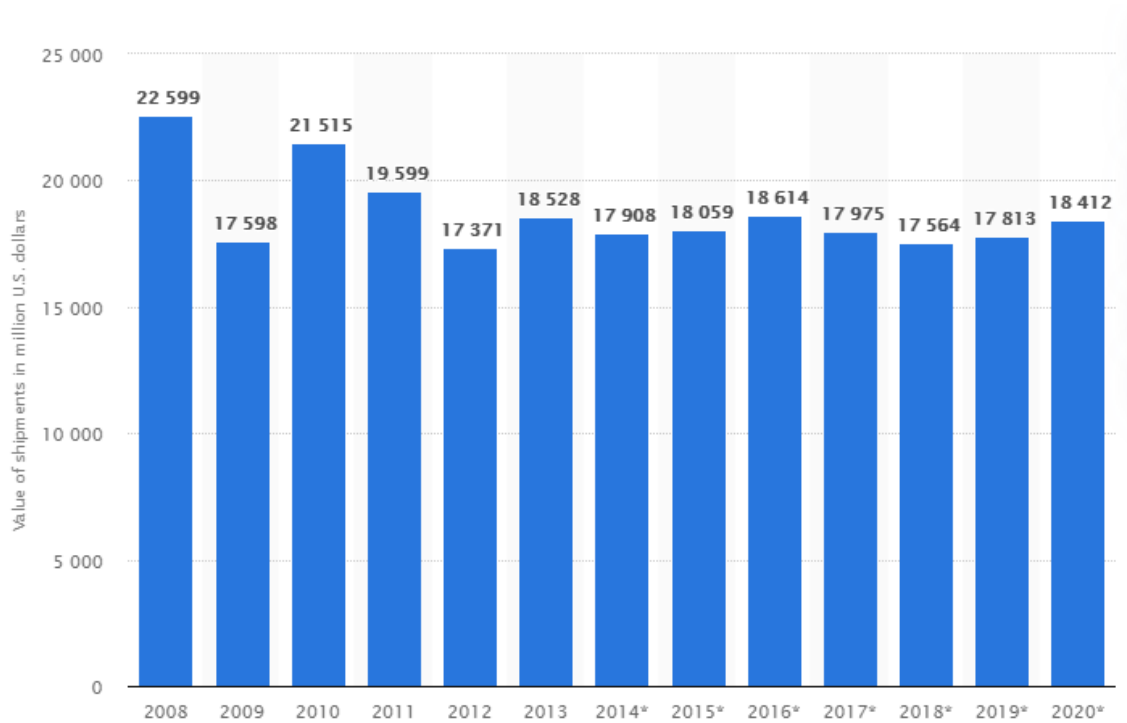


Figure 2.5: Value of shipments printed circuit assembly manufacture in US[27]

The market of PCB can clearly be understood by the budget of advertisement of the industries in this sector. In the United States, in 2012, advertising expenditures for this industry reached 20 thousand U.S. dollars. Considering the manufacturer sales or revenue, a tentative market value of PCB for few of the dominating countries can be put in Table 2.4 as shown below.

Table 2.4: Value of PCB market[28]

Country	Value of PCB	Year of the statistics	Comments
UK	90.27 million British pounds	2018	Analysis
South Korea	13.7 billion U.S. Dollars	2023	Forecast
China	60.31 billion U.S	Projected for 2016 in 2012	Forecast
United States	4.32 billion U.S. dollars	Projected for 2016 in 2013	Forecast
Global	73.3 billion U.S. dollars.	2016	Forecast

On the other hand, Table 2.5 shows the composition of the PCB, which contains 10 materials with high commercial value. Precious metals are present at concentrations of <0.1%, whereas there were higher concentrations of materials that provide structure to the PCB, such as copper (40.34%) and steel (3.5%).

Table 2.5: Percentage of materials in the printed circuit boards (PCB's) of cellphones[29]

Item	Element	PCB (% by weight)	Price (USD/ton)
1	Copper	40.34	5490
2	Tin	4.118	16,000
3	Steel	3.494	361
4	Nickel	2.598	11,788
5	Titanium	0.350	55,556
6	Gold	0.0488	40,919,295
7	Silver	0.028	553,086
8	Gallium	0.022	317,000
9	Neodymium	0.028	54,614
10	Palladium	0.00564	24,395,944

Other materials that are vital for the integration of all circuits in the PCB are also present at low concentrations, such as gallium (0.022%)—a semiconductor metal that is used for the integrated network circuits—and neodymium, which is a rare earth that serves as a magnet [30]. For this type of e-waste, it is clear that the most significant opportunity in terms of end-processing technologies centers on recovery of gold (with 79.7% of the total value in cellphone PCB materials). In terms of materials value, 97.0% is given by potential local recovery of gold, copper, palladium, and tin.

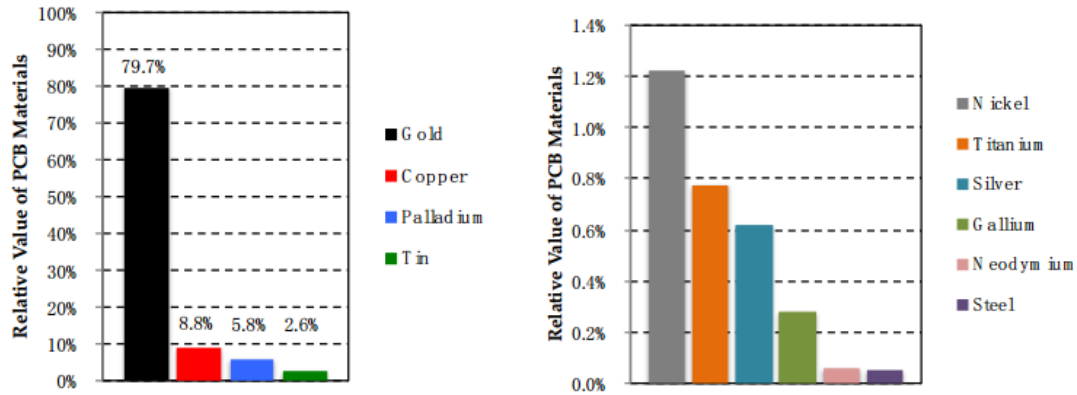


Figure 2.6: Relative value of cellphone PCB materials processed through formal channels in Mexico[29]

Although the market value of copper and tin is not nearly as high as that of gold and palladium (\$40.9 and \$24.4 million USD per ton, respectively), the relatively large proportion of these metals in cellphone PCBs makes them attractive in terms of value (Figure 2.6). Therefore, potential investment in end-processing technologies for recovery should be focused on those chemical elements.

Altogether, metal production today represents about 8% of the total global energy consumption and a similar percentage of fossil fuel-related CO₂ emissions[31].

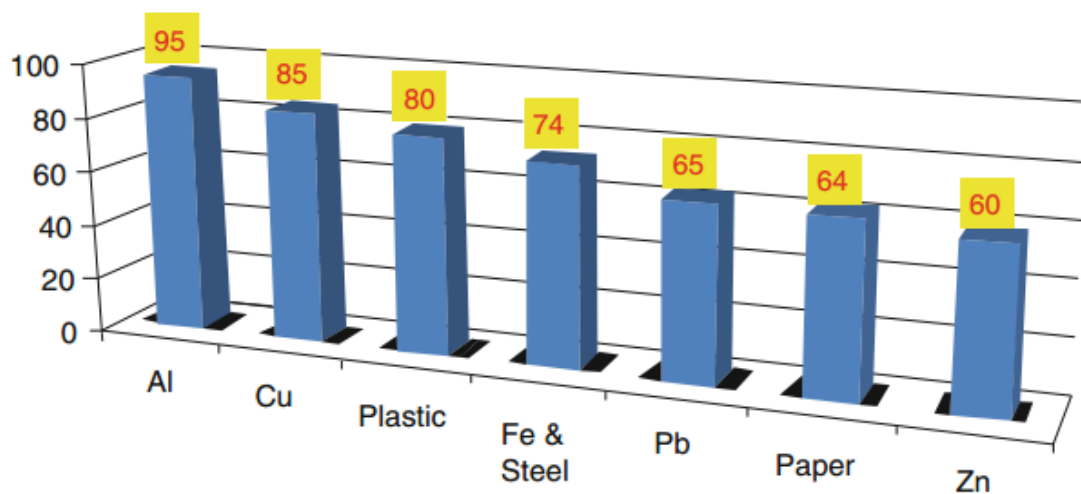


Figure 2.7: Recycled material energy savings over virgin materials[32]

Improved recycling processes can be much cheaper than primary production, primarily because they can use much less energy in production of the metal. The energy savings for a number of common metals and materials are summarized in Figure 2.7. About 60–95% energy savings are possible with WEEE recycling. Energy savings are more than 80% for Al, Cu, and plastics. Recycling often only involves the remelting of metals. Without any loss of performance, Cu is 100% recyclable. The recycling of Cu requires up to 85% of less energy than primary production.

2.5 Environmental Impacts of PCB Recycling

In the last decade, PCB has been attracted alarming attention due to the effects of hazardous components or elements present in it. The volume of E-waste generation has already become an obstruction in the way of developing the electronic industry. If we take the 10 million per year increasing sales volume into account, the recycling task will be serious in the future. According to an estimation of a research project, there were about 12.75 million retired computers in the USA in 2002, in which there were 10.2 million retired computers exported to Asia. The Silicon Valley Toxics Coalition (SVTC), a coalition advocating for a clean and safe high-tech industry, conducted an investigation that provided the basis for a report released on 25 February 2002, entitled *Exporting harm: The high tech trashing of Asia*[33]. Thus environmental issues for Asia are of much sensitivity while it is the point of recycling e-waste.

All of the naturally occurring metals and other elements are found everywhere in at least trace concentrations in soil, water, air, and organisms. Organisms require some of the trace elements as essential micronutrients, including copper, iron, molybdenum, zinc, and in some cases aluminum, nickel, and selenium. Under certain conditions, however, these same elements can accumulate to high concentrations in organisms and cause ecological damage. Trace elements that are most often associated with environmental toxicity are the heavy metals cadmium, chromium, cobalt, copper, iron, lead, mercury, nickel, silver, tin, and zinc, as well as the lighter elements aluminum, arsenic, and selenium.

Xiang et al. has studied PCB recycling and developed a sophisticated process to minimize the presence of these elements in the free environment. But this process was not enough to be

relaxed in the environmental issues but is a motivation to the way of environment friendly recycling.

Table 2.6: Element and ion concentration during the steps of PCB recycling[34]

Element	Content in 1 g ($\mu\text{g/g}$)	Metal ions content of 1 liter waste water (mg/L)	Metal elements content of 1g nonmetal particles (g/g)
Cu	992894.73	0.42	1.19E-2
Au	8.38	0.02	1.19E-5
Cd	2.81	0.015	6.85E-7
As	45.6	No detect	No detect
Pd	161.3	0.14	
Pb	3032	0.02	
Sn	3824	0.05	
Ni	24.34	0.04	4.18E-6
Ag	6.84	No detect	
Se	-	-	1.52E-4
Cr	-	-	2.20E-5

Table 2.6 shows the picture where researchers tried to reduce environmental pollution. But the real scenario is PCBs are released in to landfills, ponds, drains etc. or simply incinerated though partially collected regionally. Primary production (conventional mining) plays the most important role in the supply of metals for EEE applications since secondary metals (recycle) are only recovered in limited quantities so far. Environmental impact/footprint of primary metal production is significant, especially for precious metals and scarce metals which are low in concentration in natural ores. Considerable amounts of land are used in mining, wastewater and $\text{SO}_2(\text{g})$ are created, and the energy consumption and CO_2 emissions are large. Nowadays, the increasingly sophisticated small PCB boards make the production more and more complex and bring about a lot of wastewater full of chemical substances in the processing. PCB boards are difficult to decompose in natural environment and is disseminated everywhere. A large number of PCB boards invade the air, soil, river and ocean during the producing, processing, applying, transporting and waste handling process. Some of the PCB boards are inhaled by small marine organisms and fishes which are the food of marine life. As a result, PCB boards enter the body of all marine life, including marine

mammals. The accumulation of PCB boards in marine species is much higher than that in the water which causes a great damage to the marine ecosystem. The main pollutants in the wastewater from the design and production of PCB boards are copper, organic matter, ammonia.

Calculations of CO₂ (g) emissions associated with primary metal production (for Cu, Co, Sn, In, Ag, Au, Pd, Pt, and Ru) used for EEE manufacture in 2007 showed total 23.4 and in 2010 33.6 Mt/a[35]. Between 2007 and 2010, 65–73% of this amount comes from Cu, 17–22% from Au, 6.2% from Sn, and 2.1–3.7% from Ag metal production[31]. The recycling of old and new scrap produces 9 million tons of Cu per year. Around the world, Cu recycling only saves 40 million tons of CO₂[36]. CO₂ emissions reduced 13.2 kg CO₂/kg recovered metal from powders/residues from fluorescent lamps, 19.2 kg CO₂/kg from CRTs, 27.0 kg CO₂/kg from Li-ion batteries, and 25.9 kg CO₂/kg from PCB recycling[37]. Toxic emissions during electronic production and their recycling can be categorized in different stages as in Table 2.7.

Table 2.7: Levels of toxic emission from EEE production and e-waste recycling

Primary emissions	Secondary emissions	Tertiary emissions
Hazardous substances that are contained in e-waste	Hazardous reaction products for Improper treatment (improper incineration and smelting)	Hazardous substances/reagents used during recycling (leaching and amalgamation)
Pb, Hg, As, Cr6+, PCBs, CFCs, etc.	Dioxins, furans, BFRs	Inorganic acids, cyanide, Hg
EU RoHS Directive fully restricts these elements/substances	EU RoHS Directive partly restricts these substances	There are no necessary legislative approaches even in cleanest/ greenest inappropriate recycling

On a local-level point of view, uncontrolled discarding or inappropriate waste management/recycling generates significant hazardous emissions, with severe impacts on health and environment. In this context, there are three levels of toxic emissions.

2.6 Social Impacts of PCB Recycling:

Since the countries like Bangladesh are geographically deprived of natural resources especially metals mines, recovery of metals from e-waste or WPCB can be a solution for

them. On the other hand, the unemployment situation of hugely populated country can be resolved by creating new jobs in the recycle industries. Though few people are currently involved in this waste sector but in informal ways. When there will be an ordered structure for the sector of WEEE, the country will get more benefitted financially. For Bangladesh scenario, the WEEEs are collected mainly for export in lower price. We need to process this waste to recover metals in exchange of exporting. Also the pollution control and environmental preservation would improve the level of living of the earth's inhabitants.

The efficiency of e-waste recycling is subject to variable national legislation along with technical capacity, consumer participation, and even detoxification. E-waste management activities result in procedural irregularities and risk disparities across national boundaries. Starting from United Nations Environment Program (UNEP), European Union (EU) to U.S. Environmental Protection Agency all organizations are concerned for developing legislation for e-waste and their successful implementation. US government seriousness about the e-waste legislation has been shown in the Figure 2.8 which reveals legendary implementation of the policies.

Figure 2.8: States with Electronic Waste Recycling Programs[38]

Generally speaking, the laws in every country focused mainly to a hope that reduction of consumption will be a good approach. But the way of implementing this hope is to reuse the original product before dumping it where repairing or repurposing of the product can be a way for this. Finally, all countries focused to the philosophy that nothing is waste, every waste itself is a resource thus recycling e-waste is a must. Figure 2.9 shows the functionality of collected WEEE.

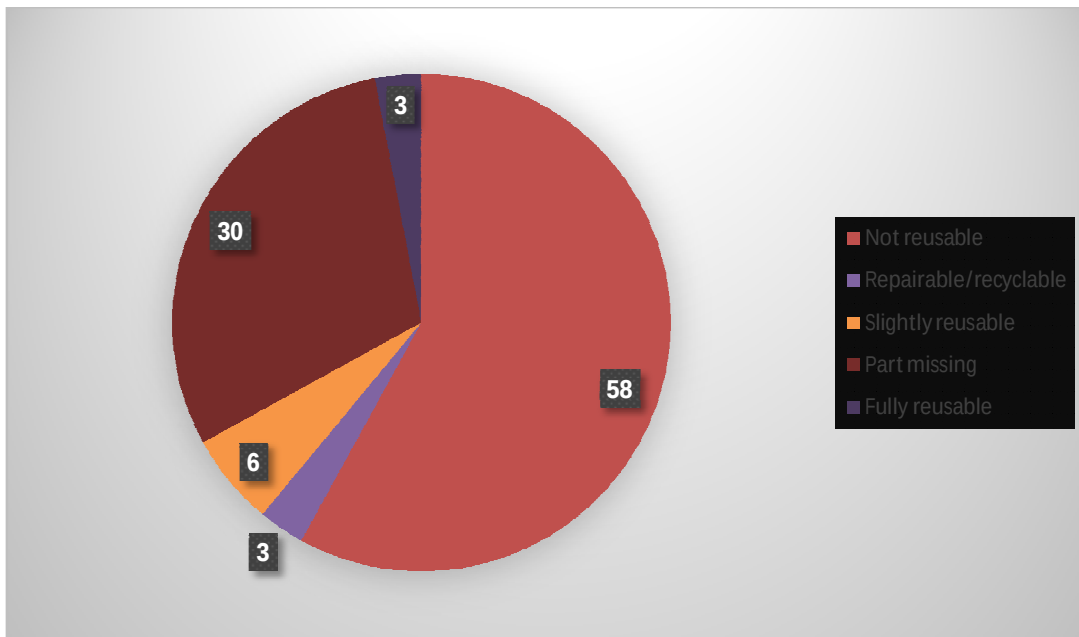


Figure 2.9: Functionality of collected WEEE[39]

Considering this necessity of e-waste legislation the government of Bangladesh took the step to frame the electronic waste management rules in 2012. In the next step these rules are Electrical and Electronic Waste (Management and Handling) Rules, 2017 and Draft National 3R (Reduce, Reuse & Recycle) Strategy. But it is yet to finalize the document. The draft rule said manufacturers, assemblers, stores, recyclers, repairer and dismantlers will have to get registered with the DoE.

2.8 Types of PCB:

PCB is used in all kinds of electronic devices depending on their purpose and functions. Types of PCBs are of varied kind when classification is made on several points of view. As for example, depending on the twisting flexibility of PCB, it is divided as rigid pcb, flexible

pcb and rigid flex pcb. On the other hand, PCB is also categorized depending on their frequency. The general categorizes of PCB are single-layer, double-layer and multi-layer PCB.

