Recovery and recycling of metals from waste PCBs using pyrolysis followed by hydrometallurgical processes and characterization

THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE

OF

DOCTOR OF PHILOSOPHY
IN
METALLURGICAL ENGINEERING

By

ANJAN KUMARI

UNDER
SUPERVISION OF

Dr. Rajendra Prasad Singh
Professor
NIT Jamshedpur

Dr. Manis Kumar Jha
Principal Scientist
CSIR-NML, Jamshedpur

Department of Metallurgical and Materials Engineering
National Institute of Technology
Jamshedpur-831014

Year: 2017

The thesis is dedicated

To

The EARTH

(The source of Life and Inspiration)

Motto of the work

To protect the environment and conserve the

natural resources by recycling of electronic waste

CERTIFICATE

This is to certify that the thesis entitled "**Recovery and recycling of metals from waste PCBs using pyrolysis followed by hydrometallurgical processes and characterization**" being submitted by **Anjan Kumari** for the Award of th**e** Degree of Doctor of Philosophy in Metallurgical Engineering is a record of bonafide research work carried out by her at National Metallurgical Laboratory, Jamshedpur, India and in the Department of Metallurgical and Materials Engineering, National Institute of Technology, Jamshedpur, India under our supervision and guidance. In our opinion, the thesis has fulfilled the requirement according to the regulations of the institute and has reached the standard necessary for the submission. The results of the work incorporated in this thesis are original and have not been submitted to any institute or university for the award of Degree or Diploma.

(Dr. Rajendra Prasad Singh)
Professor
MME Department
National Institute of Technology
Jamshedpur, India

(Dr. Manis Kumar Jha)
Principal Scientist
MEF Division
National Metallurgical Laboratory
Jamshedpur, India

ACKNOWLEDGEMENTS

I express my deep sense of respect and personal gratitude to Dr. Manis Kumar Jha, Principal Scientist, NML, Jamshedpur for the his stimulating guidance, affection and indefatigable involvement during the entire project work and Dr. R.P. Singh, Professor, NIT, Jamshedpur for his continuous encouragement and discussion to carry out the project work.

I sincerely thank to Dr. K. Muraleedharan, Director, CSIR-NML, Jamshedpur and Dr. Ram Babu Kodali, Director, National Institute of Technology (NIT), Jamshedpur and all the concerned authorities for providing me the kind opportunity for undergoing Ph.D. at this esteemed organization. I appreciate Dr. R. Kumar, MEF Division NML, Jamshedpur and Dr. R. Prasad, MME Department NIT, Jamshedpur for his kind co-operation. And appreciate to Dr. S. Ranganathan, Chief Scientist, MEF Division NML, Jamshedpur for his support in area of pyrolysis of samples.

Special thanks are also extended to my NML colleagues Archana Kumari, Rekha Panda and OM Shankar Dinkar for their personal discussion on various topics related to the subject.

Last, but not the least, I feel my pious duty to acknowledge my husband Dipankar Kumar and my parents- Sri Lalit Kumar Mishra, Smt Ram Shila Mishra, Sri R. N. Kumar & Smt Usha Kumar for their constant encouragement to pursue higher study, everlasting love and affection.

Place: *Jamshedpur*

Date: ***(Anjan Kumari)***

BIO-DATA

NAME: ANJAN KUMARI

EDUCATIONAL QUALIFICATION

B.SC CHEMICAL ENGINEERING : 1st Class with distinction

RESEARCH EXPERIENCE:

Extraction of non-ferrous metal by hydrometallurgical process.
(About 6 year experience in CSIR-National Metallurgical Laboratory (NML), Jamshedpur, India)

NO. OF PAPERS : 6 -Published and 2-Communicated

PATENT : 1

CHAPTER IN BOOK : 1

Patent

S. Ranganathan, Vinod Kumar, Manis Kumar Jha, **Anjan Kumari**. A process for the pyrolysis of depopulated printed circuit boards of e-waste. **2465 DEL 2014, Dt 29/8/2014.**

Research papers (published/accepted/communicated)

Journal (SCI)

Anjan Kumari, Manis Kumar Jha, Jae-chun Lee, Rajendra Prasad Singh, 2015. Clean process for recovery of metals and recycling of acid from the leach liquor of PCBs. *Journal of Cleaner Production* (**ELSEVIER)**, Vol. 112, part 5, pp. 4826-4834**. doi:10.1016/j.jclepro.2015.08.018 & Impact Factor-3.84.**

Anjan Kumari, Manis Kumar Jha, Rajendra Prasad Singh. Recovery of metals from pyrolysed PCBs by hydrometallurgical techniques**.** *Hydrometallurgy* **(Article in Press**). (**ELSEVIER), doi:10.1016/j.hydromet.2015.10.020 & Impact Factor-1.9.**

Anjan Kumari, Rajendra Prasad Singh, Manis Kumar Jha, 2013. Vinay Kumar. Extraction of copper from small electronic devices populated on discarded PCBs. *Journal of Indian Chemical Society*. Vol. 90, pp. 2121-2126 **& Impact Factor-0.4.**

Anjan Kumari, Manis Kumar Jha, Rajendra Prasad Singh, S. Ranganathan. Investigation of the influence of inert and oxidizing atmospheres on the efficiency of pyrolysis of waste printed circuit boards (WPCBs). *Heat and Mass Transfer* (**Revised version submitted**) **(SPRINGER) & Impact Factor-1.0.**

Anjan Kumari, Manis Kumar Jha, Rajendra Prasad Singh. Extraction of Cu, Pb and Ni from waste PCBs for recycling and protection of environment (**Communicated**).

Journal (Non-SCI)

Anjan Kumari, Archana Kumari, Manis Kumar Jha, Vinod Kumar, Rajendra Prasad Singh, Kyoungkeun Yoo. Copper recovery from small devices populated on waste

printed circuit boards. Journal of Metallurgy and Material Science. January-March 2014, pp. 41-51.

Proceedings

Anjan Kumari, Vinod Kumar., Manis Kumar Jha, B. K. Soni. Processing of polycracked ash of printed circuit boards for recovery of valuable and rare metals. Proceedings of the Xl1l *International Seminar on Mineral Processing Technology (MPT-2013),* pp. 929-933.

Vinod Kumar, **Anjan Kumari,** Manis Kumar Jha, A. Vidyadhar, B. K. Soni, Recycling of valuable metals from poly cracker ash of printed circuit boards (PCBs) by physical beneficiation and hydrometallurgical treatment. *TMS (The Minerals, Metals & Materials Society),* 2014, pp. 545-551.

Chapter in Book

Anjan Kumari, Rajendra Prasad Singh, Manis Kumar Jh**a**, Vinay Kumar. Extraction of copper from small electronic devices populated on discarded PCBs. *Education in Chemical Science and Technology*. Vol. 3 No. 1, August 2015. pp. 81-91**.**

PREFACE

In view of the increasing importance of the waste processing and recycling to meet the strict and stringent environmental regulations and conserve the natural resources, the research has been carried out by Anjan Kumari under the joint guidance of Dr. Manis Kumar Jha, Principal Scientist, NML, Jamshedpur and Dr. R.P. Singh, Professor, NIT Jamshedpur. Initially, extensive literature survey has been carried out for the generation of electronic waste and processing methods most commonly employed for recovery of metals from electronic wastes (E-wastes). The experimental studies have been made for the recovery of metals such as Cu, Ni, Pb etc. from the waste printed circuit boards (WPCBs). The thesis has been classified in different chapters dealing with both extensive literature and experimental studies. The review part describes the generation of E-waste containing Cu, Ni, Fe etc. and recovery of these metals following physical beneficiation, pyrolysis, leaching, solvent extraction, electrowinning and cementation methods.