2.8.1 Single-layer PCB:

A single-layer or single-sided PCB is one that is constructed from a single layer of substrate or base material. A thin layer of metal is applied to one side of the base material. Copper is the most popular coating due to its excellent electrical conductivity. A protective solder mask is normally added after the copper base plating, followed by the final silk-screen to mark out all of the elements on the surface (Figure 2.10). Single-layer/single-sided PCBs are simple to design and produce since all of the circuits and components are soldered to one side. Because of their popularity, they can be purchased at a low cost, especially for large-volume orders.

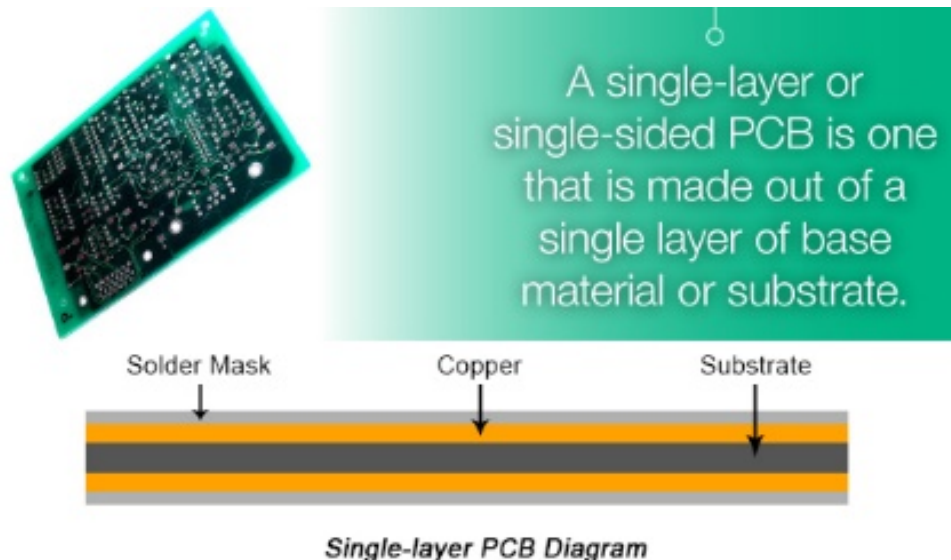


Figure 2.10: Single-layer PCB[40]

Because of their low cost and large capacity, they're widely used in calculators, cameras, radios, stereo equipment, solid state drives, printers, and power supplies, among other things.

2.8.2 Double-layer PCB:

A base material is used for double-layer or double-sided PCBs, which have a thin layer of conductive metal, such as copper, added to both sides of the surface (Figure 2.11). Circuits on one side of the board will attach to circuits on the other side of the board into holes drilled through the board. A double-layer PCB board's circuits and components are usually connected

in one of two ways: through-hole or surface-mount. Small wires, known as leads, are fed through the holes in a through-hole connection, and each end of the leads is soldered to the appropriate part.

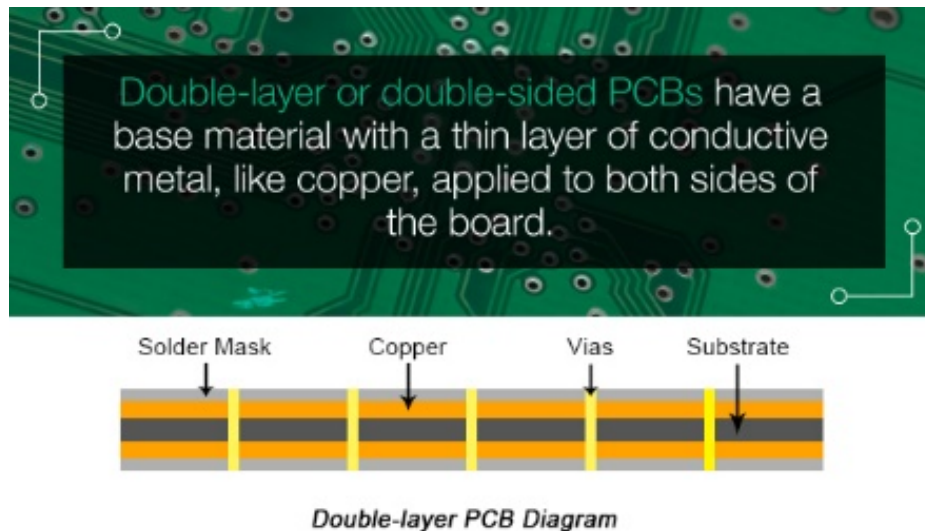


Figure 2.11: Double-layer PCB[40]

Wires are not used as connectors on surface mount PCBs. Instead, a large number of small leads are soldered directly to the board, effectively turning the board into a wiring surface for the various components. This allows circuits to be completed with less room, allowing the board to perform more functions, normally at faster speeds and with less weight than a through-hole board. Industrial controls, power supplies, instrumentation, HVAC systems, LED lighting, vehicle dashboards, amplifiers, and vending machines are all examples of applications that involve a moderate degree of circuit sophistication.

2.8.3 Multi-layer PCB:

Multi-layer PCBs are made up of three or more double-layered PCBs stacked on top of each other. These boards are then glued together with a special adhesive and sandwiched between sheets of insulation to prevent any of the components from melting (Figure 2.12). Multi-layer PCBs are available in a range of sizes, from four layers to ten or twelve layers. A 50-layer PCB was the largest multi-layer PCB ever built.

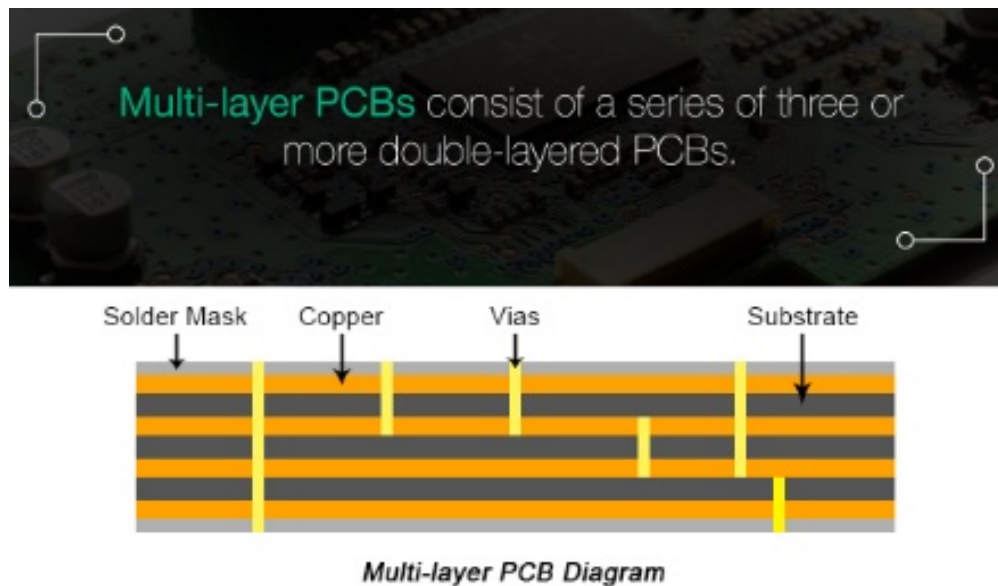


Figure 2.12: Multi-layer PCB[40]

Designers may create very dense, complex designs using several layers of printed circuit boards, which are ideal for a wide variety of complicated electrical tasks. File servers, data storage, GPS technology, satellite systems, weather forecasting, and medical equipment are all applications where multi-layer PCBs will be helpful.

2.9 Structure of PCB:

A simple PCB consists of a flat sheet of insulating material laminated to the substrate and a layer of copper foil. Chemical etching separates the copper into separate conducting lines known as tracks or circuit traces, pads for contacts, vias for passing connections between copper layers, and other features such as strong conductive areas for electromagnetic shielding or other purposes. The tracks serve as fixed wires that are separated from one another by air and the board substrate material. A coating on the surface of a PCB prevents the copper from corrosion and decreases the likelihood of solder shorts between traces or unwanted electrical contact with stray bare wires. Multiple copper layers can be found on a printed circuit board. Copper is on both sides of a two-layer board, and additional copper layers are sandwiched between layers of insulating material on multi-layer boards. Vias, which are copper-plated holes that serve as electrical tunnels through the insulating substrate, bind conductors on different layers. Through-hole part leads may also be used as vias in some cases. The next level up from two-layer PCBs is normally four-layer. Two layers are usually

devoted to power and ground planes, with the remaining two layers used for signal wiring between components. The basic materials needed to build a multi-layer board are copper foil, prepreg and inner-layer cores.

2.9.1 Copper Foil:

The copper foil used in circuit boards is typically in sheets of ½ oz. and 1 oz. per square foot in weight or 0.0007 and 0.00134 inches nominal thickness. In other words - one ounce of copper will cover one square foot when it is rolled out to a thickness of 0.00134" or 1.34 mils [41]. A sheet of heavy copper is one that contains more than three ounces of copper per square foot, or is 0.0042 inches (4.2 mils, 105 µm) thick. For high current or to help dissipate heat, thick copper layers are used. 1 oz copper per ft² (35 m) is the most common thickness on common FR-4 substrates; 2 oz (70 m) and 0.5 oz (17.5 m) thickness is also a choice. The choice is also dependent on the flexibility of substrate as the more flexible the substrate is the thinner is the metallization. Though 1/2 oz/ft² foil is not commonly used but may be used for outer layers during through holes technology.

2.9.2 Prepreg:

It is also known as Preimpregnated Bonding Sheet. Prepregs are made by curing layers of cloth or paper with thermoset resin under pressure and temperature to form an integral final piece of uniform thickness. The width and length can be up to 4 by 8 feet. To achieve the desired final thickness and dielectric characteristics, different cloth weaves (threads per inch or cm), cloth thickness, and resin percentage are used. It's the "glue" that connects the cores. There are a variety of materials available; for example FR4 – a woven fiberglass cloth pre-impregnated with epoxy resin, also known as B-stage in the industry. Pressure and heat trigger the resin, which then "melts" during the lamination process. It flows over copper features and exposed laminate on the core, bonding the foil and core layers together as it cools. The type classification (FR-4, CEM-1, G-10, etc.) and thus the characteristics of the laminate produced are determined by the cloth or fiber material used, the resin material used, and the cloth to resin ratio. The fire resistance level of the laminate, the dielectric constant (ϵ_r), the loss factor (t), the tensile strength, the shear strength, and the glass transition temperature (T_g), and the Z-axis expansion coefficient (how much the thickness changes with temperature) are all important characteristics.

2.9.3 Inner-Layer Core:

Inner layer core is nothing but the inside layers produced during the lamination process of a multi-layer PCB. Inner layer core, copper foil and prepreg are bonded together under heat and pressure, in a vacuum, during the lamination process (Figure 2.13). As a consequence, the product is inseparable in one piece.

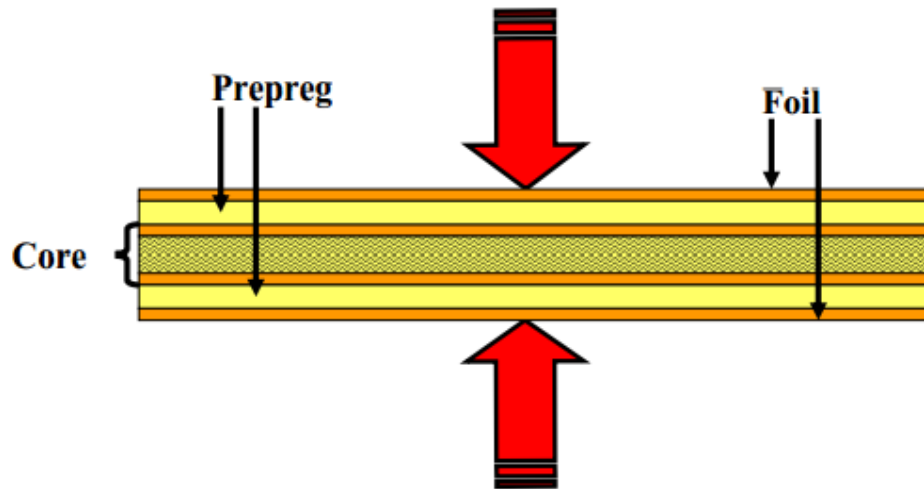


Figure 2.13: Laminated Panels[41]

Starting with a two-sided copper-clad laminate, etch the circuitry on both sides, then laminate to the top and bottom pre-preg and copper foil, a four-layer PCB can be fabricated. To get traces on the top and bottom layers, it is then drilled, plated, and etched again. Since errors cannot be reversed later, the inner layers are subjected to a thorough machine inspection prior to lamination. An image of the board is compared to a digital image produced from the original design data by automatic optical inspection (AOI) machines. Then, using a laser, Automated Optical Shaping (AOS) machines will add missing copper or eliminate excess copper, minimizing the amount of PCBs that must be discarded. The width of PCB tracks can be as small as 10 micrometers.

2.10 Mobile Phone PCB:

Mobile phones and computers, among other electronics and electrical equipment, have seen the most rapid technological advancement. Since Motorola introduced the first mobile phone in 1985, mobile phone technology has progressed to include flip phones in 1989, 2G GSM networks in 1991, SMS in 1992, vibrating phones in 1996, mobile web and the first

Blackberry mobile in 1999, internal antenna in 2000, camera embedded phones and 3G networks in 2001, and 4G in 2009[42]. Mobile phones have shrunk in size and weight through time, from 794 grams to around 100 grams now[42]. PCBs are the lifeblood of a device, supplying power to all of its components, which is why it's critical to have PCBs that are both supportive and dependable for the system. Today, mobile phones provide a technological answer for a variety of businesses, including the Internet, banking, retail, social networking, photography, and audiovisual media, to name a few. To make a device that puts the world at your fingertips, you need the correct kind of circuitry. Printed circuit boards are critical to the cell phone's efficient design and fabrication. Figure 2.14 visualizes the unmounted mobile phone PCB.

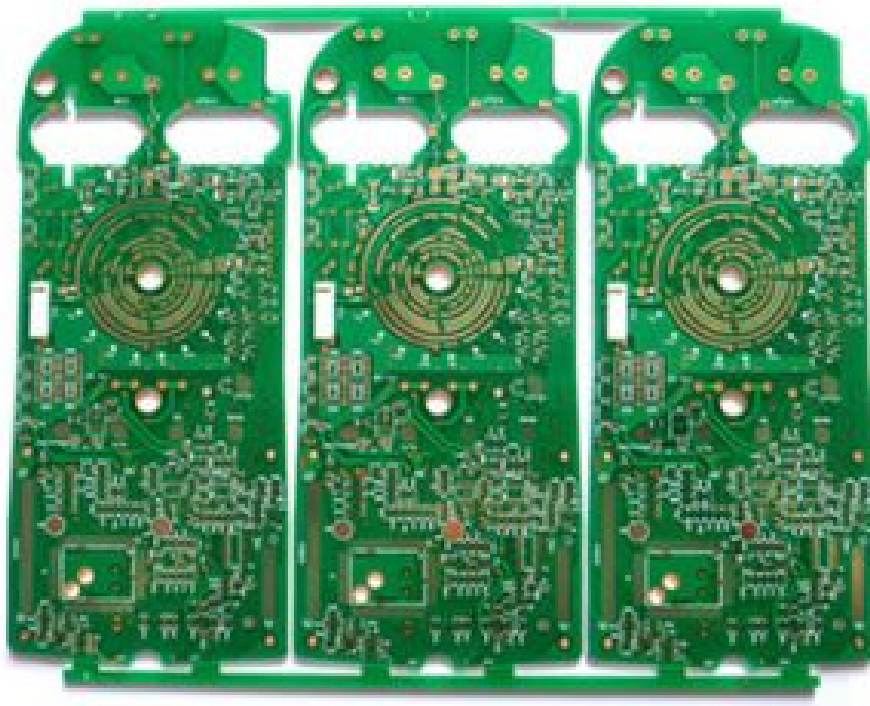


Figure 2.14: Mobile Phone PCB Boards[43]

Copper is typically used for the basic boards. A variety of flex and rigid flex materials, Pyralux TK, 370 HR, polyimide, and glass epoxy are some of the most popular circuit board materials. Dielectrics are used as a ceramic filler and glue to ensure that all of our components perform to their full potential without becoming loose or jutting out from the PCB. The components are effectively glued to the boards as a result of this.

When compared to PCBs from other electronics like televisions, refrigerators, DVD players, and calculators, computer and mobile phone PCBs contain the most valuable metals. Table 2.8 shows the metallic concentration in mobile PCB found in different studies. This feature of mobile phone PCB is expected since a small PCB in this device provides multitasking features. Metal content in the PCB also varies depending on the branded and non-branded product.

Table 2.8: Metal concentration (wt%) of PCBs as reported in different studies

Metal content	Zhang and Forssberg (1997)[44]	Shuey and Taylor (2004)[45]	Zhao et al. (2004)[46]	Wang et al. (2005)[47]	Ogunniyi and Vermaak (2007)[48]
Cu %	16.6	23.73	26.8	19.66	20
Al %	-	4.7	4.7	2.88	5
Pb %	1.35	4.48	-	3.93	1.5
Zn %	0.16	0.75	1.5	2.10	-
Ni %	0.28	3.32	0.47	0.38	1
Fe %	1.4	7.47	5.3	11.47	7
Sn %	3.24	3.65	1.0	3.68	-
Sb %	-	1.82	0.06	-	-
Ag (ppm)	1240	800	3300	500	1000
Au (ppm)	420	800	80	300	250
Pd (ppm)	10	210	-	-	110

On the other hand, as the mobile phone technologies are being changed every now and then, structure and constituents of PCB are also varied. Merve Sahan et al. studied the concentration of metals in PCB of different brands as shown in the Table 2.9.

Table 2.9: Mean concentrations of metals in the PCBs of mobile phone samples.

Element %	Asus Pegasus	NG 870	Nokia C5	Nokia 3210	Nokia 3310	Siemens C5	BB Smart*	Mixed PCB*
Cu	32.47	22.75	37.8	20.6	28.75	31.31	39.77	28.24
Fe	2.36	3.72	3.39	1.0	0.5	1.19	4.63	1.01
Al	0.89	1.04	1.15	1.07	1.18	1.63	2.01	1.59
Sn	6.27	5.18	2.83	2.96	3.55	1.30	3.30	2.71
Ni	3.23	2.38	2.10	1.10	1.58	2.70	1.70	1.50
Zn	2.81	2.12	0.23	0.35	0.72	0.51	2.69	1.36
Cr	0.019	0.39	0.033	0.013	0.029	0.044	0.044	0.014
Pb	0.16	0.73	0.26	1.63	1.79	1.0	2.73	1.56
Co	0.014	0.027	0.011	0.011	0.012	0.07	0.005	0.03
Ag	0.25	0.2	0.2	0.83	0.51	0.39	0.26	0.59
Au	0.24	0.29	0.14	0.18	0.16	0.11	0.053	0.16

*BB smart: Black Berry smart phone

Table 2.8 and 2.9 vividly stipulate the fact that besides the environmental and health issues waste PCBs are one of the most valuable sources for metals.