Initially, waste PCBs were pyrolysed under different thermal conditions followed by physical beneficiation to separate low and high metal concentrate. Further, leaching studies were carried out in different acid for dissolution of metals from pyrolysed (low and high metal concentrate) PCBs. The solution obtained after leaching were used for solvent-extraction process to extract acid and metals. Then obtained purified copper and nickel sulfate solution (after solvent-extraction) was used for evaporation, electrowinning etc. for its salts and sheet. Further, lead is extracted from leach liquor (free from acid, Fe, Cu, Ni) by cementation method. Another part of the work was also carried out for recovery of copper from the depopulated small electronic devices using physical beneficiation followed by acid leaching, solvent extraction and electrowinning techniques.

ABSTRACT

Printed circuit boards (PCBs), essential parts of all the electrical and electronic equipment (EEE), are generally composed of ~28% metallic, ~23% plastic and 49% ceramic materials. They are employed to instinctively hold the electronic components using conductive pathways of Cu circuit on its surface. The substantial increase in discarded EEEs containing PCBs has taken place due to accelerating financial growth and high technology innovation. These obsolete PCBs incorporate a noteworthy quantity of metals such as Cu, Fe, Ni, Pb, etc., some of which are lethal to life and all of which are valuable resources. These complex assemblies also embody copious materials like polymers, glass fiber, solder which eliminate harmful materials when disposed to the surroundings. But these accessible metals are being shattered due to improper recycling, causing the evolution of toxic gases and leached hazardous compounds. Thus, there is a need of appropriate execution and efficient methodologies for the recovery of metals present in PCBs, which is both profitable and environmentally worthwhile. Hence, objective of this work aims to design a commercial process to extract metals such as Cu, Ni, Pb etc, highly valued metallic element, from industrial point of view, from the PCBs of computers which appear to be particular among E-wastes available, as far as further utilization is concerned. Recovery of metals from waste PCBs using pyrolysis-physical beneficiation-leaching followed by solvent extraction-electrowinning-cementation process is focused here. Initially, waste PCBs were depopulated by IR (Infrared) heating to remove all the small electronic components followed by their treatment by pyrolysis to recover the valuable.

Investigations were carried out to study the influence of the various atmospheres such as argon, air, oxygen and vacuum on the thermal decomposition of waste printed circuit boards (WPCBs). TGA studies showed that the decomposition of the WPCBs started at about 250°C and was rapid in the temperature interval of 250-350°C. Experiments carried out in the laboratory showed that about 20.43% mass loss was observed during the pyrolysis of WPCBs in a flowing stream of argon at 275°C during a period of 4 minutes

of holding at the temperature. On the other hand, a maximum of about 2.26% mass loss was recorded when the WPCBs were heated at about 327°C for the same time interval in air. Pyrolysis under vacuum atmosphere was also carried out at 300°C for 4 minutes in which 15% mass loss of PCBs were obtained. Mass transfer during the pyrolysis of WPCBs in flowing stream of inert gas was modeled. The predictions of the model were in good agreement with experimental observations. It was found that controlling the flow rate of inert gas and the geometry of the equipment could enhance the rate of pyrolysis significantly. This can lead to significant savings in energy and improvement in the efficiency of pyrolysis. The fumes generated during the pyrolysis process got condensed to generate marketable LD-oil (low density oil). About 10% of the mass of the WPCB could be recovered as oil during experiments which were conducted in argon and vacuum atmosphere. The oil was characterized using FT-IR and found to contain radicals of O-H, C-C, C-H and C-O.

The pyrolysed PCBs sample containing metallic components and carbon fractions were used for further set of experiments. The poly-cracked (pyrolysed) PCBs were subjected to comminution to separate the metallic component from non-metallic fractions using double roll crusher/scutter crusher/ball mill. Further, the ground poly-cracked PCBs was scrubbed/washed with water without using any additives to enrich the metallic concentrate up to 98%. Thereafter, this enriched poly-cracked (pyrolysed) PCBs were further screen analyzed to separate high and low metal concentrate (small fraction). These fractions of pyrolysed PCBs were subjected to hydrometallurgical treatment for recovery of metals.

The small fraction (-10 mesh size i.e., <2 mm size) of poly-cracked PCBs was leached in 2.4M H_2SO_4 at 150°C maintaining 20 bar pressure and pulp density 100 g/L. Systematic scientific studies were also carried out to recover base metals (Cu, Fe and Ni) from leach liquor of small fraction of poly-cracked PCBs. To recover acid by solvent-extraction process from the leach liquor, the experiments were carried out using 70% TEHA diluted in kerosene, which resulted in the extraction of 99.99% H_2SO_4 in three stages at O/A ratio 2/1 in 5 min. The recovered acid could be recycled for leaching of materials in the continuous close loop of operation. Subsequently, air sparging was performed to separate and recover Fe as a precipitate. After the recovery of acid and iron from the leach liquor,

the solution was further processed to recover Cu using 10% LIX 84IC diluted in kerosene. 99.0% copper was found to be extracted in two stages at pH 2.5, O/A ratio 1/1 in 5 min, leaving Ni in the raffinate. Further, nickel was separated completely from the solution in two stages using 1% LIX 84IC at pH 4.58, O/A ratio 2/1 in 15 min.

The high metallic concentrate (+10 mesh size i.e., >2 mm size) of poly-cracked (pyrolysed) PCBs was leached in 4M HNO_3 at 90°C for 60 min using 30 g/L pulp density and maintaining stirring speed 250 rpm showing complete dissolution for most of the metals present viz. Cu, Fe, Pb and 57.5% Ni. Systematic scientific studies were also carried out to recover acid and metal from leach liquor of the poly-cracked PCBs. To recover nitric acid from the leach liquor, the experiments were carried out using 60% TBP diluted in kerosene, which resulted in the extraction of 99.99% HNO_3 in three stages at O/A ratio 3/1 in 12 min. Subsequently, air sparging was performed to separate and recover Fe as a precipitate. After the recovery of acid and iron, the leach liquor was further processed to recover Cu using 25% LIX 84IC diluted in kerosene. The copper was found to be extracted 99.99% in two stages at pH 2.5, O/A ratio 1/1 in 20 min, leaving Ni and Pb in the raffinate. Cu solution was stripped from loaded organic using 10% H_2SO_4. Further, the raffinate was processed for the recovery of Ni by solvent-extraction and Pb by cementation process. Cu metal sheet was obtained from the strip solution by electrowinning process in 4 hours at temperature 30°C using cathode current density 200 A/m^2.

Another part of the work was also carried out for recovery of copper from the depopulated small electronic devices using physical beneficiation followed by acid leaching, solvent extraction and electrowinning techniques.

The novel pyro-hydro hybrid metallurgical process consisting of pyrolysis-beneficiation-leaching-solvent extraction-electrowinning-cementation for the recovery of metals from waste PCBs has been reported. The developed process is cleaner and environmental friendly with zero waste generation concept and has potential to be commercialized after validation on pilot scale trials.