2.11 Recycling of PCBs

WPCBs are often PCB assemblies rather than bare PCBs. ECs are always used to mount PCBs. Unpopulated/bare PCBs or printed wiring boards are PCBs without ECs (PWB). The chemical compositions of WPCBs are more sophisticated and diversified, containing a wide range of useful elements. As a result, the recycling of WPCBs is significantly more difficult. At the time of disposal/dismantling, the majority of ECs are functional and useable. To conserve scarce resources, reuse functioning ECs, and remove potential exposure to dangerous elements, removing ECs from WPCBs is a critical stage in the WPCB recycling chain from both the standpoints of materials recovery and EC reuse. For example, in WPCB recycling, poisonous (mostly in electrolytes), explosive, and combustible elements must be removed and disposed of from Al electrolytic capacitors (AEC). The following recycling procedures are commonly used in today's general material and component recovery methods. The recycling process for e-waste is divided into four key parts[49].

- Collection and presorting

- Pretreatment (includes dismantling, size reduction for liberation, and granulometric classification)
- Preprocessing (includes separation, upgrading, and extraction)
- Endprocessing (purification and refining)

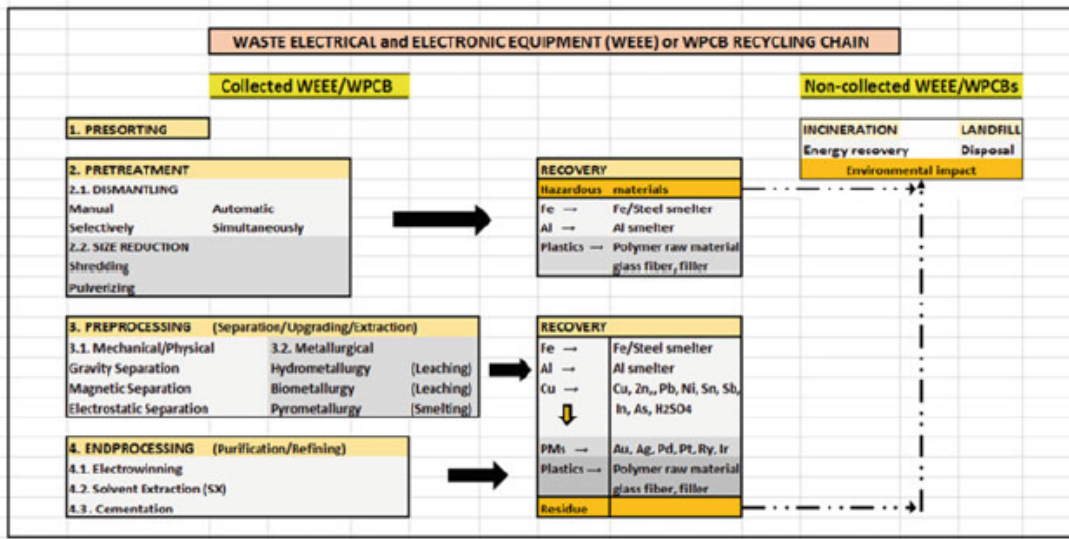


Figure 2.15: E-waste recycling chain and end-of-life WEEE/WPCB treatment options[31]

Collective municipal or commercial collection, individual producer and retailer collection, and informal sector collection are the main possibilities for postconsumer goods collection (waste pickers). Getting rid of post-consumer garbage is a logistical nightmare. In contrast to Europe, where consumers pay for collection and recycling, garbage collectors in developing countries typically pay consumers for outmoded appliances and metal scrap. Individuals and small enterprises comprising collectors, merchants, and recyclers are typically organized in informal waste sectors, each providing value and creating jobs at every point in the recycling chain. Because many poor people rely on the little revenues created by this chain, collection rates of up to 95 percent of total generated waste are noteworthy. This demonstrates how a strong economic motivation for collection is a critical component of successful collection, a feature that may be overlooked in today's organized takeback systems. End-of-life WEEEs/PCBs are treated in one of four ways: landfill, incineration, shredding, or disassembly (Figure 2.15).

2.12 Pretreatment of waste PCB for recycling

Mechanical processing causes significant losses of PMs (precious metal) and SMs (scarce metal) in WPCB. This issue is caused by incomplete liberation of minor and significant metals in complex materials, as well as losses of metallic dusts during ceramic component shredding. Separation occurs as a result of imperfect emancipation. Physico-mechanical preprocessing separation produces various grades/quantities of recyclates. EEEs do not usually require extensive preparation; depending on the final processing tiny EEEs, such as cell phones and MP3 players, can be handled promptly once the battery has been removed (without size reduction). Dismantling and sizing are the two physical pretreatment adopted extensively for WPCB recycling.

2.12.1 Dismantling/Disassembly

The goal of dismantling is to free the materials and send them to the appropriate pre- and post-treatment processes. Hazardous compounds must be removed and carefully stored or handled, whereas valuable components/materials (PCBs, HDs, etc.) must be removed and directed to efficient recovery operations. The first and most significant phase in a recycling chain is dismantling ECs on WPCBs, which can help conserve scarce resources, establish component reuse, and remove dangerous elements from the environment. In recycling technology, manual disassembly is the most expensive and time-consuming activity. When considering the number of WPCBs in use around the world, the creation of an automatic disassembly procedure is critical. Manual disassembly is the most common method for processing of WPCBs since it is low-cost, uses simple electrical/pneumatic instruments, and can be done by people with little or no education with the right instruction. Disassembly can be done manually or automatically, and it can be done sequentially or concurrently. The ECs are all evacuated from WPCBs at the same time. Mixed EC disassembly can help you save time. The dismantling is done in a semi-automated/automated manner. On a big scale, automated disassembly allows a cost-effective recycle with minimal manpower. Radio-frequency identification (RFID) tags will be extremely useful in identifying ECs on WPCBs[50]. Critical issues with regard to occupational health should be implemented during deconstruction and downward recycling streams, and significant dust exposure should be avoided as much as feasible. Due to the nature of the metal-nonmetal interface, the limitations of purely mechanical process routes are effectively concerned with PM loss from component

structures on populated boards, and an effective automated disassembly methodology could well expand the potential for mechanical turnkey approaches for all grades of WPCBs.

Although WPCBs are supposed to last 500,000 hours, the average End of Life for ECs is only 20,000 hours, or less than 5% of the time. As a result, many ECs are still functional and usable when they are discarded as e-waste. To save finite resources and avoid potential exposure to hazardous elements, dismantling ECs from WPCBs is a first and critical step in the WPCB recycling chain[51]. ECs are often separated into two categories: (i) functioning and useable ECs that may be reused for new goods and repairs, and (ii) damaged ECs that can be recycled for metal. The disassembly (demanufacturing/inverse manufacturing) process separates reusable, recognizable, or toxic ECs and/or materials in order to optimize economic return and reduce environmental damage, allowing succeeding processes to run more effectively. The systematic removal of ECs, components, a collection of parts, or a subassembly from e-waste is known as disassembly. Soldering, bolting/riveting, gluing, coating/painting, and foaming are the most common methods for connecting ECs to PCBs. Table 2.10 demonstrates the features of connection types in terms of their degree of specificity and nonrandomness of liberation behavior following shredding with various connection complexities. Fracturing, drilling, ungluing, heating, and lubricating procedures can be employed to disassemble ECs. Special equipment, simple tools, or disassembly by hand are all options for disassembly.

Table 2.10: Characteristics of connection types related to their specific degree and nonrandomness of liberation behavior after shredding with different connection complexities

Connection type	Liberation after shredding
Bolting/riveting	High liberation, high randomness
Gluing	Medium liberation, medium randomness
Coating/painting	Low liberation, low randomness
Foaming	Medium liberation, medium randomness
Connected materials/components of different levels of complexity	High/medium liberation from structure, high/medium randomness
Heterogeneous/high number of connections per surface area	Low liberation on component, low randomness
Material properties, low complexity, low number of joints	High liberation, high/medium randomness

Due to inefficiency and detrimental effects on the environment and human health, current WPCB dismantling techniques prohibit e-waste recycling[52]. As a result, an environmentally acceptable dismantling method is required. Within any WEEE recycling approach, manual disassembly and sorting are a substantial cost element and a high labor strain. Disassembly can be done in stages or in its entirety. The components are reuse oriented selective disassembly technology for WPCBs with wet chemical selective desoldering, which can reduce pollution and recover expensive solder/tin. Desoldering is required to remove ECs from WPCB assemblies. To open solder connections and separate various types of metals and components, the current informal manual selective dismantling method employs chisels, hammers, and cutting torches. Another manual procedure is cooking on a coal/electric-heated plate and melting solder in order to sell the chips and other recovered components to acid strippers for further processing. Manual informal dismantling has a foul odor, black vapors, and is a prohibited process.

2.12.2 Size Reduction

Recycling and managing e-waste is not a simple or straightforward procedure. WPCBs have a very different mineralogy than natural ores used in metal processing. Many elements are intertwined with complicated assemblies and subassemblies, and metals are also intertwined with hazardous organics. In addition to the liberation goals, the particle size must be compatible with the processing method. The approach of size reduction will be determined by the diverse material behaviors. Shredding, crushing, and sequential sorting/classification employing mechanical processing procedures are used to free metals from organic nonmetals and other metals. The main cause of resource loss is incomplete material liberation from WPCBs.

Because of randomness and physical qualities, imperfectly liberated particles end up in the wrong recycle streams, but also because of related materials that impact physical properties and therefore separation (Figure 2.16).

Crushing, grinding, or shearing, together known as "shredding," is used to reduce the size of materials, however it rarely results in complete liberation. Separation occurs as a result of imperfect emancipation. The size of the particles has a considerable impact on the separation and extraction operations that follow. With lower particle sizes and a narrow size distribution, mechanical separation of metallic components from WPCBs is easier to achieve[53], [54].

Because of the huge surface area, metals dissolve best at the smallest particle size fractions during leaching. Particle sizes ranging from 37 to 4750 μm were employed in previous research[55].

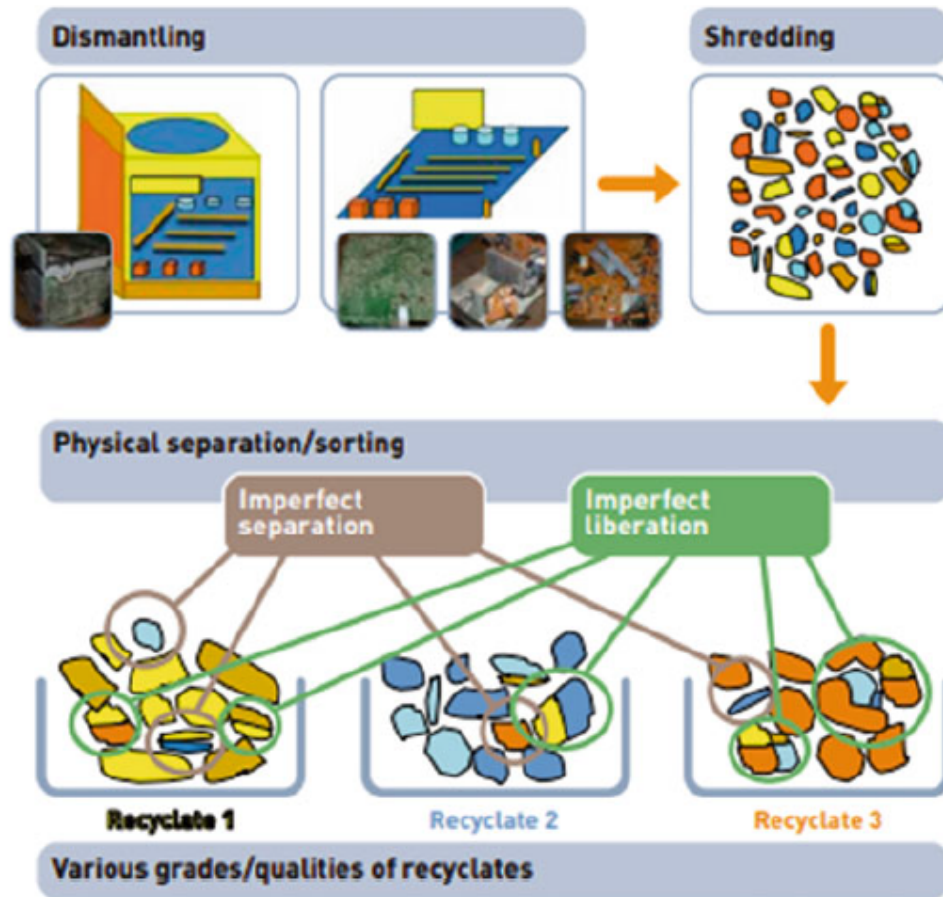


Figure 2.16: Imperfect liberation leads to imperfect separation[31]

Laboratory-scale investigations (in μm size, i.e., 53–150 μm) use far coarser particle sizes (in mm size, i.e., 5–50 mm) than industrial-scale plants (in mm size, i.e., 5–50 mm). In PCB recycling, calcination following size reduction is an environmentally unsuitable procedure[56]. Shredding, according to Chancerel et al. (2009), increases PM loss and has a detrimental influence on PM recovery[57]. Plastics and ferrous metals absorb some of the PMs. The concentration of PMs in PCBs decreases as the amount of shredding increases. Pd is found in ceramics that are broken down to dust and end up in filter dust during

shedding. The first and most straightforward strategy to reducing PM losses during shredding and sorting is to limit the amount of PMs entering the shredder by manually sorting the materials at the start of the process to remove the majority of PM-rich items. Shredding should be avoided for PM-rich WEEEs and instead immediately fed into appropriate metallurgical recovery processes for PMs and SMs.

2.13 Traditional processes for waste PCB recycling

Thermal or nonthermal, chemical or mechanical, pyrometallurgical or hydrometallurgical, advanced or traditional/conventional, primitive or direct, or according to reaction atmosphere, WPCB treatment and recycling processes can be classified. Direct treatment, which includes uncontrolled burning, mechanical separation, and primitive crude acid leaching processes are all examples of traditional recycling techniques.

2.13.1 Uncontrolled Incineration

Incineration is the process of burning WPCB by converting its calorific value to energy and emitting the gas either directly or after treatment, with the primary goal of removing the nonmetallic component (around 70 wt percent). It has the advantage of reducing the volume of WPCB by 50%, and the calorific value of WPCB is quite high when compared to municipal solid waste, which is around 9.9×10^4 kJ/kg. Because of the simplicity of the procedure, incineration is still commonly employed in America, Asia, and Europe today. In the absence of post-purification, harmful pollutants such as heavy metals, fly ash, PCDD/Fs, and PBDD/Fs are discharged into the atmosphere during the combustion of WPCB. Cd, Cu, Ni, Pb, and Zn will be evaporated and released into the environment in the order of their melting points[58]. As a result, given the harmful emissions, cremation as a treatment method for WPCB is not an environmentally beneficial alternative. Furthermore, the development of an incinerator facility is a significant financial investment for local governments.

2.13.2 Mechanical Separation

The rules of physics and material properties are used to separate materials in generic mechanical and physico-mechanical separators. Sorting and gravity separation are the most common mechanical separations, whereas physico-mechanical separation combines gravity, magnetic, and electrostatic separations. Mechanical separation is a traditional treatment

method for WPCBs, while physico-mechanical separation is a more advanced treatment method. Separation is influenced by a number of factors[31]:

- Fluid viscosity (ease of flow).
- Solid volume concentration (significantly affects viscosity).
- Flow turbulence (and turbulent energy dissipation).
- Boundary flow along the separator walls.
- Eddy flows, i.e., swirls that dissipate energy and efficiency.
- Particle shape affecting terminal velocity, e.g., platelike particles will fall differently than more spherical ones (shape factor).
- Hindered settling, i.e., particles affect each other's flow.
- Momentum transfer between phases and within a phase.
- Uneven force field separation, e.g., due to technological constraints.
- Zeta potential, e.g., the electrical surface charges on particles.
- pH of fluid.
- Physical distribution of particle properties, e.g., density, conductivity, and magnetism (and other properties than those used for separation)

Shredding and grinding of the entire mixed e-waste is followed by separation and concentration utilizing gravity, magnetic, and/or electrostatic separators. As a result, mechanical approaches, particularly for PMs, do not yield great recovery rates. Purely mechanical preprocessing results in significant losses of PMs, particularly in the dust and ferrous fractions. Due to a liberation problem between metals and polymers, the potential loss of PMs in dry mechanical separation methods could be as high as 10–35 percent. A three-stage dust removal system is often used to avoid contamination from dust. In impoverished and emerging countries, e-waste is handled improperly by informal sectors. As a result, it's critical to create straightforward physical material recovery processes that can be used in both formal and informal sectors.

2.14 Advanced Methods for WPCB Recycling

2.14.1 Pyrometallurgy

The most important alternative approach for treating complex e-waste is thermal/thermochemical processes at high temperatures. Direct treatment (without size reduction or removal of connected ECs) targets Cu and PM recovery in pyrometallurgy. The initial pyrometallurgical stage is usually followed by hydrometallurgical and electrometallurgical procedures in this situation. During the last three decades, pyrometallurgical techniques for extracting metals from diverse waste sources have been used. E-waste recycling procedures include smelting in furnaces, incineration, combustion, and pyrolysis.

2.14.1.1 Direct Smelting

Mixed WEEE is burned in the blast/shaft furnace to obtain 75–85 percent black Cu, then oxidized in the converter, and finally reduced in the anode furnace in the direct smelting process. The majority of impurities are separated into the vapor phase and released in the off-gas. H₂SO₄ can be used to purify anodic Cu, as well as Ni, Zn, and Fe[59]. As a result of the deterioration of epoxy and the volatilization of metals, thermal procedures emit dangerous substances into the atmosphere and water (including Pb, Sn, As, and Ga). These operations are energy intensive and necessitate the use of costly exhaust gas purification systems and corrosion-resistant equipment[60]. Metals are melted at roughly 1200 °C in an air-blown furnace during direct smelting.