Contents

	Page No.
Certificate	III
Acknowledgement	IV
Bio-Data	V
List of publications	VI
Preface	VIII
Abstract	IX
List of Tables	XV
List of Figures	XVII
Chapter-1. Introduction	1
Chapter-2. Electronic wastes (E-wastes) generation/scenario/management	4
Chapter-3. Literature review on process for metals recovery/recycling from electronic waste	25
3.1. Physical beneficiation of waste printed circuit boards (WPCBs)	26
3.2. Pyrolysis of waste printed circuit boards (WPCBs)	27
3.3. Hydrometallurgical processing for the recovery/recycling of metals	31
3.3.1. Leaching of metals	31
3.3.2. Solvent extraction of mineral acid and metals from leach solution	38
3.3.3. Lead cementation	47
3.3.4. Copper electrowinning	49
3.4. Conclusion	51
Chapter-4. Pyrolysis of waste printed circuit boards (WPCBs)	54

4.1. Introduction	55
4.2. Experimental studies	56
4.3. Results and discussion	58
Chapter-5. Leaching of metals from different metallic fractions	73
5.1. Introduction	74
5.2. Experimental studies	74
5.3. Results & discussion	76
Chapter-6. Solvent-extraction	103
6.1. Introduction	104
6.2. Extraction of sulfuric acid and metals from leach liquor-I	104
6.2.0. Materials & methods	104
6.2.1. Results & discussion	105
6.3. Extraction of nitric acid and metals from leach liquor-II	121
6.3.0. Materials & methods	121
6.3.1. Results & discussion	121
Chapter-7. Cementation of lead	133
7.1. Introduction	134
7.2. Materials & Methods	135
7.3. Results & discussions	135
Chapter-8. Electrowinning of copper	141
8.1. Introduction	142
8.2. Materials & methods	143
8.3. Results & discussion	144

Chapter-9. Copper recovery from small electronic devices populated on waste printed circuit boards (WPCBs)	149
9.1. Introduction	150
9.2. Material & methods	151
9.3. Results & discussion	154
Chapter-10. Major conclusion	161
Equipments used during the experiments	165
Future scope of research activity	171
References	172
Publications	189

List of Tables

	Page No.
Chapter- 2	4
Table 1 E-waste generated in top ten states.	7
Table 2 Domestic sales data of desktop in India.	8
Table 3 Growing trends of E-waste.	8
Table 4 Composition of E-waste for different kind of electronic appliances.	11
Table 5 World copper production (1000 tonnes).	19
Table 6 Trends in world production and use of refined copper (1000 tonnes).	19
Table 7 Trends in copper production in India (tonnes).	19
Table 8 Consumption of lead in various industries.	21
Table 9 The world mine production and reserves of lead (1000 tonnes).	21
Table 10 Reserves of nickel in metric tonnes.	23
Table 11 Mine Production (metric tonnes) of nickel.	23
Chapter-4	54
Table 1 Chemical analysis of depopulated WPCBs.	57
Table 2 Pyrolysis of WPCBs in tubular furnace.	64
Table 3 Effect of temperature on vacuum pyrolysis of waste printed circuit boards (WPCBs) for 4 min.	70
Chapter-5	73
Table 1 Chemical composition of poly-cracked (pyrolysed) PCBs.	75
Table 2 Chemical analysis of high metal concentrate (+10 mesh size) and low metal concentrate (-10 mesh size) of poly-cracked PCBs.	77

Table 3 Calculated values of rate constant, Kct for the fraction of the reacted copper phase (X) of the low metal concentrate (-10 mesh size i.e. < 2mm) of poly-cracked (pyrolysed) PCBs for different models.	81
Table 4 Regression co-efficient, R^2 values for different shrinking core models for the kinetics of the leaching of the low metal concentrate (-10 mesh size i.e. < 2mm) of poly-cracked (pyrolysed) PCBs.	81
Table 5 Calculated values of Kct for the fraction of the reacted copper of high metal concentrate (+10 mesh size, i.e. >2mm size) pyrolysed PCBs for different models.	95
Table 6 Regression co-efficient, R^2 values for different shrinking core model for the kinetics of the leaching of the copper metal from high metal concentrate of pyrolysed PCBs.	95
Table 7 Calculated values of Kct for the fraction of the reacted lead of (high metal concentrate i.e. >2mm size) pyrolysed PCBs for different models.	96
Table 8 Regression co-efficient, R^2 values for different shrinking core model for the kinetics of the leaching of the lead metal from high metal concentrate of pyrolysed PCBs.	96
Table 9 Calculated values of Kct for the fraction of the reacted nickel of (high metal concentrate i.e. >2mm size) pyrolysed PCBs for different models.	97
Table 10 Regression co-efficient, R^2 values for different shrinking core model for the kinetics of the leaching of the nickel metal from high metal concentrate of pyrolysed PCBs.	97
Chapter-8	141
Table 1 Effect of nickel concentration on electrowinning of copper.	147
Chapter-9	149
Table 1 Analysis of the metallic content in different fraction of crushed MOSFETs.	153

List of Figures

	Page No.
Chapter-2	4
Fig. 1 The conventional E-waste processing and recycling.	13
Fig. 2 Industry consumption of copper in 2011.	20
Fig. 3 Nickel consumption by the country and industry.	24
Chapter-4	54
Fig. 1 Experimental apparatus for pyrolysis under argon atmosphere.	58
Fig. 2 Thermo-gravimetry of WPCBs heated in argon, oxygen and air.	59
Fig. 3 Percentage mass change in argon atmosphere.	61
Fig. 4 Percentage mass change in oxidising atmospheres.	61
Fig. 5 Kinetics of oxidation of metals in WPCBs.	62
Fig. 6 Kinetics of vapourization of volatile matter in WPCBs.	63
Fig. 7 Thermo-gravimetry of WPCBs at different heating rates.	63
Fig. 8 Influence of gas flow rate and system geometry on rate of pyrolysis.	68
Fig. 9 Photograph of oil collected during pyrolysis.	71
Fig. 10 FTIR of oil collected during pyrolysis.	71
Chapter- 5	73
Fig. 1 Pressure leaching of low metal concentrate (-10 mesh size) of pyrolysed PCBs.	78
Fig. 2 Pressure leaching of crushed (-10 mesh size) untreated (before pyrolysis) PCBs.	79
Fig. 3 Kinetics studies of copper metal leaching from pyrolysed (-10 mesh size) PCBs.	82

Fig. 4 EPMA and EDS of leached residue showing spherical particles.	82
Fig. 5 Effect of different acids on recovery of Cu, Pb & Ni from high metal concentrate (+10 mesh size) poly-cracked of PCBs.	85
Fig. 6 Effect of nitric acids on recovery of Cu, Pb & Ni from high metal concentrate (+10 mesh size) poly-cracked (pyrolysed) PCBs.	87
Fig. 7 XRD of the leached residues in different time interval.	88
Fig. 8 Effect of pulp-density on recovery of Cu, Pb & Ni from poly-cracked (pyrolysed) PCBs.	90
Fig. 9 Effect of temperature on recovery of Cu, Pb & Ni from poly-cracked (pyrolysed) PCBs.	92
Fig. 10 Kinetics studies of Cu, Pb and Ni metals leaching from high metals concentrate of (>2mm size) pyrolysed PCBs.	98
Fig. 11 EPMA and EDS of leached residue showing spherical particles.	99
Fig. 12 Process flow sheet for recovery of metals from WPCBs.	102
Chapter-6	103
Fig. 1 Effect of extractant concentration on extraction of sulfuric acid.	106
Fig. 2 Log D vs Log [TEHA].	106
Fig. 3 Effect of temperature on extraction of sulfuric acid.	107
Fig. 4 Effect of O/A ratio on extraction of sulfuric acid.	108
Fig. 5 Mc-Cabe Thiele plot for extraction of sulfuric acid.	108
Fig. 6 Effect of time on extraction of Cu using 10% LIX 84IC.	110
Fig. 7 Effect of pH on extraction of Cu using 10% LIX 84IC.	111
Fig. 8 Effect of extractant concentrations on extraction of Cu.	112
Fig. 9 Log D vs Log [LIX 84IC].	112
Fig. 10 Effect of O/A ratio on extraction of Cu.	113
Fig. 11 Mc-Cabe Thiele plot for extraction of Cu.	114

Fig. 12 Loading capacity of 10% LIX 84IC.	115
Fig. 13 Stripping of loaded 10% LIX 84IC.	115
Fig. 14 Effect of pH on extraction of Ni using 1% LIX 84IC.	116
Fig. 15 Log D vs pH.	116
Fig. **16** Effect of extractant concentration on nickel extraction.	117
Fig. 17 Effect of O/A ratio on extraction of Ni.	118
Fig. 18 Mc-Cabe Thiele plot for extraction of Ni.	118
Fig. **19** Process flow sheet for recovery of metals from low metal concentrate (-10 mesh size) of pyrolysed PCBs.	120
Fig. 20 Effect of extractant concentration on extraction of nitric acid.	122
Fig. 21 Log D vs. Log [TBP].	123
Fig. 22 Effect of O/A ratio on extraction of nitric acid.	124
Fig. 23 Mc-Cabe Thiele plot for extraction of nitric acid.	124
Fig. 24 Effect of pH on extraction of Cu using 25% LIX 84IC.	126
Fig. 25 Log D vs pH.	126
Fig. 26 Effect of O/A ratio on extraction of Cu using 25% LIX 84IC.	127
Fig. 27 Mc-Cabe Thiele plot for extraction of Cu.	128
Fig. 28 Effect of pH on extraction of Ni using 1% LIX 84IC.	129
Fig. 29 XRD of copper sulfate salt obtained after evaporation.	130
Fig. 30 XRD of nickel sulfate salt obtained after evaporation.	131
Fig. 31 Process flow sheet for recovery of metals from high metal concentrate (+10 mesh size) of pyrolysed PCBs.	132
Chapter-7	133
Fig. 1 Effect of different reagents on lead cementation.	136

Fig. 2 Effect of aluminum foils quantity on the cementation of lead.	137
Fig. 3 Effect of temperature on the cementation of lead.	138
Fig. 4 Effect of pH on the cementation of lead.	139
Fig. 5 XRD of lead cemented residue.	140
Chapter-8	141
Fig. 1 Effect of Cu concentration on current efficiency.	144
Fig. 2 Effect of Cu concentration on energy consumption.	145
Fig. 3 Effect of Cu concentration on the applied voltage.	145
Fig. 4 Effect of cathode current density on current efficiency.	146
Fig. **5** XRD of copper metal sheet.	147
Chapter-9	149
Fig. 1 Waste PCBs showing the presence of MOSFETs.	152
Fig. 2 +14 mesh size (BSS) of MOSFETs.	152
Fig. 3 XRD of +14 mesh size (BSS) of MOSFET samples.	153
Fig. 4 Leaching of copper at different concentration of nitric acid.	154
Fig. 5 Effect of pulp-density on leaching of copper from crushed MOSFETs.	155
Fig. 6 Effect of temperature on leaching of copper in different time.	156
Fig. 7 XRD of dry residue which is left after leaching in 3M HNO_3.	157
Fig. 8 Effect of Cu Concentration on current efficiency.	159
Fig. 9 Complete process flow sheet for recovery of copper from small electronic devices (MOSFETs) depopulated from waste PCBs.	160

CHAPTER-1

INTRODUCTION

Introduction

Advancement in the field of science and technology had brought industrial revolution which made discernible a new age in human civilization. With the passage of time, the information and communication uprising has brought massive changes in our lives, economies, industries and institutions, thus enhancing the quality of our living. At the same time, these incessant augmentations in the living standard have led to manifold problems including the generation of massive amount of hazardous and other wastes from electric products which pose a great threat to the human health and environment. Thus, proper management of electronic waste (E-waste) is necessary as it constitutes a severe defy to the modern societies and requires coordinated efforts to address it for achieving sustainable development. Wastes are substances or objects, which are disposed of or are intended to be disposed of, or are required to be disposed of because of their hazardous properties. A wide variety of different wastes is arising from different sources being used in our daily activities. Among these wastes, E-waste is emerging as a risk to the whole society as they are hazardous in nature and are ignitable, corrosive, reactive, toxic, explosive, poisonous or infectious. Hence, they pose a substantial or potential threat to public health and the environment.

Base metals viz. copper (Cu), iron (Fe), nickel (Ni), zinc (Zn) and lead (Pb) are generally known as industrial metals and these metals are used in a wide variety of applications from electrical wiring (Cu) to batteries (Pb), strengthen and harden metal alloys (Ni) and to coat and protect more reactive metals, such as Fe. These metals are less expensive than precious metals as they occur more widely and are readily extracted. Nowadays, the use of these metals is incessantly increasing in the production of electrical and electronic equipment (EEEs) with the development of science and technology. But the accelerated economic growth and technological modernization of different electronic devices, has generated a huge amount of E-waste. PCBs, especially of computers are the most idiosyncratic for further utilization as it incorporate a noteworthy quantity of metals viz. Pb, Fe, Cu, Ni, etc, some of which are lethal to life and all of which are valuable resources. But their heterogeneous mixture makes the recycling of this scrap difficult. Waste PCBs are removed from electronic equipment during the dismantling phase and recovery of metals from scrap/waste printed circuit board (PCB) may contribute to reduce

the environmental impacts caused by the extraction of high-valued and/or highly toxic materials from nature. These PCBs could be processed either by pyrometallurgical or hydrometallurgical method after pre-treatment process which is essential for effective liberation and separation of metallic from non-metallic fractions as pyrometallurgical treatment generates carcinogenic gases and direct hydrometallurgical method rarely extracts metals due to encapsulation of epoxy resin, ceramics and plastic materials.

The PCBs encapsulated with epoxy resin hinders the leaching reaction due to restraining of surface contact [1]. A pre-treatment process such as pyrolysis, physical beneficiation, organic swelling etc. is essential for the recovery of metals from waste PCBs by hydrometallurgical techniques. Various efforts have been made to break the encapsulation by using organic swelling, physical beneficiation and pyrolysis [2-4]. Physical beneficiation and organic swelling process are energy and cost intensive respectively. However, treatment of PCBs after pyrolysis is comparatively low acid consuming technique. After pyrolysis, plastic and other volatile compounds are liberated easily from PCBs and thus, make leaching reaction faster even with low acid concentration.

Nitric acid/sulfuric acid is used as lixiviant for the dissolution of metals. The metal from leach solution could be recovered by different methods such as solvent extraction, precipitation, cementation, electrowinning, etc.

The solvent extraction process is a technique in the hydrometallurgical treatment of concentrate. It is used for purification and separation of metals from leach solution. The quality of metal produced by solvent extraction method is also of high purity as compared to the existing processes. Electrowinning is the electrodeposition of metals from the solution obtained by the treatment of ores/scraps followed by their purification by solvent-extraction. In electrowinning, a current is passed from an inert anode through a liquid leach solution containing the metal so that the metal is extracted as it is deposited in an electroplating process onto the cathode. Cementation is the terminology of those spontaneous electrochemical reactions in which a metal ion in the solution is reduced to the metal with the concurrent oxidation of a less noble metal placed in the same solution.