2.14.1.2 Incineration

Unlike smelting, incineration does not result in the creation of melts. The goals of incineration are to minimize the amount of WPCB and to accomplish partial heat recovery by burning WPCB when the heat released is sufficient. Small-scale e-waste with high PM content can be burned at roughly 850 °C with around 6% oxygen in rotary furnaces. The burned substance loses around 20% of its weight. The incinerated material is brittle and crushed to a fineness of 0.2 mm. Hg is often volatile during the burning of WEEE and batteries. If off-gas treatment systems are not used, Ni, Mn, and Cd are also emitted.

2.14.1.3Pyrolysis

Pyrolysis is regarded as a viable technology for utilizing WPCB resources. The potential utility of recycling should be considered while using pyrolytic oil (PO). However, due to its complex chemical composition, it has not been used on a big basis. Pyrolysis is the thermochemical degradation of organic materials (plastics, paper, etc.). In the absence of oxygen/air, resin) is heated to a high temperature. Pyrolysis is the process of changing the chemical composition and physical phase of a substance. Pyrolysis produces no direct gas emissions. The primary goal of WPCB pyrolysis is to recover resources. Gases produced by pyrolysis could be used as a source of energy or chemical compounds. Vacuum pyrolysis of organic materials yields combustible gases (high in CO, CO₂, CH₄, H₂, etc.) (syngas) and liquid products (oil), as well as a carbon-rich solid residue (char) (i.e., glass fiber, ECs, metals, other inorganic materials, etc.).Pyrolysis produces gases that can be utilized as a source of energy or to make chemical compounds. Combustible gases (high in CO, CO₂, CH₄, H₂, etc.) and liquid products (oil) are produced by vacuum pyrolysis of organic materials, as well as a carbon-rich solid residue (char) (i.e., glass fiber, ECs, metals, other inorganic materials, etc.).Liquid products are formed up to 400 degrees Celsius, and over 800 degrees Celsius, the high molecules are broken, resulting in smaller organic molecules.In general, the process of PCB waste LtP (180–350°C) can be divided into three steps. While the first phase's products were mostly H₂O and CO₂, the flame retardants, coupling agents, and curing accelerators also degraded, producing gaseous products such as HBr, H₂O, CO₂, and other molecular hydrocarbons in the second phase (methane, ethane, and butane).During the third phase, when complete pyrolysis and carbonization happened, gases and liquid compounds degraded by resin were released. Furthermore, when the temperature hit 300°C, the process resulted in fast mass loss. The vacuum situation obviously helps the pyrolysis treatment procedure greatly[61].

2.14.1.4Gasification

It is a method that allows for the complete removal of organic components to the gaseous phase when the system's oxygen potential is low. Steam, oxygen (air, oxygen enriched air), or CO₂ (much less) reagents are employed in gasification.Pyrolysis, incineration, and gasification can all be done in the same reactor. The sole change was the gaseous phase used in the reactor for pyrolysis, incineration, and steam gasification — Ar/N₂ for pyrolysis, air for incineration, and distilled water for steam gasification.A 1.2 m quartz tube reactor furnace

can be utilized in laboratory-scale incineration testing. From one side of the reactor, Ar, air, or gases are introduced, and reaction gases are collected from the other side by a Liebig condenser[62].The release of polymers from WPCBs is not significantly affected by heat treatment at 300 degrees Celsius. The temperature range of 400–500 C produced the most pyrolysis (decomposition).

2.14.2 Hydrometallurgy

2.14.2.1 Solvent Leaching

In general, hydrometallurgical leaching technology is more precise, predictable, flexible, and easy to manage in material extraction from resources, and it has been used in WPCB recycling for about three decades with the use of mechanical crushing as a pretreatment. To selectively dissolve and precipitate metals, hydrometallurgy employs a variety of lixiviants/chemicals (such as strong acids, caustic watery solutions, halides, or microorganisms).The primary disadvantages of leaching solvents are corrosion, toxicity, high consumption, sluggish leaching rate, high cost, low stability, and environmental irritations. When various types of leaching reagents are utilized, corrosion poses challenges for the equipment. Due to the slow leaching rate, the leaching process usually takes a long time to obtain a metal-rich solution, making it a time-consuming operation.

Table 2.11: Comparison of most commonly used two mineral acids, AR and ionic liquids, used in base metal leaching[31]

Reagents	Pros	Cons
H ₂ SO ₄	Strong proton donor Its cost is much less than other inorganic/mineral acids Handiness makes suitable lixiviant in the leaching process Highly hygroscopic Highly selective, well-established process for Cu	At elevated temperature Corrosive
HCl	Fast kinetics at room temperature High dissociation constant (ka) High solubility and activity of base metals oxides Low toxicity Neutralized with NaOH to produce NaCl	Excessive corrosion Difficult electrowinning of Cu Poor quality of Cu
Aqua regia (AR) (3HCl + 1HNO ₃)	Fast kinetics Effective	High reagent cost Highly corrosive Low selectivity

mixture)		
Ionic liquids (ILs)	Thermally stable Environmentally friendly	High cost Excessive dosage

Electrochemistry, pre-pyrolysis, supercritical extraction, and mechanical treatment have all been investigated as ways to strengthen the driving force and expedite the leaching rate. The most often utilized H_2SO_4 and HCl mineral acids, aqua regia, and ionic liquids (IL) in leaching are compared in Table 2.11.

HCl has a high dissociation constant and dissolves a variety of base metal oxides with ease. NaCl is produced during neutralization with NaOH . The main disadvantages are excessive corrosion, difficulty in Cu electrowinning, and poor Cu purity. Proton donor H_2SO_4 is a powerful substance. It is the most affordable mineral acid. Its portability makes it ideal for the leaching process. Cu is extracted using H_2SO_4 , which is a highly selective and well-established method. Corrosiveness and high temperature requirements are a couple of drawbacks. AR has a high kinetic and efficacy when used in leaching. AR has a number of limitations, including high reagent costs, corrosivity, and limited selectivity. Ionic liquids are thermally stable and environmentally friendly, however they are costly and utilized in excessive dosages. Mineral acids pollute the environment and can dissolve unwanted pollutants. Carbonaceous compounds including inorganic acids may result in the creation of CO_2 pressure as a result of rapid dissolution, posing a concern.

In hydrometallurgical processing, selectivity and efficacy of valuable metals leaching are always significant. Chemical leaching is faster and more efficient, but it always results in the production of wastewater and waste gas. To recover BMs, traditional hydrometallurgical extraction techniques use acid leaching. Cu , Pb , Zn , and other metals can be extracted using $\text{HCl}/\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HClO}_4$. Aqua regia can also be used to digest base (Cu , Pb , and Zn) and precious (Ag and Au) metals from WEEE in a nonselective and aggressive manner. Order of corrosivity has been postulated as $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$ toward Cu , Fe , and brass [63]. HNO_3 and HCl have been thoroughly researched, however due to environmental regulations and the corrosive character of these leaching agents, they are just as suitable as the less hazardous H_2SO_4 [64]. The most harmful to the environment is HNO_3 [65].

Ayorinde Emmanuel Ajiboye et al. reported the extraction efficiencies of base metals for HCl and H₂SO₄ leaching as showed in the Figure 2.17 [66]. Cu extraction efficiency improved significantly as the concentration of HCl was increased from 0.5 to 2.5 M. When the HCl concentration was increased from 0.5 to 2.5 M, Cu efficiency increased from 65.1 percent to 80.1 percent. Increases in concentration from 2.5 to 5.0 M HCl showed little influence on efficiencies, which were slightly reduced due to inadequate dissociation equilibrium caused by insufficient hydration. Increases in HCl concentration, on the other hand, had no discernible influence on Zn extraction efficiency, with 58.5 percent to 62.3 percent removed when the HCl concentration was increased from 0.5 to 5.0 M, respectively. Other metals (Fe, Ni, Al, Pb, and Sn) were co-extracted with Ni, with extraction efficiency increasing proportionately with increases in HCl concentrations.

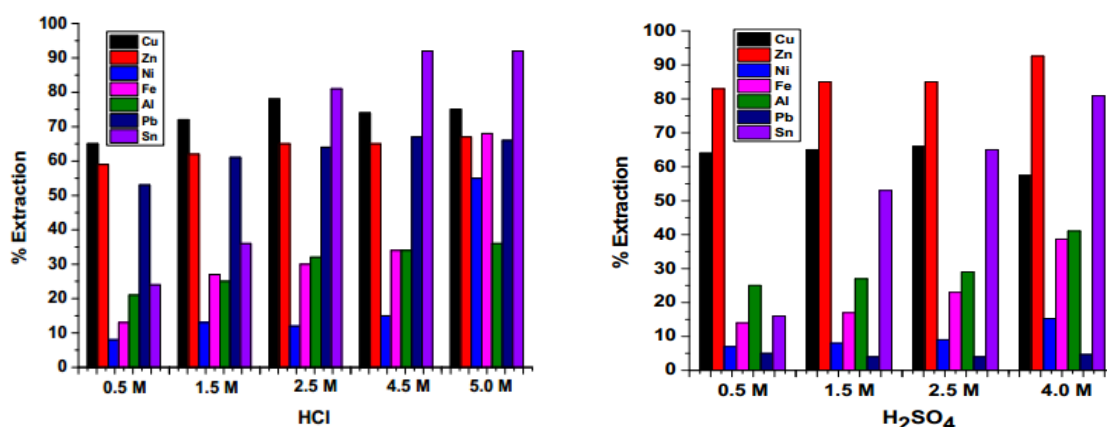


Figure 2.17: Comparative extraction efficiencies of different metals from WPCBs using HCl and H₂SO₄ lixivants, 50 g/L pulp density, 25 °C, 300 rpm, and 12 h[66].

In contrast to the results of HCl lixivants, the examination of H₂SO₄ lixiviant had a high extraction efficiency of Zn (Figure 2.17). The high corrosion potentials of H₂SO₄ (0.98 mV.SCE) compared to HCl (1.0 mV.SCE) caused this behavior[67]. Increases in the concentration of H₂SO₄ lixiviant resulted in proportionate increases in the extraction efficiency of iron (Figure 2.17). Cu extraction efficiency improved steadily as concentration climbed from 1.0 to 3.5 M, according to the results. The extraction efficiency was unaffected by a further increase in concentration to 4.0 M. In contrast, high Zn extraction efficiency was also attained in HNO₃ lixivants, with the exception of 4.0 M HNO₃, when Zn extraction was shown to be reduced[66].

2.14.2.2 Biometallurgical Leaching

Bioleaching is the process of removing a metal from a solid material with the help of microorganisms (bacteria, archaea). The method relies purely on the natural interaction of biological organisms and does not require any of the ecologically destructive processes present in traditional refining methods. The method has also been successful in recovering minerals from low-grade ore and tailings that were previously deemed waste. Biological mineral refining holds considerable potential in the extraction of a variety of elements from their ores, such as copper, gold, uranium, nickel, and cobalt. Despite being an environmentally benign and cost-effective method, bioleaching is unsuitable for industrial use due to its slow pace and long leaching time [68]. To recover Cu from WPCB fine powder, Liang et al. (2013) utilized a mixed culture of *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*. The bacteria can bioleach elemental S by oxidizing it in H_2SO_4 and then extracting the metal from the broth. At pH 1.56, elemental sulfur (S^0) 5.44 g/L, and 16.88 g/L $FeSO_4 \cdot 7H_2O$ concentration, the maximum Cu recovery rate (98.4%) was obtained. However, increasing the amount of WPCB in the culture from 18 to 32.4 g/L reduces the Cu recovery rate from 98.3 percent to 87.2 percent [69]. Bacteria that are mesophilic, chemolithotrophic, cyanogenic, or mildly thermophilic are also widely employed. Biometallurgy recycling strategies work in a similar way to hydrometallurgy recycling procedures since they both involve leaching. Biometallurgy recycling approaches, on the other hand, typically utilise chemicals created by the microorganism itself, such as organic/inorganic acids, cyanide, or sulfate ions, rather than adding leaching reagents. The metal ions form complexes or precipitates after leaching, and they are therefore isolated from the culture broth for immediate application or additional refinement. Ilyas et al. (2007) investigated the bioleachability of metals from e-waste by acidophilic chemolithotrophic and acidophilic heterotrophic bacteria that are moderately thermophilic. *Sulfobacillus thermosulfidooxidans* and an unidentified acidophilic heterotroph (code A1TSB) were among those found in the area. A mixed consortium of metal adapted cultures was able to leach more than 81 percent of Ni, 89 percent of Cu, 79 percent of Al, and 83 percent of Zn at T, 45 °C; t, 8 days; pH, 2; and N, 180 rpm at a scrap content of 10 g/L. Although Pb and Sn were also leached out, they were discovered in the bioleaching precipitates [70]. The implementation of the biometallurgical treatment method is hampered by the low extraction rate in high WPCB dose due to limitations in air dispersion and oxygen mass transfer [71]. Furthermore, bacteria are generally vulnerable to heavy metals, and their

growth is impeded as a result of metal toxicity[72].Although some bacteria or fungi can adapt to the situation and attain a good recovery rate after a long period of adaptation, the time necessary for this adaptation is extraordinarily long (more than a week)[73].Furthermore, biometallurgical treatment takes much longer to recover than pyrometallurgy or hydrometallurgy recycling approaches, affecting the process's good rating.

2.15Recovery of Metals

Several techniques are available for metal recovery depending on the previous process adopted during WPCB recycling. Precipitation, electrowinning, cementation, and ion exchange are the four basic processes of metal recovery (Figure 2.18).

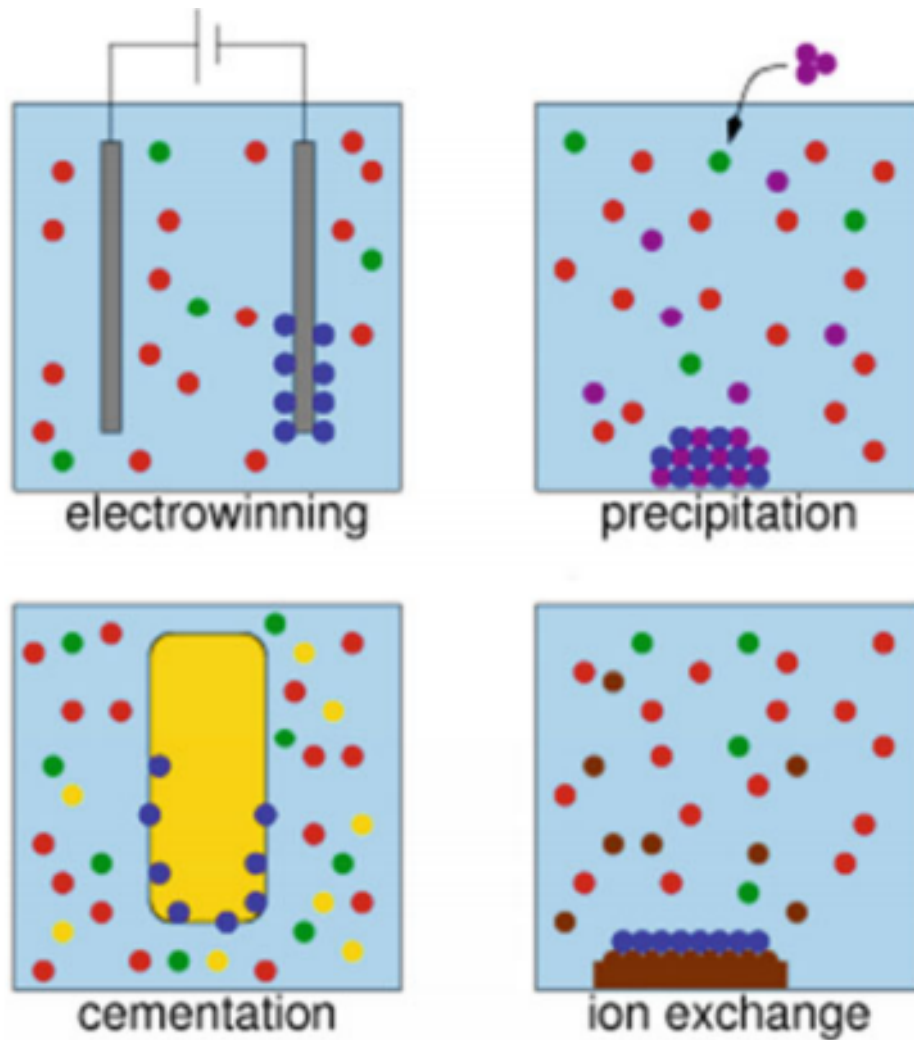


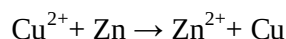
Figure 2.18: Metal recovery techniques[31]

2.15.1 Chemical Precipitation

When metals are precipitated out of aqueous solution, the pH of the solution is usually adjusted or chemical precipitants and flocculants are added, but the procedure utilized is determined by the solubilities of the metals in solution. Hydroxides, sulfides, and carbonates are common metal precipitates. The pH of the solution was varied to 1.5, 3, 6, and 8 to recover Sn, Fe, Cu, and Zn from leach solutions via chemical precipitation. Filtration can be used to remove precipitated metals after precipitation. pH can be adjusted with base like NaOH and acid like H_2SO_4 .

2.15.2 Cementation

Metal ions are converted to their elemental state at a solid metal contact during cementation. It's a popular way to get rid of one metal from a solution that isn't vital enough to be electrowon. Cementation is a form of precipitation, a heterogeneous process in which ions at a solid metallic surface are reduced to zero valence. Leach solutions are typically refined using this method. Scrap Fe or Zn dusts can be used to cement Cu in solution as per the following reaction, and Zn powders can be used to precipitate Ag in solution.