In the present studies, a new route consisting of pyrolysis-physical beneficiation-leaching-solvent extraction-electrowinning-cementation is developed for recovery of

copper, nickel, iron, lead from waste PCBs. Initially, extensive literature survey has been carried out on the generation of E-waste and processing methods most commonly employed for the recovery of these metals from waste PCBs. The literature showed that hydrometallurgical processing as the suitable option in comparison to pyrometallurgical approach as the hydrometallurgical process can control different level of impurities using a selective leaching agent.

After literature review, it noticed that combined process of pyrolysis-physical beneficiation-leaching-solvent extraction-electrowinning-cementation for the recovery of metals from waste PCBs is not reported yet. The developed process is cleaner and environmental with zero waste generation concept and has potential to be commercialized after validation on pilot scale trials. Initially, waste PCBs were pyrolysed under different atmosphere at different temperature followed by physical beneficiation to separate low and high metal concentrate. Pyrolysed PCBs here termed as poly-cracked PCBs, after physical beneficiation these (poly-cracked) pyrolysed PCBs were analysed with respect to metallic constituents and phase present in it. Leaching studies were carried out in different acid for dissolution of metals from pyrolysed PCBs. Various process parameters like acid concentration, solid: liquid ratio, temperature, kinetics etc. were studied during leaching of poly-cracked (pyrolysed) PCBs. The solution obtained after leaching in nitric acid and sulfuric acid is used for solvent-extraction. Initially, acid was recovered from both leach liquor (high and low metal concentrate) of poly-cracked (pyrolysed) PCBs. Iron is removed by air sparging as precipitate formed from acid-free leach liquors. Subsequently, the solvent extraction studies have been carried out for recovery of metals such as Cu & Ni from acid and iron free leach liquors of poly-cracked (pyrolysed) PCBs using LIX 84IC as a solvent. Various process parameters like pH, O/A ratio, extractant concentration, stripping of loaded organic, stage requirement for continuous extraction of metal etc. were studied for solvent extraction of metals (Cu & Ni). Obtained purified copper and nickel sulfate solution was used for evaporation, electrowinning, crystallization etc. for its salts and sheet. Lead is extracted from leach liquor (free from acid, Fe, Cu, Ni) by cementation method. Leach liquors left after extraction of acid and metals (Cu, Fe, Ni & Pb) will be used for other metals extraction by ion-exchange method.

CHAPTER -2

E-waste- Generation/Scenario/Management

Generation of E-waste & its Scenario

E-waste has been escalating rapidly with the increase in the application of advanced information technology in the society. It is the fastest developing sector of the municipal solid waste stream.

The information technology has revolutionized the system of our living, bringing countless benefits and affluence to all its users. The creation of innovative technologies, advancement in living standard combined with incessantly escalating demand of latest product leading to obsolescence in the electronics industry and the globalization of the economy have made these latest products reasonable to the people changing their lifestyles altogether. But, this innovation has also led to unrestrained resource consumption and an alarming waste generation. Both developed countries and developing countries like India is facing the problem of E-waste management. Huge amount of waste electrical and electronic equipment (WEEEs) is being produced internationally, particularly in industrialized countries such as USA, Europe, Korea, India, Greece, China, etc. [5]

The Indian market for E-waste management is "not-organized" and E-waste is a severe matter because of the casual recycling actions. Therefore, quantification of E-waste in India is exceptionally troublesome [6]. Actual and reliable data on the generation, both domestic and import of E-waste, is not currently available in India. A few studies have been conducted by various organizations to devise an inventory of E-waste in the country. Most of these studies depend on the model of obsolescence of electronic products, which needs to be validated with the field data [7].

In India, it is estimated that the E-waste is 0.1-0.2% of the aggregate municipal waste. In case of PCs, 22% of the e-waste is generated by domestic use where as business sector which is responsible for the 78% of the E-waste, as 83% of household customers are buy the PCs first. So business sector is mainly responsible for the waste generation. Additionally, about 1050 tonnes per year of computer waste comes from retailers and manufacturers [6]. The beginning evaluations carried out by national WEEE team in 2005 advice that total E-waste or WEEE generation in India is approximately 146,000 tonnes per year [8].

A more recent study by GTZ (Deutsche Gesellschaft für Technische Zusammenarbeit) has put a much higher number of E-waste generated in India [6]. It is estimated the amount to be 330,000 tonnes for the year 2007. Complementing this, Cobbing et al. 2008 put the view in India as 0.33 million tonnes of E-waste in 2007 [8]. Wath et al. 2010 has put the figures as 420,000 tonnes in the year 2009 [9]. Skinner et al. 2010 argued that of the estimated 382,979 tonnes of E-waste generated in India, 144,143 tonnes entered the waste stream in the year 2007 [10]. However, the complexity of E-waste flows within India and insufficient record-keeping by industry members make an estimation of the amounts of E-waste inside of India troublesome [11].

The western part of India generates the highest amount of E-waste i.e., 35%, whereas northern, southern and eastern regions generate 21%, 30% and 14% respectively. UNEP, listed the equipment wise E-waste generation in the country as over 100,000 tonnes from refrigerators, 275,000 tonnes from TVs, 56,300 tonnes from personal computers, 4700 tonnes from printers and 1700 tonnes from mobile phones [12]. As far as sales of computers and mobile phones are concerned, the sale of computers and laptops has grown at 18% in 2009-10 as compared to 2008-09 [13]. Whereas, the mobile subscriber base is concerned, the total wireless subscribers (CDMA & GSM) have reached 391.76 million. There were only 261.07 million subscribers in 2007-08 but in 2008-09 additional 130.69 million subscribers were added with annual growth rate of 50.06% [14].

There is an immediate need to decide a strategy for E-waste problem in developing countries like India. The report predicts that by 2020, E-waste from old computers across India will increase to 500%; from discarded mobile phones will be about 18 times high, from televisions will be 1.5 to 2 times higher, from discarded refrigerators will double or triple, than its respective 2007 levels [15]. E-waste generated in top ten states is shown in Table 1.

Table 1. E-waste generated in top ten states [15-16].

Indian states	WEEE (Tonnes)	Percentage (%)
Maharashtra	20270.59	19.8
Tamil Nadu	13486.24	13.1
Andhra Pradesh	12780.33	12.5
Uttar Pradesh	10381.11	10.1
West Bengal	10059.36	9.8
Delhi	9729.15	9.5
Karnataka	9118.74	8.9
Gujarat	8994.33	8.8
Madhya Pradesh	7800.62	7.6
Punjab	6958.46	-----

European studies estimate that the volume of E-waste is expanding by 3-5% per year, which is almost three times quicker than the growth of municipal waste stream. Today, E-waste consists of more than 5% of all municipal solid waste being generated. For instance, newer software renders the old ones archaic as well as the cheaper and attractive hardware causes rapid obsolescence of computers. It has been reported that between 1994 and 2003, 500 million PCs reached the end of their service lives and found to contain around 2,872,000 tonnes of plastics, 718,000 tonnes of lead, 1363 tonnes of cadmium and 287 tonnes of mercury. The growth in the waste stream is quickened because of a fast reduction in the lifespan of computers from 4-6 years in 1997 to 2 years in 2005 [17]. Analysts estimate that in California alone more than 6,000 PCs get to be out of date every day. In Oregon and Washington, it is estimated that 1,600 computers become obsolete each day [18]. In India, around 2.25 million units of obsolete computers were reported in 2005, which touched to 8 million units by 2010 at an average annual growth rate of approximately 51%. Table 2 depicts the domestic sales data of desktop in India.

Table 2. Domestic sales data of desktop in India.