2.15.3 Electrowinning (EW)

By sending a current through aqueous solutions having positive redox potentials, metals such as Au, Ag, and Cu can be recovered. However, for some metals such as Cr, EW is less effective, and for metals like Al, it is practically impossible. The metal ions on the cathode are chemically reduced by electrons from the current, resulting in a solid metal complex. In modern metal recovery, mining, refining, and wastewater treatment applications, electrowinning is a commonly utilized method. The pH of a solution affects its potential window and the solubilities of any metal compounds dissolved in it, hence the electrowinning process is typically sensitive to pH changes. An overpotential in water can result in hydrogen gas evolution at the cathode and oxygen gas evolution at the anode, causing embrittlement, a decrease in electrodeposition quality, and low current efficiency. In the presence of solutions, electrowinning is done in a split cell with anode and cathode. Important variables include ion concentrations, temperature, current density, acidity, and cell voltage. The key cell performance parameters are cathodic current efficiency and cell voltage. Current efficiencies that are higher are preferable. Current efficiency in the catholyte increases as the dissolved ion concentration rises. The most important aspects of electrowinning are choosing the correct electrodes and determining the voltage or potential needed to separate the metals from the AR medium. The electrodes are selected based on the galvanic series, and the potential is determined using electrochemistry's Nernst equation. The electrodes will be chosen depending on the galvanic series or reactivity. The anode is the active metal, and the cathode is the passive or inert metal. The electron is given by the anodic material, and the metal precipitated from the solution is deposited on the cathode. As a result, anode material should have a higher reactivity than cathodic material. Cu can be utilized as a cathode; the Cu

extracted will be deposited on a pure Cu rod, increasing it and saving money. Other metals, which are PMs, employ stainless steel (SS) as both anode and cathode, and utilizing it as a cathode would be inefficient. When a voltage is applied to this configuration, the anode loses electrons that are acquired by metallic ions in the liquid and deposited on the cathode. As a result, metal extraction is dependent on the voltage required to lose an electron as well as the conversion of metals in the liquid to ions. Cu is recovered first, followed by Ag, Pd, and Au in the EW process. The metal from the solution is collected at the cathode as the DC current is applied. The reaction is in progress, as evidenced by the bubbling. The bubbling eventually ceases, indicating that the reaction is complete. Scrape off the powder that has accumulated on the cathode end.

2.15.4 Solvent Extraction (SX)

Solvent extraction is a method for separating two or more components in two immiscible liquid phases due to their differing solubilities. It's a common method for separating metal ions from their solutions in hydrometallurgy.

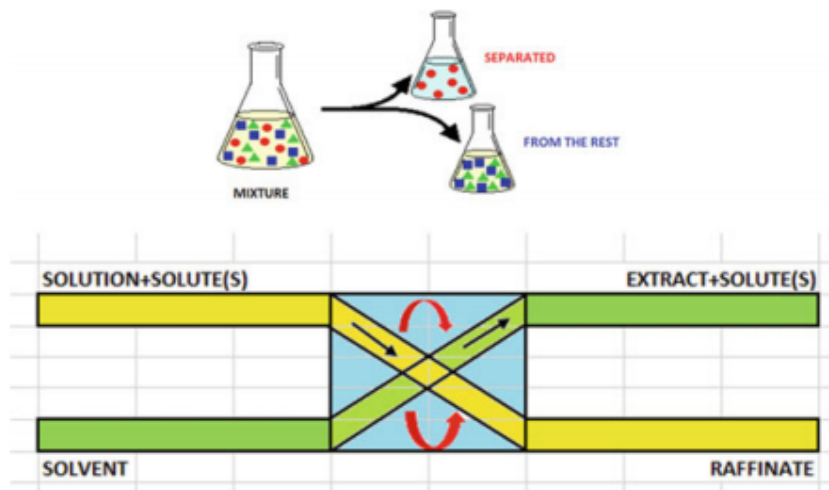


Figure 2.19: Solvent extraction process feeds and products[31]

SX is the process of transferring one (or more) solutes from a feed solution to an immiscible liquid (solvent). The feed solution that is depleted of solute(s) is termed raffinate, and the solvent that is enriched in solute(s) is called extract (Figure 2.19).

2.15.5 Ion Exchange (IX)

Ions are exchanged between two electrolytes or an electrolyte solution and a solute or complex in ion exchange. Typically, the sacrificial metal is of poor value. Ion exchange reactions remove dissolved ions from solution and replace them with other similarly charged ions in a reversible chemical reaction. Ion exchange is a reversible electrostatic adsorption event that occurs when two oppositely charged surfaces (solute molecules and resin) come into contact[74]. The medium ions exchange the positive and negative ions. Cation and anion exchangers are the two types of ion exchangers which can be organic and inorganic. Kim et al. examined Au recovery by the IX method utilizing three resins (Amberlite XAD-7HP, Bonlite BA304, and Purolite A-500) (2011)[75].

2.16 Scope of the work

Many approaches have been developed for recovering copper from waste PCBs and repurposing it. Pyrometallurgy, hydrometallurgy, biotechnology, and mechanical methods are among the technologies considered. Hydrometallurgical techniques, with their cheap capital costs, lack of gas/dust production, operational selectivity, and applicability for small-scale applications, are promising options for the treatment of waste PCBs. The majority of hydrometallurgical operations, on the other hand, were primarily focused on copper leaching. After hydrometallurgical procedures, the copper-contained leach liquor of waste PCBs requires further processing or purification in order to obtain high value added products that can be reused in commercial or industrial settings. Because of their unique characteristics and vast range of prospective applications in numerous fields, ultrafine Cu and its oxides have gotten a lot of interest in the last two decades. Catalysis, magnetic materials, solar energy conversion, sensors, material additives, negative electrode material for lithium ion batteries, microelectronics, and optoelectronics are among the topics covered. This work presented a simple and feasible approach for preparing high value added copper nanoparticles from waste PCB leach liquor using electrometallurgical process.

CHAPTER 3

EXPERIMENTAL

3 Experimental

3.1 Introduction

The experiments performed under this study were conducted adopting the basic steps from earlier studies discussed in the literature review, and improvising upon a long array of trial and error. An overview of the experimental path finding can be visualized in table 3.1.

Table 3.1: Overview of the experimental path

Bat ch no.	Description	Obstacle	Decision
01	Working with the whole mobile phone PCB just after manual dismantling of small parts	Aqueous solution does not reach inner layers because of upper surface polymeric layer	Removal of upper polymeric layer with NaOH solution
02	Working with the whole mobile phone PCB (MPCB) after treating with NaOH solution	Still solution is not capable to react with all the inner layers	Shredding the whole PCB to increase the reacting surface area
03	Shredded MPCB, NaOH treatment, HNO ₃ treatment for solder removal, Cu leaching through HCl solution	Presence of excessive magnetic element in the Cu reach solution	Removal of shredded magnetic parts with magnetic separator
04	Shredded MPCB, NaOH treatment, HNO ₃ treatment for solder removal, Magnetic separation, Cu leaching through HCl solution	Reaction rate is very slow	Addition of H ₂ O ₂ into the HCl solution to expedite the oxidation rate
05	Shredded MPCB, NaOH treatment, HNO ₃ treatment for solder removal, Magnetic separation, Cu leaching through H ₂ O ₂ added HCl solution	Expected Cu pregnant solution but synthesis of Cu is not complete	Adopting electrolysis process for Cu reclamation

06	Cu pregnant solution electro winning where pure copper bar used as cathode and anode	Corrosion of anode	Use of Graphite as anode
07	Cu pregnant solution electrolysis where cathode is a Cu rod and Graphite rod stripped out from battery is anode	A black color layer from graphite is found in the cathode though deposition of Cu was successful	Using Graphite as both anode and cathode
08	Cu pregnant solution electro winning where graphite is used as cathode and anode	Size of Cu particle is not in the Nano range	Application of heat and stirring condition
09	Electro winning process with heat and stirring condition	Multiple trial and error conditions faced	Successful completion of experiment after applying the heat and stirring condition

3.2 Materials and Equipments

3.2.1 Materials:

Waste Printed Circuit Boards of Mobile Phones (A mixture of different brands) were collected from the local scrap market (Elephant road, Dhanmondi, Dhaka). Visualization of raw materials could be seen in figure 3.1. The chemical reagents (HCl, NaOH, H₂O₂ and HNO₃) used in this study were of analytical grades (Merck, Germany and Scherlue, Spain) purchased from Paradise Scientific Stores, Hatkhola, Dhaka. For all purposes de-ionized water (pH 6.5 - 7.5) was used.

3.2.2 Instrumentation

The particle size distribution was analyzed using a laser-based particle size analyzer (Manufacturer: Microtrac, Model: S-3500, USA). Phase identification data of several synthesized products were obtained using XRD (Brand: Bruker, Model: D8 Advance, Origin: Germany). Concentration of ions in different intermediate solutions was characterized by an

AAS (Brand: Shimadzu, Model: AA7000, Origin: Japan). A (Brand: Jeol, Model: 71031SE2A, Origin: Japan) FESEM was used to acquire micrographs and EDX analysis was done by the same instrument for the estimation of elemental contents of product samples.

3.3 Methods

3.3.1 Manual dismantling:

Several small parts like various types of Integrated Circuit (Network, Audio, Logic, Flash IC etc.), RAM, CPU, BSI, Antenna Switch etc. are mounted all over the printed circuit board. These small parts mounted over the PCB surface were differed in quantity since locally purchased MPCBs were mixtures of several brands. On the other hand, while these PCBs were collected in the whole sale shops located in Elephant Road and Nimtoli, few of the parts were isolated due to rough handling. Figure 3.1 shows a common scenario of MPCBs with small machineries connected to them.

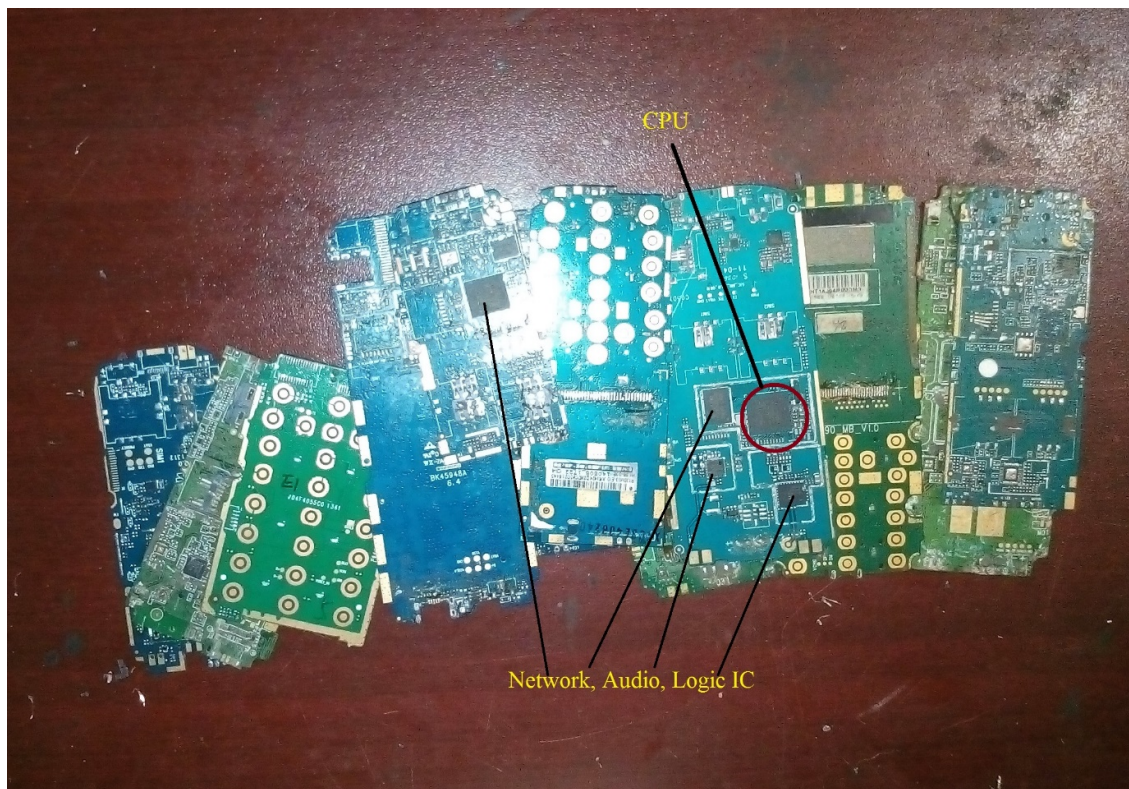


Figure 3.1: Locally purchased MPCBs showing different small parts mounted

Before starting the main experimental part, these tiny parts were dismantled from the PCB with bare hand or with a pliers and a screw driver where necessary. After removing these parts PCBs were looked like shown in the Figure 3.2.



Figure 3.2: Surfaces of MPCBs after removing the tiny parts

Different electronic parts, plastic casings and in few cases plastic cover of the keypad were carefully isolated and stored in a separate box. Since types of PCBs were randomly mixed during purchasing, the dismantling process was adopted on need basis like using pliers for some parts, while bare hand or screw driver used for few parts. But the process was manual.

3.3.2 Size Reduction:

An approach was made to follow the hydrometallurgical route with the whole PCB. This was the main reason of dismantling the electronic components (ECs) mounted over the PCB surface. Later, it had been seen that intact piece of PCB is not well processed for a speedy leaching process. In fact, reducing the PCB size will allow more leaching solution to interact with, by increasing the surface area. In this experiment, size reduction was done with a shredder which is capable to maintain the dimension of small pieces in 2-4 mm range. Figure 3.3 is an image of shredder with inside view used in this experiment. For shredding, one batch of sufficient quantity PCB was placed inside the shredder and then switch was pushed

on. The shredding process was completed automatically inside the machine and when the size reduced to the required one shredded pieces were relieved into the box placed below the machine.



Figure 3.3: Shredder used for size reduction

Required amount of small pieces of PCB was shredded repeating this process (Figure 3.4).



Figure 3.4: Shredded PCB

Since PCBs were finally shredded into small pieces, manual dismantling of the PCB was not much necessary in the final experimental batch. But it is better to go through the dismantling step. But, considering the industrial approach and to reduce the time consumption, in this experiment manual dismantling part was omitted in the final batch, shredded PCBs.

3.3.3 Removal of polymer coating:

Though polymeric coating is applied on PCB to protect the unit from shock, vibration, radiation, moisture, fungus, salts, solvents, etc. but mainly as solder mask. Solder mask, also known as solder stop mask or solder resist, is a thin lacquer-like film of polymer that is applied to the copper traces of a printed circuit board (PCB) to protect them from oxidation and to prevent solder bridges from forming between solder pads that are close together. Thus, removing or loosening up this coating is necessary for better contact of solution with the upper copper layer. For this purpose, Sodium Hydroxide (NaOH) treatment was done where molarity of NaOH was 2 M. Initially this treatment was done on whole PCB (Figure 3.5), then later it was concluded to work with Shredded PCB for better result.



Figure 3.5: NaOH treatment of whole PCB

In the final run, 500 gm of shredded PCB was treated with 2 M NaOH solution and solution molarity was maintained by dissolving 80 gm NaOH to 1000 ml de-ionized water.

Teflon stirrer was used during this operation to maintain equilibrium condition all over the beaker. This treatment was done for 48 hours maintaining the stirring speed around 350

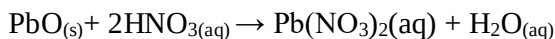
rpm. Then the solution was filtered using a Whatmann filter paper to collect the NaOH treated shredded PCB which was then sun dried in the open air.

After drying, these treated PCBs were weighed for 453 gm and the weight loss included some dusts or particles produced during shredding. These PCBs were used in the further final processing steps.

3.3.4 Solder Removal:

Solder is a fusible metal alloy that is used to bind electrical wiring and electronic components (ECs) to printed circuit boards (PCBs). Before starting the final leaching process for copper recovery, it was necessary to remove the soldering metals in order to reduce the concentration of unwanted elements in the Cu rich solution. On the other hand, while solders were removed the copper leaching solution was expected to react faster than direct leaching process. Since higher concentration of nitric acid would dissolve Cu which we wanted to leach selectively, low concentration solution of HNO_3 was selected to remove soldering and other metals partially if not completely. To maintain a homogeneous condition leaching was done under a motor based teflon stirrer having digital display. Conventional solders comprised of Sn and Pb, while Pb free solders are a variety of alloys which include elements like Sn, Zn, Cu, Bi, Sb, Al etc. Along with these elements, Fe was also been leached during this step so that in the final Cu leaching solution its concentration remain as low as possible.

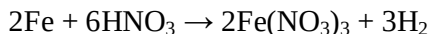
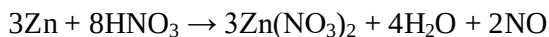
For this solder removal treatment 1000 ml solution of 0.3 M HNO_3 was prepared by adding 20 ml HNO_3 into 980 ml deionized water. Previously dried 453 gm NaOH treated shredded PCBs were then treated with this 0.3 M HNO_3 solution. During the lead dissolution reaction, HNO_3 oxidizes Pb to PbO , which then forms lead nitrate, as shown below:



While Pb remained in the solution as lead nitrate, Sn reacted with nitric acid and precipitated as metastannic acid following the reaction shown below:



While these are the mandatory reactions occurred during this treatment, Fe and Zn also dissolved into the nitric acid solution as per the reactions shown below:



(a) HNO_3 solution filtering



(b) HNO_3 treated air dried PCB sample

Figure 3.6: HNO_3 solution filtering(a) and HNO_3 treated air dried PCB sample

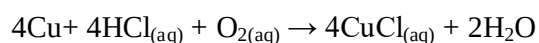
This step was run for 24 hours with a stirring speed of around 350 rpm which ensured the equilibrium leaching condition. After 24 hours of nitric acid treatment, this solution was filtered to collect the treated PCBs. These PCBs were then air dried and weighed for 411 gm (Figure 3.6 b) which indicated a total removal of 42 gm metals into liquor.

3.3.5 Magnetic Separation:

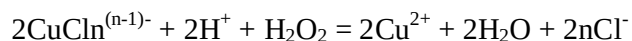
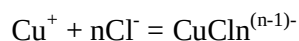
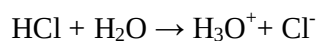
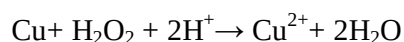
During the shredding process, few of the PCB particles were entangled by the metallic parts. Meaning, these metallic parts were bended due to the shredder forces and in their bending gap PCB particles were stuck. This was a reason of conducting the magnetic separation step after the desoldering step. After the nitric acid treatment, due to the loss of metals and solder removals the mechanical bonding between the bended metallic parts and PCBs was loose, thus allowed the shredded particles to be released. Thus, magnetic separation in this step reduced the error in mass balance. This operation was done by the local magnetic separator made in the experimental laboratory. For proper removal of magnetic part, this operation was repeated 3 times. After the operation magnetic and nonmagnetic part were weighed for 51 gm and 360 gm respectively. These, nonmagnetic part of PCB was then used for the final extraction of copper.

3.3.6 Leaching of Copper:

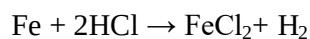
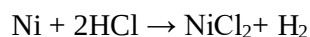
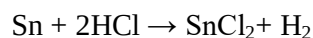
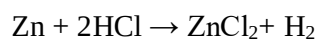
Because of its high dissociation constant, quick kinetics at room temperature, and ease of dissolving different base metal oxides, HCl was chosen for copper leaching. NaCl is generated after neutralization with NaOH. In a reaction beaker, 1000 ml solution of 4M HCl was produced for this final extraction step. For increasing Cu extraction, 50 ml H₂O₂ was added to the 4M HCl solution which is basically 5% of the total 1000 ml solution. Previously treated and nonmagnetic parts of the PCBs were added to this solution for leaching process under the motor based Teflon stirring condition having digital display. Reactions during the extraction are versatile as HCl is non-oxidizing agent. The oxygen from the ambient atmosphere reaches the solution during the leaching process and serves as an oxidizing agent:

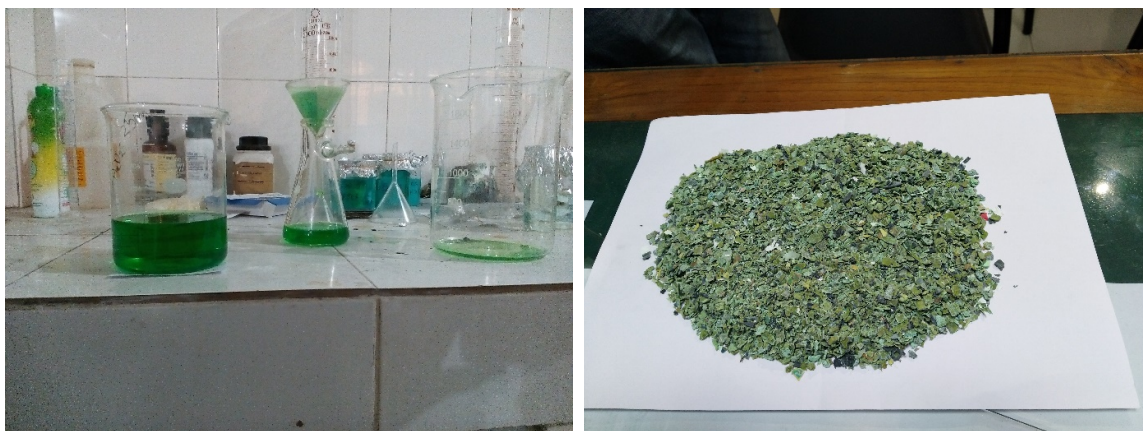
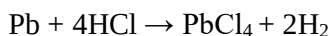
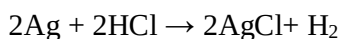
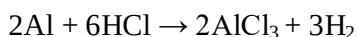


On the other hand, in acidic solutions, metallic copper was oxidized by H₂O₂ to cupric ions. With the leaching of metallic copper from waste PCBs in acidic H₂O₂ solutions, the Cu²⁺ concentration in solutions rises, and the other reaction between metallic copper and Cu²⁺ in chloride media occurs.



Besides during this extraction process Zn, Sn, Ni, Fe, Al and Ag metals react immediately with HCl to form metal chlorides.





(a) HCl+H₂O₂ solution filtering

(b) HCl+H₂O₂ treated air dried PCB sample

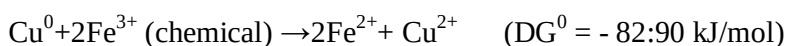
Figure 3.7: Visualization of HCl+H₂O₂ solution filtering (a) and HCl+H₂O₂ treated air dried PCB sample

This leaching process was allowed to run for 24 hours while maintaining a stirring speed of about 350 rpm. Then the liquid solution with metallic ions and residue of treated PCBs were isolated through filtering. Figure 3.7 shows the air dried PCB residue after all the hydrometallurgical treatments. These PCBs were then weighed to 325 gm indicating a total of 35 gm metallic dissolution in this step.

3.3.7 Recovery of Copper:

One of the most common methods for recovering metal(s) from an acidic solution is electrowinning. An electrical current is passed from an inert anode through a leach solution containing the dissolved metal ions in electrowinning to recover the metal as it is deposited onto the cathode in an electroplating phase. The pregnant leach solution (PLS) derived from the leaching of printed circuit boards (PCB) can contain a number of impurity metals, which can have a complicated effect on copper electrolysis. For example, Co²⁺ can reduce the rate of anode corrosion [76], while Fe³⁺ has a negative impact on current performance [77]. Electrowinning cell used for this study was 250 mL pyrex beaker and 100 ml solution was used to test a number of anodes and cathodes. A digitally controlled DC source was used to power the anode and cathode. Initially, rectangular pure copper bar was used for anode and cathode. Since pure copper is almost inert according to the reactivity

series of common metals, the anode copper bar was not supposed to corrode. But experimentally anode was corroded which may be attributed to the pregnant leach solution chemistry and presence of impurity ions with varied concentrations. One of many probabilities can be shown through the exothermic reaction below:



Later, copper anode was replaced by graphite rod stripped out from pencil battery. But during the experimental period, a black color layer of graphite was surrounding the cathode and also floating throughout the leach solution (Figure 3.8 a). Thus the final recovery of copper was complicated from stripping out of cathode and was also contaminated. Finally, rectangular graphite electrode bought from the local market was used for both anode and cathode.

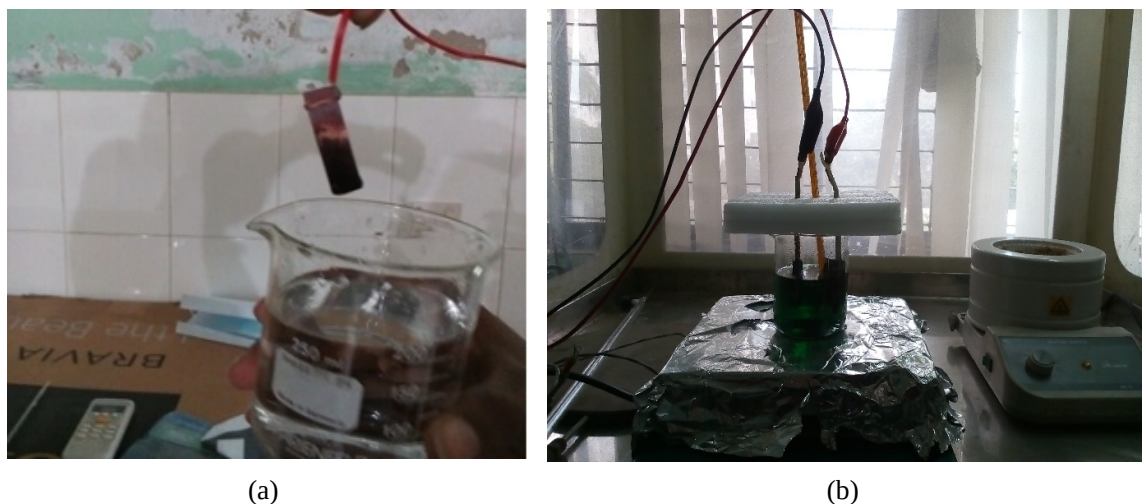
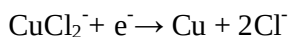
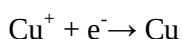
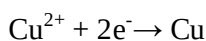


Figure 3.8: Graphite layer issue while using pencil battery graphite rod (a) and electrowinning using locally purchased graphite electrode (b)

These locally served electrodes were enough compact with smooth surface finish thus worked as expected. All the experiments were done in the constant voltage mode while current was fluctuating into a range maintaining the compatibility of leach solution chemistry. Dominating ionic species in the PLS were Cu^{2+} , Cu^+ , CuCl_2^- , Fe^{2+} , Fe^{3+} , Ni^{2+} , Co^{2+} , H^+ , Cl^- , OH^- ions etc. The followings are the reactions of greatest interest during electrowinning:



Several experiments were done using voltage range 3.6-5.0 V and reclamation of copper was successful. But the particle size was not in the nano-range. To obtain copper nanoparticles, a variety of combinations were tried among the voltage, temperature and solution agitation. The cell was agitated using a magnetic stirrer at a constant speed of 800 rpm. Finally, copper nanoparticles were deposited maintaining the voltage 5.0 V in the DC source while cell temperature was 65°C.

3.3.7.1 Collection of Copper Particles:

After having the electrowinning run time 5 minutes, cathode was brought out of the cell. Cu particles deposited on the cathode surface were washed by DI water to store in a petri dish. This particle suspended DI water was then used to centrifuge the solution with an aim to reduce the dealing of excessive water and collecting the nanoparticles in a single tube.



(a) Centrifuging Instrument



(b) Micro tubes placement inside the centrifuge



(c) Sonication of primary solution



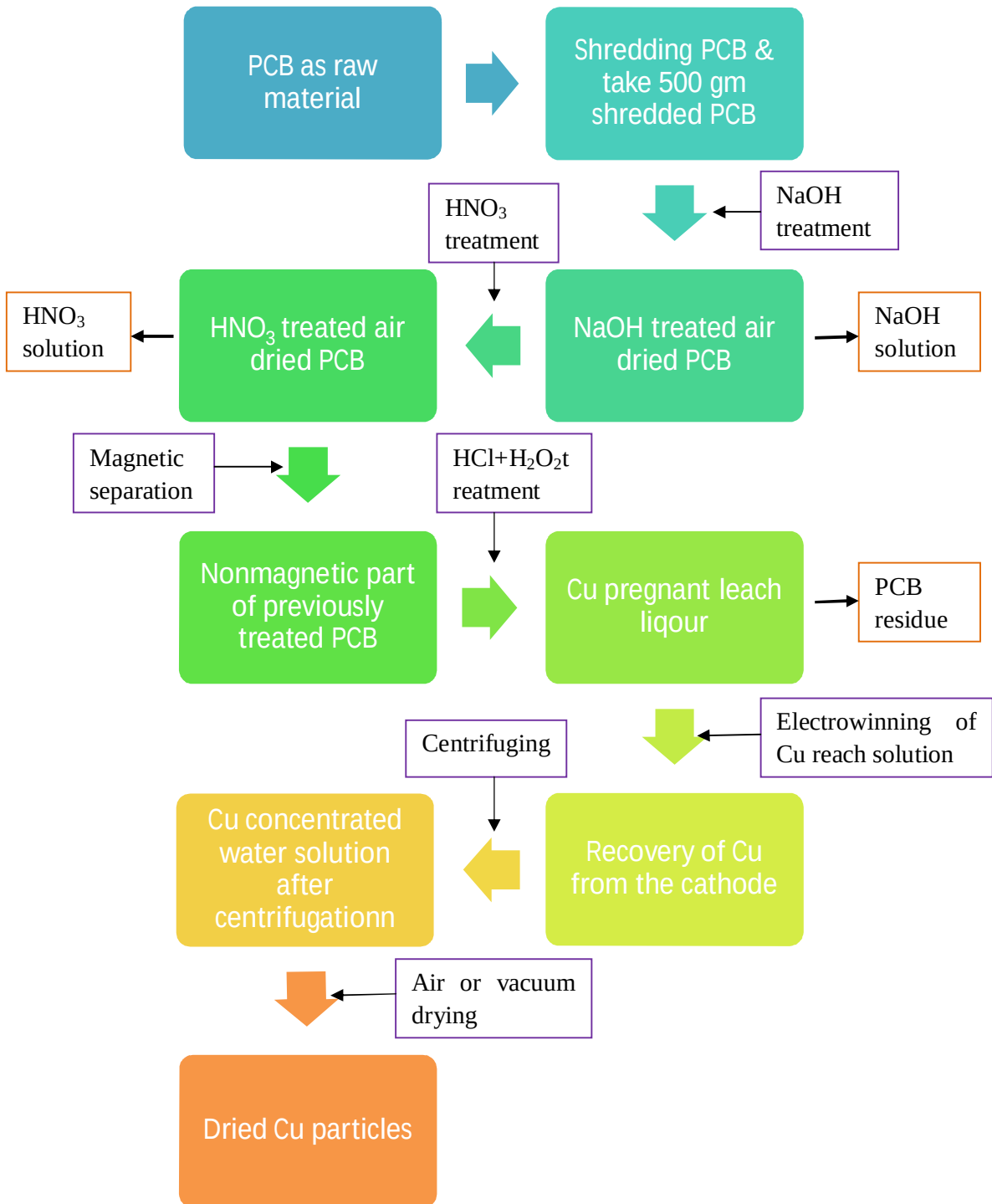
(d) Cu particles after water decantation

Figure 3.9: Visualization of various steps during centrifugation

For centrifuging purpose micro tubes were used and before refilling these micro tubes the primary DI water solution was ultrasonicated for 1-2 minutes (Figure 3.9). Centrifuging was done for 5 minutes maintaining the rotation at 13,500 rpm. Then the micro tubes were decanted to release the extra clear water. These tubes were again refilled from the primary solution and passed through the centrifugation. Finally, particles were collected in a relatively bigger tube and sent for air or vacuum dryer.

3.4 Summary:

The experimental procedure can be summarized as the following flow chart:



CHAPTER 4

RESULTS AND DISCUSSION

4 RESULTS AND DISCUSSION

4.1 Dismantling and Shredding

Dismantling of electronic components mounted over the PCB surface was an effective step since it separates the unwanted parts and reduce the presence of unwanted elements in the liquor. This process was found so easy that dismantling was done by bare hands except for some of the components which required pliers and a screw driver. This process also enables the solvent to react faster with the targeted parts. Most importantly, after the separation of surface mounted parts, removal of the surface polymer coating became easier and more effective.

The function of shredding was diversified and more effective than the dismantling process. Obviously, shredding can be done following the dismantling process however, to adopt this sequence study of economical and industrial viability is mandatory. Since dismantling was a manual process for this experiment, final process was developed using the shredded PCB as raw material. As expected, shredding reduced the size to 2-4 mm thus increased the surface area which removed or loosened up the polymeric coating more efficiently. Visual inspection of shredded PCB after the NaOH treatment confirmed the effectiveness of this process. Besides, during the shredding electronic components mounted over the PCB were broken down thus also dismantled. From this point of view, shredding was more effective than the dismantling process since it worked for both purposes namely dismantling the small parts of PCB and reducing the size. Moreover, shredding also expedited the successive leaching process by increasing the interaction between leaching liquor and PCB.

4.2 AAS of Leaching Solution

Target of this study was to recover Copper as nanoparticles from the waste PCB. Thus leaching steps focused only to the copper reclamation. Low concentration Nitric Acid solvent was used to leach solders and other elements and to protect the leaching of Copper in this stage. The next step leaching done by Hydrochloric Acid was solely focused on the leaching of Cu. For this study which focused only to reclaim Cu as value added product, two stage

leaching process as mentioned was very effective. This resolution can be confirmed by the Table 4.1 which shows the AAS data of Nitric and Hydrochloric Acid leach liquor.

Table 4.1: AAS data of Leach Liquor

Solution ID	Cu (PPM)	Fe (PPM)	Zn (PPM)	Pb (PPM)
Nitric Acid solution	102.5	3531.88	67.69	150
Hydrochloric Acid Solution	29437.5	461.88	2034.06	268.75

As HCl solution is the final liquor from which Cu was recovered, the target of this experiment was to minimize the Cu leaching in the nitric acid treatment and maximizing it in the hydrochloric acid solution. Table 4.1 shows that concentration of Cu was 102.5 ppm in the nitric acid solution while this concentration was around 30,000 ppm in the hydrochloric acid solution which reflects the target of adopting this two stage leaching process. Moreover, as Fe was not the targeted element in any of the steps of this experiment, it was necessary to reduce the concentration of Fe in the final Cu pregnant solution. AAS data reveals that concentration of Fe was approximately 8 times higher than the final liquor. Thus the interference of Fe in electrowinning solution was less. On the other hand, though concentration of Zn and Pb was comparatively higher in HCl liquor, it is certain that if the nitric acid leaching was not adopted the concentration would be higher. One reason of this scenario might be due to low concentration of nitric acid and the better reactivity of Zn and Pb with higher molarity HCl solution.

4.3 Selectivity Ratio

This selectivity experiment was carried out with the goal of justifying the process steps up to final leaching. As Cu was the target element of this study all other elements are count as impurity for the final electrowinning solution. It is mentionable that, in this study removal of these impurity from the final solution achieved after the HCl treatment was not done purposely. Since feasibility of electrowinning process was studied without further purification, it was necessary to design the leaching process in a way to reduce the impurity percentage. Ayorinde Emmanuel Ajiboye et al. after studying 6 lixiviants including HCl and

HNO₃ for multiple molarity solution, suggested 5 as the minimum standard selectivity ratio for considering as effective lixivants[66]. Selectivity ratio for the final leach liquor of this study is presented below.

Table 4.2: Selectivity Ratio data for final leach liquor

Element	Con. in HCl sol. (ppm)	Selectivity Ratio			Standard Ratio
		Cu/Fe	Cu/Zn	Cu/Pb	
Cu	29437.5				5 Source: Ayorinde Emmanuel Ajiboye et al.[66]
Fe	461.88	63.73			
Zn	2034.06		14.47		
Pb	268.75			109.53	

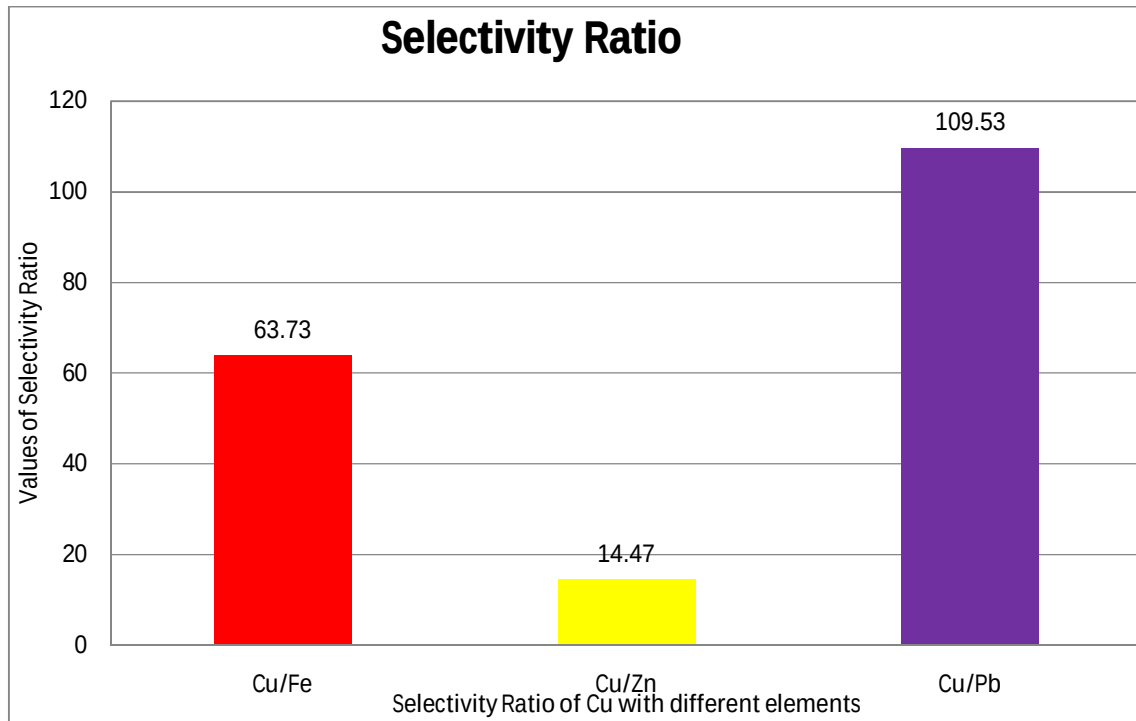


Figure 4.1: Representation of Effectiveness of Selectivity Ratio

Figure 4.1 resembles that the selectivity ratio for Cu as target element in respect to Fe and Pb is around 63 and 110 respectively which indicates that the process route was effective while considering the interference of impurity. In case of Zn, though the selectivity ratio is not as high as Fe and Zn but it is around 3 times better than the standard ratio suggest by Ayorinde

Emmanuel Ajiboye et al. Thus, when Cu is the target element the interference of impurity element is not much high for the hydrometallurgical process route adopted in this study.