Year	In Million Unit
1995	0.37
1997	0.79
1999	1.45
2001	1.67
2002	2.29
2003	3.03
2004	3.63
2005	4.61
2007	5.52

India is expected to generate about 4.1 million tonnes of E-waste by 2015 and 8 million tonnes by 2025 growing at the rate of 10% [16]. In India, decontamination, dismantling, hammering (pulverization), shredding and density separation using water are some methodologies used to recover useful components and metals. There are about 47 recycling companies accounting for only 27% of E-waste, leaving 73% into the environment. China is expected to generate 10.68 million tonnes of E-waste by 2015 and 21 million tonnes by 2025 (Table 3). Guiyu, E-waste town in China, consist of 500 villages which recover gold and silver discarding 80% into the environment, polluting ground water and creating human health hazards.

Table 3. Growing trends of E-waste.

Country	Year 2015 (Million Tones)	Year 2025 (Million Tones)
India	4.1	8
China	10.68	21
USA	9.5	18
Europe	10.53	18
World	77.8	130

The USA is an industrialized nation which is the largest producer and consumers of electronic goods. Annually around 48.5 million computers are discarded in USA, out of which 1.5 million ends up in landfills. Europe and the USA are likely to generate 18 million tonnes of E-waste each by 2025. There are 500 recycling companies in USA

alone but only 20% of e-waste is recycled and the rest is discarded into environment. World is expected to generate 77.8 million tonnes of e-waste by 2015 and 130 million tonnes by 2025 (Table 3). World average stands at 20% of recycling of E-waste till now. Thus, there is an urgent need to find suitable newer recycling and technology management methodologies for reducing of pumping of hazardous materials into environment to protect environment, ground water contamination and human lives.

Sources of E-waste

Developed countries like the US, a few West Asian and European countries, produce massive amounts of E-waste each year. The greater part of this is sent out to developing nations like India, China, Pakistan, Malaysia etc. because exporting would be much cheaper than managing it. Additionally, these developing nations have a workforce willing to discard the hazardous waste for very low wages. Electronic waste is produced by three major sectors:

Individuals and small Businesses: In India, these segments represent for about 24% of the total E-waste generation [19]. Electronic equipment and computers, in particular, are frequently discarded by households and small businesses, sometimes not because they are broken but simply because new innovation has left them obsolete or undesirable.

Large corporations, institutions, and government: Large companies upgrade their employee computers periodically. For example, Microsoft, with over 50,000 employees worldwide (some of whom have more than one computer) replaces each computer about every three years. Factories and industries replace the older equipment with new ones, bringing about more E-waste and so on. Subsequently, this part adds to around 74% of the aggregate waste generation in India alone [19-20].

Original equipment manufacturers (OEMs): OEMs generate E-waste when units coming off the production line don't meet quality standards, and must be disposed of. It is estimated that around 1050 tonnes per year of waste comes from this sector [20].

E-waste Management

Ideal and proficient utilization of natural resources, minimization of waste, development of environmentally sustainable recycling process and disposal of waste are some of the issues which need to be addressed by all concerned while ensuring the economic growth and enhancing the quality of life. Two noteworthy difficulties in this business are low

awareness level among the companies and individuals about the recycling and the collection of the waste products. Because of low infrastructure, the collection of electronics for recycling becomes much more costly affair. It is estimated that 75% of electronic items are stored due to the uncertainty of how to manage it. These electronic junks lie unattended in houses, offices, warehouses etc. and usually combined with household wastes, which are finally disposed of at landfills. This requires implementable management measures. However, some already existing modes of disposal cause a significant amount of harm to the surrounding ecosystem. Some of these and their consequent harms are mentioned below [21].

Incineration: This is a controlled way for discarding the E-waste and it includes combustion of electronic waste at high temperature in specially designed incinerators. This E-waste disposal method is quite beneficial as the waste volume is reduced to a greater extent and the energy obtained is also utilized separately. However, it is not free from disadvantages like emission of the harmful and carcinogenic gases such as dioxins and furans [22].

Landfilling: This is the most well-known method used for the E-waste disposal. Soil is unearthed and trenches are made for covering the E-waste in it. An impervious liner is made of clay or plastic with a leachate basin for collection and transferring of the leachate from the E-waste to the treatment plant. However, the landfill is not an ecologically sound process for disposing of the e-waste toxic substances like cadmium, lead and mercury which are capable of contaminating the ground water and degrading the quality of the soil [22-23].

Recycling: Recycling E-waste can be a big source of many valuable substances, but they are worth only if they are extracted by proper means. Most of the methods used today for recycling move the hazards into secondary products that eventually have to be disposed of. Due to halogenated substances found in plastics, both dioxins and furans are generated as a consequence of recycling the metal content in E-waste. Hazardous emissions to the air also result from recycling of E-waste containing heavy metals such as lead and cadmium. These can be significantly reduced by pre-treatment operations. Hence, most of the methods used today for dismantling and disposal of electronic waste are causing more contamination and hazards to the ecosystem, contrary to what their

purpose is. Therefore, a suitable alternative is required for these processes. Various factors can play a significant role in managing the E-waste.

E-waste compositions

Electronic appliances are made out of many distinctive materials that can be both toxic and equally of high value. While the greater part of these materials, for example, iron, aluminum, plastics and glass account for over 80 weight % of E-waste, whereas valuable and toxic materials are found in smaller quantities but are still of high importance. The material composition of different appliances is often similar, but the percentage of different components can vary a lot. The precious metals such as gold, silver, copper, platinum etc., turns recycling of E-waste into a beneficial business opportunity. On the other hand, the recycling of hazardous E-waste which possesses carcinogens such as lead and arsenic is critical and cause serious health risks and environment dangers if not properly took care of. Composition of E-waste for different kind of electronic appliances is shown in Table 4.

Table 4. Composition of E-waste for different kind of electronic appliances [16].

Materials Large	Household appliances	Small household appliances	ICT and consumer electronics	Lamps
Ferrous metal	43	29	36	-
Aluminum	14	9.3	5	14
Copper	12	17	4	0.22
Lead	1.6	0.57	0.29	-
Cadmium	0.0014	0.0068	0.018	-
Mercury	0.000038	0.000018	0.00007	0.02
Gold	0.00000067	0.00000061	0.00024	-
Silver	0.0000077	0.000007	0.0012	-
Palladium	0.0000003	0.00000024	0.00006	-
Indium	0	0	0.0005	0.0005
Brominated plastics	0.29	0.75	18	3.7
Plastics	19	37	12	0
Lead glass	0	0	19	0
Glass	0.017	0.16	0.3	77
Other	10	6.9	5.7	5
Total	100	100	100	100

Health hazards of E-waste

Since E-waste is a diverse combination of the various type of harmful components, which are capable of creating an irreversible effect to the environment and human health if not handled appropriately. The health hazards of few toxic elements are given below [16, 24].

Americium- This radioactive element is present in smoke alarms. It is known to be carcinogenic.

Mercury- It is available in fluorescent tubes, tilt switches (mechanical doorbells, thermostats) and flat screen monitors. Health effects include sensory harm, dermatitis, memory loss, and muscle weakness. Health effects in animals include death, reduced fertility and slower growth and development.

Sulphur- It is found in lead-acid batteries. Health effects include damages to vital organs such as liver, kidney and heart and also causes eye and throat irritation. When released into the environment, it causes acid rain.

BFRs- It is used as flame retardants in plastics in most of the electronic devices. Health effects include impaired development of the nervous system, thyroid and liver problems.