4.4 Recovery of Copper element

Reclamation of copper from the hydrochloric acid leach liquor was done by several trial and error processes using a digital DC voltage source. Final Electrowinning was done for 100 ml solution using graphite electrodes. During the electrowinning it was found that stirring and temperature has effect on the particle size. Firstly, electrowinning was done to reclaim copper without applying temperature and stirring which produced comparatively larger particle though in nano range. Later it was found that temperature and stirring has positive effect towards smaller particle sizes. Final recovery was done applying 65°C temperature and 750 rpm rotation by magnetic stirrer which produced comparatively better nanoparticles.



Copper powder with stirring and temperature (a)



Copper powder without stirring and temperature (b)

Figure 4.2: Image of reclaimed copper (a) with stirring and temperature effect (b) without stirring and temperature effect

Figure 4.2 depicts the color difference of larger particles and smaller particles. Visual inspection of these samples also revealed the difference of particles smoothness and surface

roughness. Larger particles were comparatively less sticky than smaller particles and had less motion inertia inside the container while tilting.

4.5 Particle Size Analysis

Particle size analysis was done for both the samples, without temperature & stirring effect (Sample-1) and with temperature & stirring effect (Sample-2). Analysis of sample-1 reveals that distribution of particle size was diversified and random. Figure 4.3 depicts that while temperature and stirring was not applied during electrowinning, particles showed two differently identifiable peaks. Both of the peaks are enough broad to make a resolution that size distribution was random. First peak is found having peak intensity at 336 nm and this peak starts at 200 nm which ends at 500 nm. Second peak starts at around 500 nm and ends after crossing the 1200 nm range which have average particle size of 1205 nm.

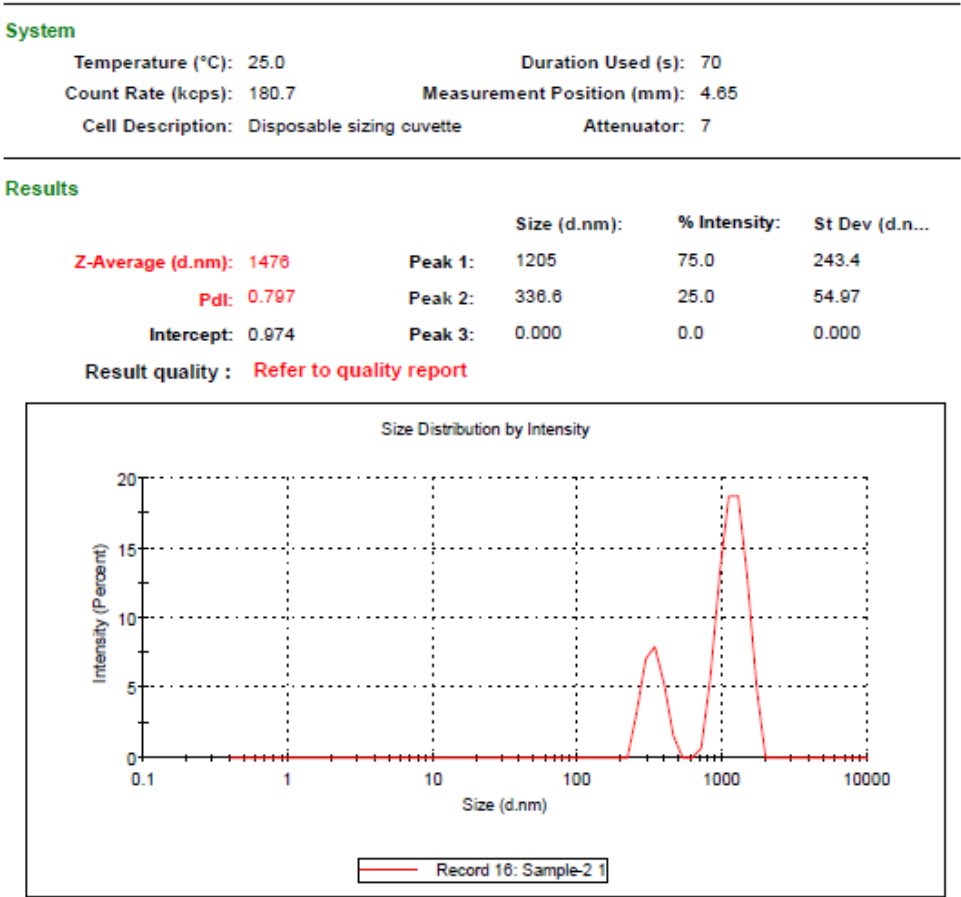


Figure 4.3: Particle size analysis of copper (sample-1) without temperature and stirring

It was also evident that the amount of smaller particles were less compared to the larger particles, since the area covered by the second peak is higher than the first peak.

With the aim of having better particle size distribution and smaller particles, temperature and stirring were applied during electrowinning. Adoption of this step provided better result compared to the earlier one. Result of Particle size distribution of sample-2 presented below.

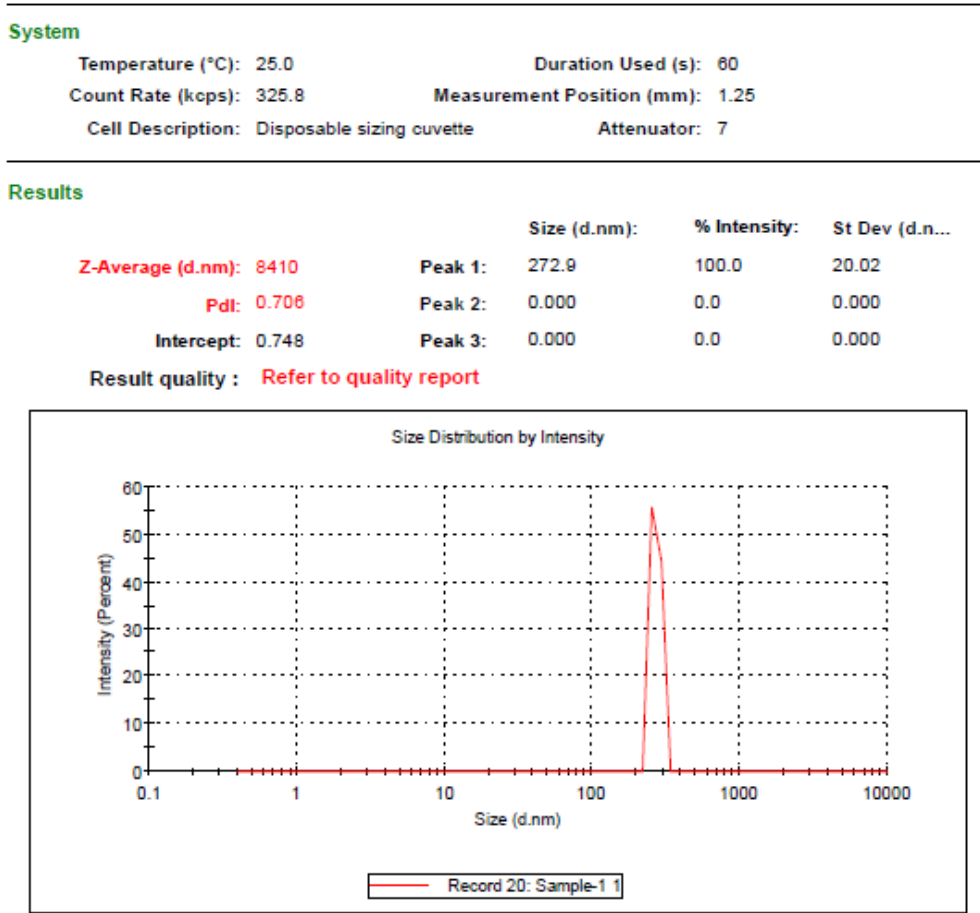


Figure 4.4: Particle size analysis of copper (sample-2) with temperature and stirring

Figure 4.4 resembles that after applying the temperature and stirring condition average size of the particles dropped down to 270 nm which is much finer than the smaller particles of sample-2. This result may be attributed to the fact that increased ion mobilization assisted by the higher temperature inhibited the particle growth by creating more nucleation sites which was further aided by the stirring condition. Moreover, size distribution analysis of sample-2 showed only a unique peak unlike the sample-1 which means the particles are in the same

range. Figure 4.4 also resembles that the peak is enough sharp to start at near 100 nm and to end after crossing the 200 nm marking. This analysis reaches to the resolution that stirring and temperature conditions play a significant role to produce copper nanoparticles by electrowinning.

4.6 SEM Micrographs

The result of SEM analysis also supports the resolution of particle size distribution which is stirring and temperature conditions affect the particle size during electrowinning.

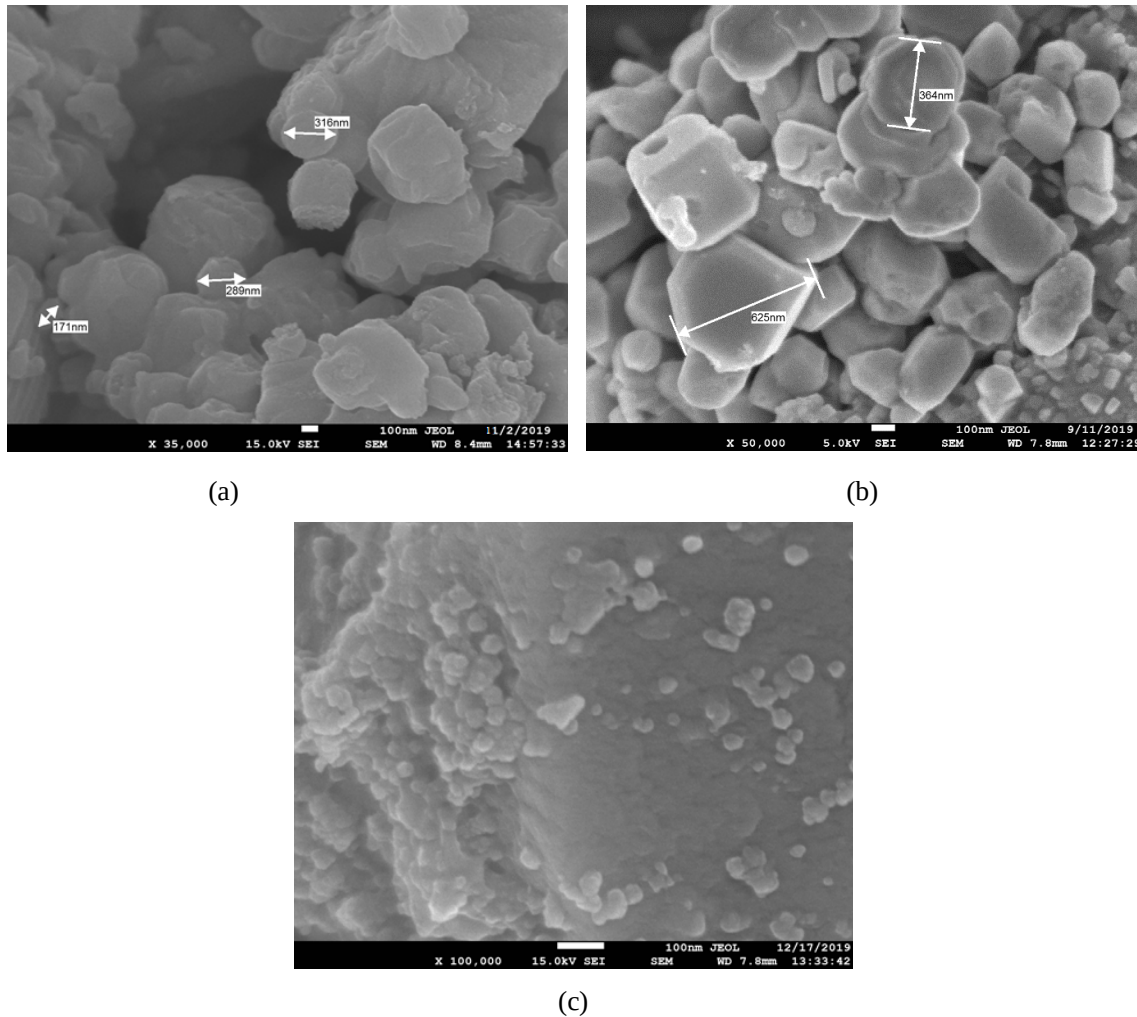


Figure 4.5: SEM Micrographs of Copper particles without stirring and temperature conditions (Sample-1) (a) 35,000 magnification (b) 50,000 magnification (c) 100,000 magnification

Figure 4.5 depicts the SEM micrographs of sample-1 for 35,000 magnification, 50,000 magnification and 100,000 magnification, all of which resemble the presence of nanoparticles. From Figure 4.5 (a) it is clear that particles are in a broad dimensional range which is approximately 150-500 nm. Besides, it provides a hint that particles agglomeration was a significant phenomenon for this sample. In Figure 4.5 (c) agglomeration was clear though it possess a lot of circular plate shape nanoparticles mounted over the agglomerated bulk surface like Figure 4.5 (a). Three-dimensional structure of sample-1 is best pictured from Figure 4.5 (b) where it is evident that along with the circular plate shape particles there are presence of cuboidal, rectangular and round phase particles.

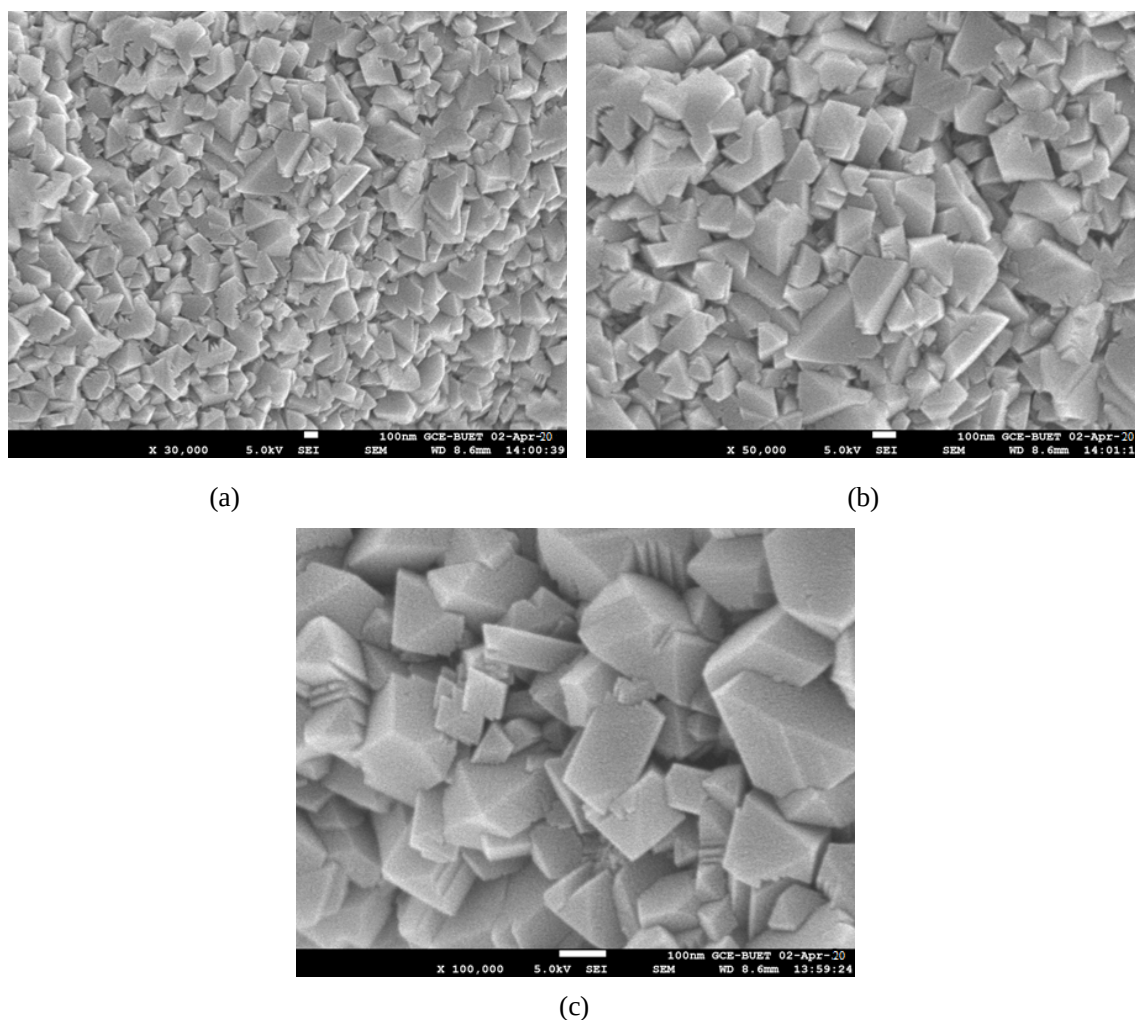


Figure 4.6: SEM Micrographs of Copper particles with stirring and temperature conditions (Sample-2) (a) 30,000 magnification (b) 50,000 magnification (c) 100,000 magnification

After applying the stirring and temperature conditions in the electrowinning cell, particles size of sample-2 dropped down to smaller nano-range. Unlike the sample-1 micrographs of sample-2 (Figure 4.6) reveal unique shape of particles which looks like sliced mango. This phenomenon can be attributed to the stirring effect. It seems that circular movement of electrolyte struck the deposited particles in a specific manner which was expected since the magnetic rotation was constant. Though the particles are of irregular shape they possess no three-dimensional structure variation like sample-1. Moreover, all the particles are of almost same size and most of them are below 150 nm. On the other hand, it is clear from the Figure 4.6 that particles did not agglomerate within each other. The nucleation rate and grain size are both influenced by the current density, hence the grain size is significantly reduced at higher temperature. Primary result for size reduction of particles may be the increment of current density with the increasing solution temperature[78]. The deposits formed at low current densities were made up of only a few nuclei[79]. However, when the current density grew, the number of growth sites increased and the deposit's grain size reduced. When nucleation sites are increased they don't get enough time and space to grow thus particles become smaller. Additionally, the stirring condition also inhibits the growing of one nucleation site and assist ions to deposit on the different nucleation sites. Along with the stirring effect, electrolytic cell temperature increased the current density which increased the nucleation rate, resulting in a reduction in particle size.