Cadmium- It is found in light-sensitive resistors, corrosion-resistant alloys for marine and aviation environments and nickel-cadmium batteries. The sale of nickel-cadmium batteries has been banned in the European Union except for medical use. When not properly recycled, it can leach into the soil, harming microorganisms and disrupting the soil ecosystem. The inhalation of cadmium can cause severe damage to the lungs and is also known to cause kidney damage.

Lead- It is used as a soldering agent, in CRT monitor glass, lead-acid batteries, etc. Adverse effects of lead exposure include impaired cognitive function, behavioral disturbances, attention deficits, hyperactivity, conduct problems and lower IQ.

Beryllium oxide- Filler in some thermal interface materials such as thermal grease used on heat sinks for CPUs and power transistors, magnetrons, X-ray-transparent ceramic windows, heat transfer fins in vacuum tubes, and gas lasers.

Hexavalent chromium- A known carcinogen after occupational inhalation exposure. The above health effects show that precautions have to be taken in handling the e-waste to overcome the health hazards.

Non-hazardous Substances [24]

Tin- It is used as solder materials, coatings on component leads etc.

Copper - It is used as a copper wire, printed circuit board tracks component leads etc.

Aluminum- It is used in nearly all electronic goods using more than a few watts of power (heat sinks), electrolytic capacitors.

Iron - Applications of iron are steel chassis, cases, and fixing etc.

Silicon- It is used as a glass, transistors, ICs, printed circuit boards etc.

Nickel- It is used in alloy steels, rechargeable batteries (nickel-cadmium batteries), catalysts and other chemicals, coinage, foundry products and plating.

Lithium- It is used in lithium-ion batteries etc.

Zinc- Application of zinc for plating in steel parts.

Gold- It is used in connector plating, primarily in computer equipment.

Recycling of E-waste

Electronics recycling is an environmentally friendly process because the re-use of electronic goods limits the pollutions generated, to make or reproduce the new product and also to reduce the need for the metals used in electronics. Computer and their components are the world's biggest items in the recycling field, approximately 60% by weight of all electronic recycled goods. In every nation, the municipalities have electronic recycling collections. However, the conventional E-waste treatment and recycling is basically a five-step process as presented below in Fig 1.

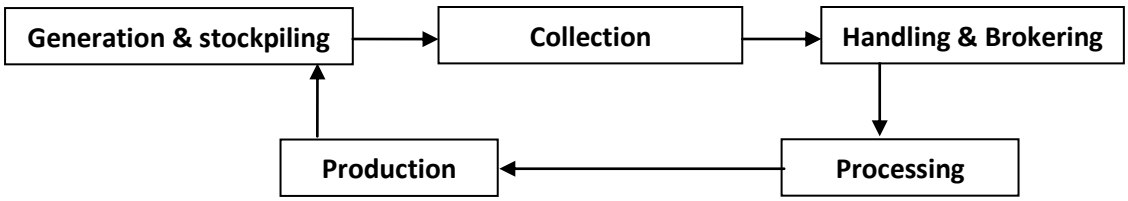


Fig. 1. The conventional E-waste processing and recycling.

Recycling/Recovery System

Recuperation of metals by PCB recycling could be achieved by mechanical processing, pyrometallurgy, pyrolysis, hydrometallurgy, bio-hydrometallurgy or via blending of these techniques. As may be predictable, all of the work undertaken on mechanical systems has been with the primary objective of enhancing separation yield of the various fractions, particularly the one bearing valuable metals. The basic mechanical techniques deployed in the treatment of waste PCBs and electronic assemblies have been adapted or adopted from the raw materials processing sector and refinement has sought to address both yield constraints and ultimately cost effectiveness of the approaches, either used singly or in an integrated manner.

Recycling of metal fractions of PCBs

In spite of the fluctuant average scrap composition amongst the different WEEEs, mobile phones, calculators and PCB scraps uncover that more than 70% of their value relies on their high content in metals. Metallurgical recovery of metals from WEEEs is, therefore, a matter of relevance and has been recently reviewed underlining three possible approaches: pyrolysis, pyrometallurgy and hydrometallurgy.

Pyrolysis: Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures (generally without the participation of oxygen). It includes the simultaneous change of chemical composition and physical phase and is irreversible. It can be considered as an alternative method for recycling PCB, because in the pyrolysis process, the organic part is decomposed to low molecular products (liquids or gases), which can be used as fuel or chemical source, furthermore PCB changes brittle, undergoes delamination which could be easily crushed, while the inorganic part such as glass-fibre remain fairly intense, which can be recycled into other composites or any other materials.

Pyrometallurgy: Pyrometallurgy is a branch of extractive metallurgy consisting of thermal treatment of minerals and metallurgical ores as well as concentrates to bring about physical and chemical transformations in the materials to enable recovery of precious metals. Pyrometallurgical treatment may produce saleable products such as pure metals, or intermediate compounds or alloys, suitable as feed for further processing. Pyrometallurgical processes are generally grouped into one or more of the following categories: Calcining, Roasting, Smelting and Refining. Most pyrometallurgical

processes require energy input to sustain the temperature at which the process takes place. The energy is usually provided in the form of fossil fuel combustion, exothermic reaction of the material, or from electrical heat. However, pyrometallurgical processing of e-waste suffers from some limits, in particular, the recovery as metals of aluminum and iron transferred into the slag is difficult, the presence of brominated flame retardants in the smelter feed can lead to the formation of dioxins unless special installations and measures are present and precious metals are obtained at the end of the process. Furthermore pyrometallurgy results in a limited upgrading of the metal value and thus, hydrometallurgical techniques and/or electrochemical processing are subsequently essential to make refining.

Hydrometallurgy: Hydrometallurgy is a technique within the field of extractive metallurgy involving the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials. The complement to hydrometallurgy is pyrometallurgy, which is a conventional technology. The Hydrometallurgical route is widely used for the recovery of precious metals from E-waste due to its low processing time and high metal recovery with less emission of harmful gases. Moreover, it is less energy intensive and cost effective process. Hydrometallurgical method is also said to be more precise, more predictable and easily controlled compared to pyrometallurgical processing. Hydrometallurgical processes are mainly used for recycling of the metallic ferrous materials of the waste where the extraction of the metal content is profitable. Hydrometallurgy is typically divided into three general areas: Leaching, Solution concentration and Purification as well as metal recovery.

Advantages of recycling E-wastes

- It will give way to the perfect management of E-waste.
- As there will be virtually no land filling or incineration, the hazards to the environment will be avoided.
- Waste disposal costs will be reduced for organizations handling their own e-waste.

- It will generate a good quantity of raw materials for various other industries. Moreover, the cost of this raw material will be much less than that obtained from its original source.
- Widely used metals like copper, platinum have to be dug out from their ores. Acquiring them this way will not only be a cheaper, less time-consuming mean, but will also result in reduction of waste, and its hazards by reuse.
- Plastics can be reused relatively many times. So recycling them from E-waste makes use of this advantage of plastics.
- It will have better and safer working conditions relative to backyard stripping corporations. This means protected means of dismantling and recycling of E-waste.
- It will generate many employment opportunities for people from many disciplines.

Perspectives and aims of thesis

The current thesis is focused on the recovery of valuable and hazardous metals from waste electrical and electronics equipment (WEEEs), particularly from printed circuit boards (PCBs) of spent computer.

In order to achieve the underlying objective, research aims were designed as following:

- Literature review of the focused metals (copper, nickel and lead) was done.
- Pyrolysis of waste printed circuit boards (PCBs) of personal computers was carried out at different thermal conditions.
- Recovery of valuable/hazardous metals from the Poly-cracked (pyrolysed) PCBs sample adopting hydrometallurgical route of acid leaching followed by solvent extraction-cementation-electrowinning techniques were studied.
- Characterization study of the leached residue and the final products was done.