4.7 EDX Analysis

EDX analysis was performed in macro scale thus whole compositional scenario of samples were found not of a specific particle.

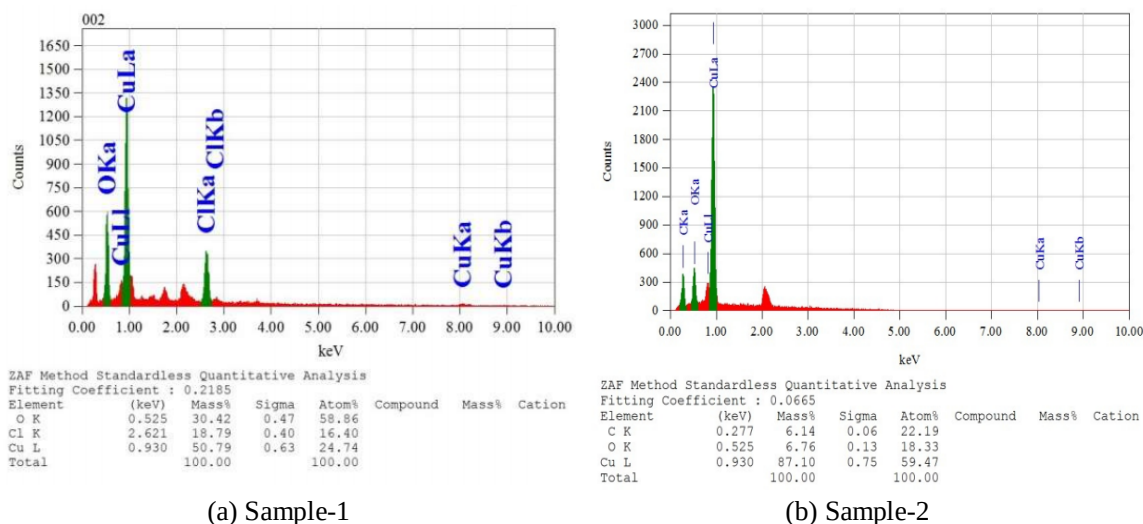


Figure 4.7: Macro Scale EDX of (a) Sample-1 and (b) Sample-2

Unidentified peaks of the graphs belonged to the EDX process parameters like C from the carbon tape and Pt from the Pt sputtering done before putting the sample into the SEM instrument. Summary of the EDX analysis is presented in Table 4.3.

Table 4.3: Composition of sample-1 and sample-2 summarized from EDX analysis

Element	Sample-1		Sample-2	
	Mass %	Atom %	Mass %	Atom %
O	30.42	58.86	6.76	18.33
C	-	-	6.14	22.19
Cl	18.79	16.40	-	-
Cu	50.79	24.74	87.10	59.47
Total	100.00	100.00	100.00	100.00

Figure 4.7 and Table 4.3 confirm the presence of Cl in sample-1. This might be reason of sample-1 not being properly cleaned through the DI water. Noting this issue, careful cleaning

of sample-2 was able to remove the presence of Cl. Another significant issue was the presence of O which is very high in sample-1. This point should be attributed to the air drying of sample-1. It is mentionable that, when sample-2 was processed through vacuum dryer presence of O dropped down approximately 24%. Trace amount of O present in sample-2 might be the result of handling sample-2 in open air and storage container air tightness. Sample-2 as the final product contains Cu 87% which would be more than 90% if C was not counted in the calculation, while sample-1 contains only 50%. Thus, this discussion comes to the resolution that proper cleaning, drying and storage process has significant role in the final product.

4.8 XRD Analysis

The XRD analysis of sample-1 (Figure 4.8) detected the presence of cuprous oxide (Cu_2O) (JCPDS: 01-071-3645) which is a metastable oxide and still in active state. SEM with EDX showed that this sample contains 30% O which formed this cuprous oxide. This metastable phase also indicate that the synthesized product was initially Cu and later formed this metastable Cu_2O phase. Moreover, this oxidation may be the result of stored sample handling during SEM and XRD analysis.

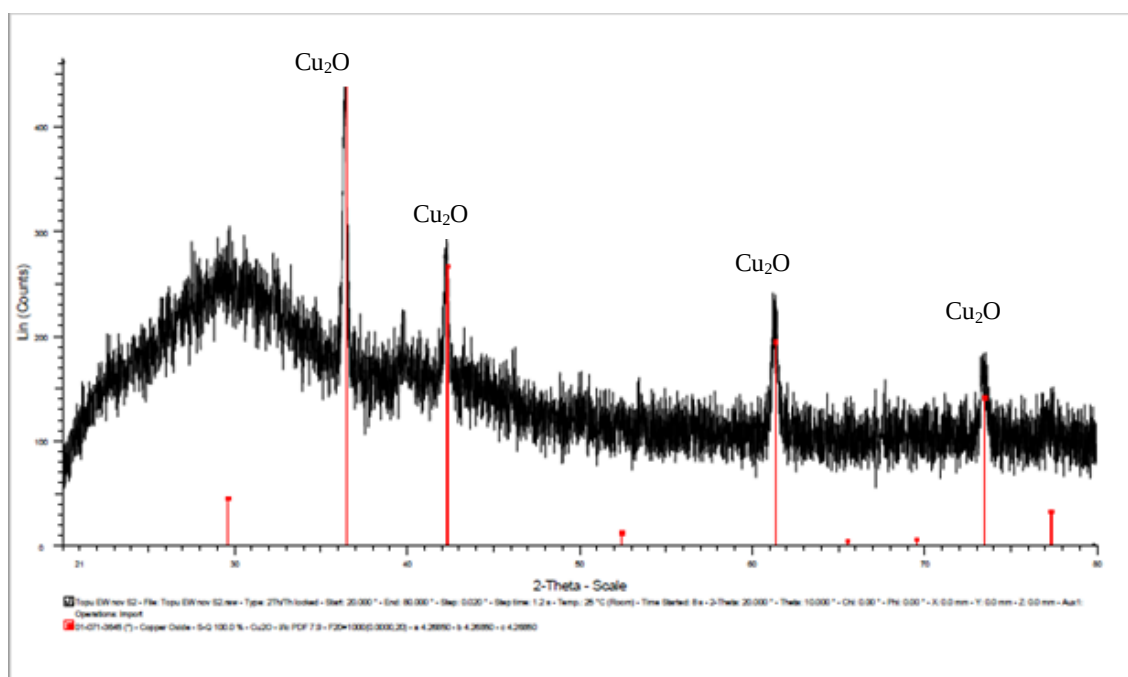


Figure 4.8: XRD analysis of sample-1

An initial hump of XRD scan (Figure 4.8) also provides hint of the presence of moisture which may be the reason of air drying process or moisture contamination in the later stage.

On the other hand, XRD analysis of sample-2 (Figure 4.9) detected mainly elemental copper (Cu) (JCPDS: 00-004-0836) phase with the presence of metastable cuprous oxide (Cu_2O) (JCPDS: 01-071-3645) phase.

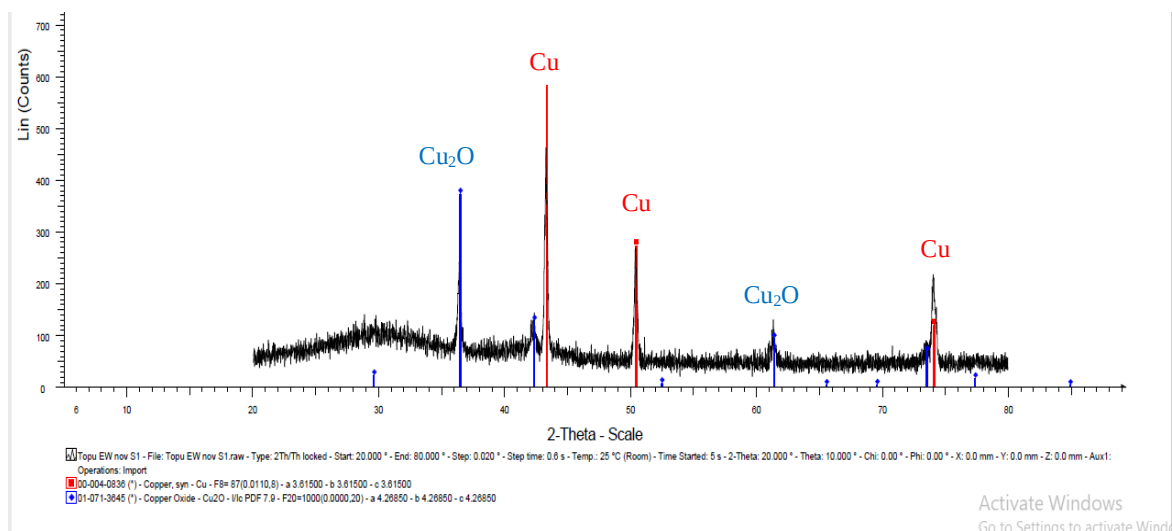


Figure 4.9: XRD analysis of sample-2

The sharp peaks of the scanned graphs resemble a high degree of crystallinity and presence of either single crystal or very small grains. Metastable cuprous oxide phase is the result of increased reactivity of the copper nanoparticles as smaller size increases the surface area and reactivity. Unlike the sample-1 peak broadening of cuprous oxide phase in sample-2 is very low which might be the result of vacuum drying. Drying samples in a vacuum dryer is mandatory since air drying process resulted no copper phase whereas sample-2 represented primarily copper after passing through vacuum dryer.

4.9 Rietveld Refinement

Rietveld refinement of samples provided the crystallite parameters of both sample-1 and sample-2.

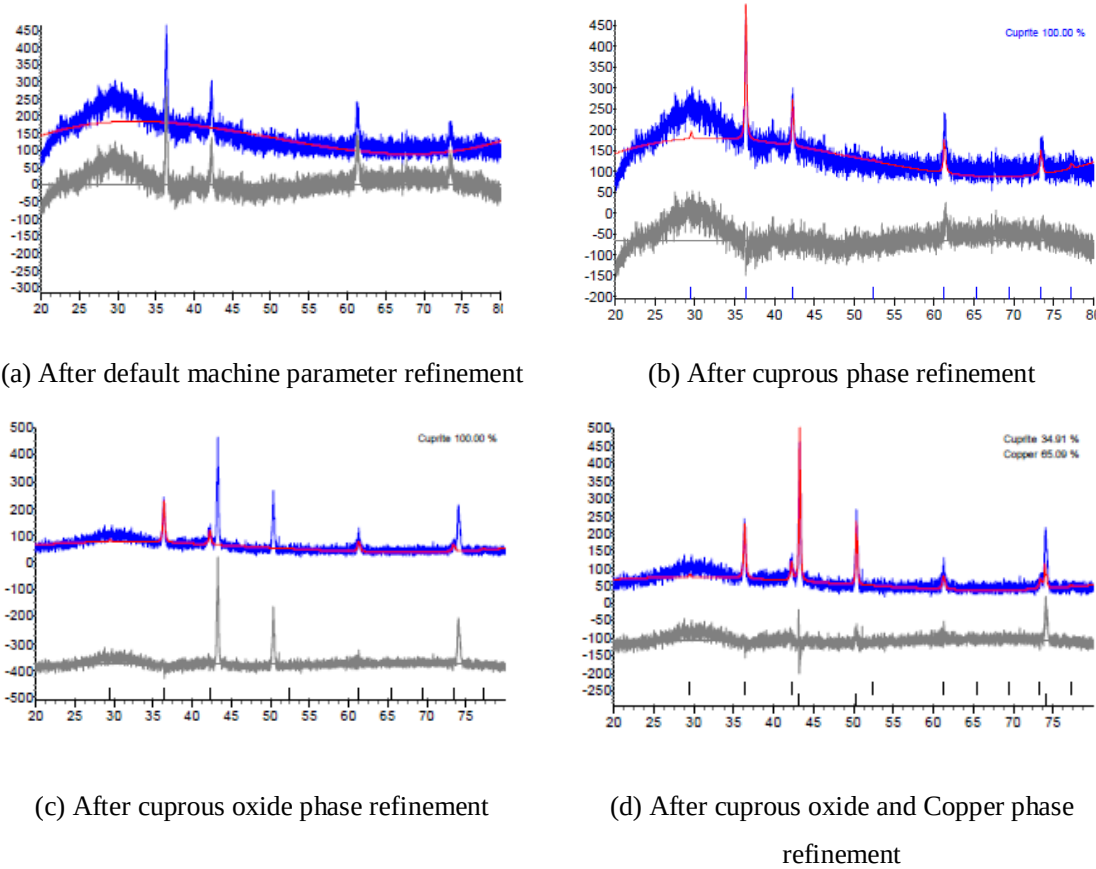


Figure 4.10 Presentation of achieved accuracy during rietveld refinement: a & b for sample-1 and c & d for sample-2

Refinement process perfectly matched all the peaks (Figure 4.10) for both of the phases except the last peak of copper phase (Figure 4.10 d) which was matched partially. This peak looks like a twin phase which may be the reason of this minor error. Overall, after the refinement completion, both graphs had become almost straight which indicated a good accuracy of rietveld refinement.

Crystallite parameters found from the Rietveld Refinement analysis indicated several features of both sample-1 and sample-2 as shown in Table 4.4. Sample-2 contains 65% copper phase and 35% cuprous phase where sample-1 have 100% cuprous phase.

Table 4.4: Summary of crystallite parameters found from the Rietveld Refinement

Parameters	Sample-1	Sample-2	
	Cuprous phase	Copper phase	Cuprous phase
Phase %	100	65.093	34.907
Crystallite size (nm)	55.8	76.7	41.5
Lattice parameter a (Å)	4.2780054	3.6205411	4.2763106
Crystal Density (g/cm ³)	6.070	8.894	6.077

Crystallite size of copper phase belonging to the sample-2 is 76.7 nm. Besides, cuprous phase crystallite size decreased from 55.8 nm in sample-1 to 41.5 nm in sample-2 which might be the consequence of applying heat and stirring conditions in the electrolytic cell. Moreover, this phenomenon also represents that smaller particles are more prone to oxidation and thus form metastable cuprous phase. Rietveld refinement showed that unit cell of all the phases are belonged to the cubic structure having lattice parameter 3.62 Å and 4.27 Å for copper phase and cuprous phase respectively. An indication of reduced porosity is observed as the crystal density of Cu₂O increased for 0.007 g/cm³ in sample-2 while copper phase crystal density almost reached to theoretical density 8.96 g/cm³.

4.10 Comparison with Literature Data

Table 4.5 compares the achieved results found in studied literature with this work. Considering the leaching parameters, having 10 times higher solid to liquid (S/L) ratio and without temperature application concentration of Cu in the leach liquor has been found approximately 1.5 times rich. For Cu recovery when solvent extraction process was adopted use of modifier was necessary which made the process complex since handling of additional chemical became mandatory. Moreover, this route found the particles in the micrometer (µm) range not even in the Nano range. In the super critical methanol process, higher temperature condition compared to this study was adopted which found the particles in a range of 100-500 nm without further purification of leach solution. On the other hand, purified leach solution was able to synthesize particles of 50-300 nm while this study found the particles size in 30-200 nm. It could be mentioned that purification of leach liquor is laborious, chemically more complex, time consuming and economically unpractical. Another point to mention about the

current study is that it uses the most efficient leaching process and a simple metal recovery technology to reduce process complexity and potential operational costs.

Table 4.5: Comparison with literature data

Leaching parameters			Cu conc. (ppm)	Cu recovery process			Particles size		Source
Chemical	Temp. (°C)	S/L ratio (g/ml)		Method	Temp. (°C)	Purification (or phase modifier)	Avg. size	Size range	
Ammonia – ammonium sulfate	35	0.05	22,175	Solvent Extraction	--	TBP modifier	1.5 μm	(0.6-8 μm)	Yang et. al[80]
HNO ₃	90	--	18,200	Super critical Methanol	300-360	Without purification	300 nm	100-500 nm	Xiu et. al[81]
						With purification	180 nm	50-300 nm	
HCl+H ₂ O ₂	Room	0.5	29,437	Electrowinning	65	Nothing	130 nm	30-200 nm	This work

CHAPTER 5

CONCLUSIONS

5 CONCLUSIONS

The growing use of electronic devices has constructed a global environmental problem fueled by technological trash. These valuables buried in such garbage has justified the development of long-term recovery procedures. The current project's goals are based on such urgency, and it focuses on wasteprinted circuit boards (WPCBs), which are used in all kinds of electronic devices. Specifically, this study focused on the recovery of copper from WPCB as a value added product like Cu nanoparticles.

- The physical treatment along with the chemical treatment and leaching process successfully prepared a Cu rich solution having the Cu concentration 29,437.5 ppm.
- Using this Cu pregnant solution as electrolyte in the electrowinning process, Cu was reclaimed as nanoparticles in the range of 30 nm to 200 nm where solution temperature was 65 °C along with 800 rpm stirring condition.
- Average crystallite size of these particles was found to be 76 nm having the density 8.894 gm/cm³ compared to the theoretical density 8.96 gm/cm³.
- It is possible to recover Cu nanoparticles as value added product from waste PCB leach liquor by electrometallurgy without further purifying the leach solution.
- Elevated temperature and stirring conditions during electrowinning have significant role in the particle size. In this study, these conditions assisted for the reduction of sizes and homogenization of the particles shape.
- Cu nanoparticles have a tendency for oxidation particularly forming the metastable cuprous oxide phase which can be controlled and minimized by vacuum drying instead of oven drying and careful storage & handling of the product.

This approach has been proved to be efficient, simple, and cost effective using several characterization techniques.

5.1 Future Work

This study recommends the following points for further study in this area:

- Relationship of current density and current efficiency with impurities of the leach solution
- Effect of current density and current efficiency on the particle size
- Dynamic study for particle size and morphology dependency on the temperature and stirring conditions
- Dependency of the copper particles purity on impurity concentration and electrolyte temperature

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