CHAPTER-3

LITERATURE REVIEW

CHAPTER-3

LITERATURE REVIEW

The current intensity of research works and scientific understandings in the field of electronic waste management both in developed and developing countries is briefly discussed. Nowadays, due to rapid economic growth, advancement in living standards and continuous launching of new and improved products, there has been a tremendous increase in the sale of electrical and electronic equipment (EEE). The rapid replacement of old by latest advanced models causes mass generation of waste electrical and electronic equipment (WEEE). The use of electrical and electronic equipment (EEEs) has become an integral part of today's life over this earth. Presented here also include the theoretical cohesions and confrontations among scholars to tackle the challenges of electronic waste. This is to addresses the conversation of research activities in the field and to contextualize the thesis work.

Copper: Cu, which is present in larger amount, ~20-25% (wt) in waste PCBs due to its fine conductivity, greater residence to electro-migration and thermal properties. It is a soft and pliable in its pure form, it is a good conductor of heat and electricity. It is a slow corrosive metal which doesn't react with water but reacts to atmospheric oxygen and forms a layer on the surface. It is an important and valuable metallic element from both industrial and environmental point of view and is widely used in its pure state as well as in alloys with other metals [25]. It is used in defense, space program, railways, power cables, mint, telecommunication cables, etc. In addition, copper is essential element for all living organisms in traces as a dietary mineral. Copper compounds are also used in fungicides and wood preservatives. World copper reserves reported to have assessed at 680 million tonnes in terms of copper content within them. Chile has the largest share of about 27.94% of world reserves, followed by Australia with 12.65%, Peru with 11.18%, the USA with 5.73%, Mexico with 5.59%, China and Russia with 4.41% share each as reported by the Indian Bureau of Mines. World copper production is shown in Table 5 and Trends in world production and use of refined copper is shown in Table 6.

Table 5. World copper production (1000 tonnes) [26-27].

Country	2009	2010	2011	2012	2014
Chile	5394	5419	5260	5370	5800
China	1070	1200	1310	1500	1620
Peru	1276	1247	1240	1240	1400
U.S.	1180	1110	1110	1150	1370
Australia	854	870	958	970	1000
Russia	676	703	713	720	850
Zambia	698	686	668	675	730
World	15500	15600	16100	17000	1870

Table 6. Trends in world production and use of refined copper (1000 tonnes) [27].

Year	Production	Use	Stocks
2008	18214	17888	1102
2009	18249	17894	1376
2010	18984	19129	1199
2011	19596	19697	1210
2012	20128	20386	1381
2013	20995	21267	1336

Copper production in India is not enough to meet domestic consumption requirements and is supplemented with imports to a large extent. India is the 7thlargest producer of refined copper although it lags much behind in terms of mine production. Copper mine production in India is primarily concentrated in Madhya Pradesh, Rajasthan and Jharkhand states. Trends in copper production in India (tonnes) is shown in Table 7 and industrial consumption of copper is shown in Fig. 2.

Table 7. Trends in copper production in India (tonnes) [27].

Year	Mine	Smelter	Refined
2010	37656	678500	661440
2011	38051	707171	677595
2012	38056	781500	705312
2013	38166	661500	600500
2014	39000	738500	732500

Source: Thomson Reuters as estimated in Feb 2014

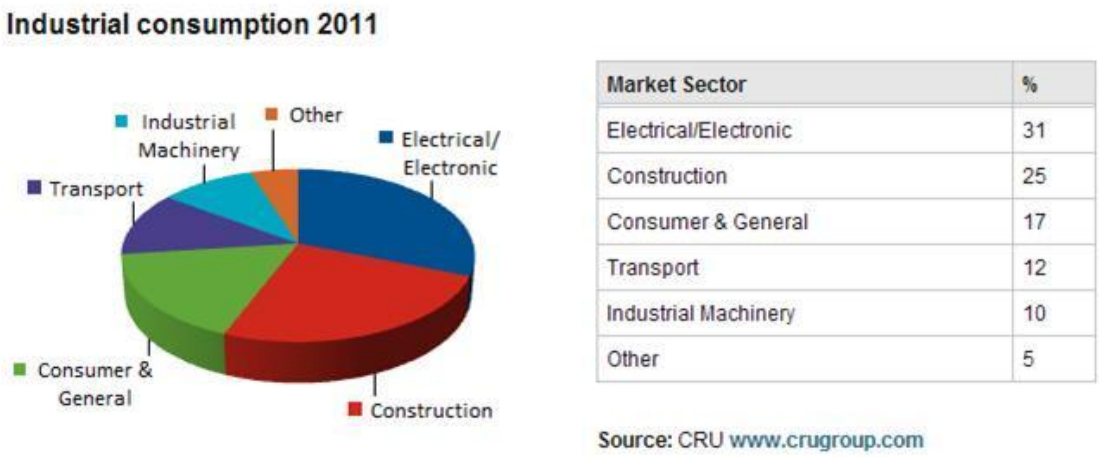


Fig. 2. Industry consumption of copper in 2011 [26].

In electronic industry, copper is widely used as an interconnecting material for the manufacturing of electronic components due to its higher conductivity and greater residence to electro-migration [28]. The recovery/removal of copper from the E-wastes have received considerable attention on account of economic and environmental reasons. The excessive intake of copper by human leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [29]. Copper may be recovered from electronic scrap via pyrometallurgical processes which raises the energy consumption and cost of transportation [30]. Generally, hydrometallurgical route consisting of leaching/solvent extraction/electrowinning, etc. is found suitable to process such wastes [31-33] due to reduced processing cost and lower power consumption [34] and it can be economically operated even on a small scale. Thus, apart from protecting environment there is an economic interest in the extraction and recovery of copper from WEEEs.

Lead: Lead is an imperative base metal, obligatory for a variety of applications in various metallurgical and chemical industries due to its malleability, low melting point and high resistivity to corrosion. It is mainly used as a pure metal, alloyed with other metals, or as chemical compounds [35]. The chemical and physical characteristics of lead are now often used to line tanks that store corrosive liquids and as a shield against x-rays and gamma-ray radiations. Other uses include the manufacture of paints, lead-acid-

batteries, pigments, etc [36]. The consumption of lead is shown in Table 8. Global mine production of lead was expected to increase from 2011 to 2012 by 11% i.e. 5.20 million tonnes. The world production and reserves of lead are shown in Table 9. One of its applications in the manufacture of electrical and electronic equipment (EEEs) was, indeed, used in machines of all kinds, not as a structural material, but where its fusibility and workability were an advantage [37]. Lead metal is chiefly recovered from primary sulfide concentrates which is not measured economical.

Table 8. Consumption of lead in various industries.

Industrial Consumption	**%**
Alloys	1.0
Cabel Sheathing	3.0
Sheet & Extrusions	7.0
Ammunition	6.0
Pigments & Chemicals	12.0
Batteries	71.0

Table 9. The world mine production and reserves of lead (1000 tonnes).

Countries	**2011 (Mine production)**	**2012 (Mine production)**	**Reserves**
United States	342	345	5,000
Australia	621	630	36,000
Bolivia	100	110	1,600
Canada	59	53	450
China	2,350	2,600	14,000
India	115	118	2,600
Ireland	45	50	600
Mexico	220	245	5,600
Peru	230	235	7,900
Poland	60	60	1,700
Russia	105	105	9,200
South Africa	55	55	300
Sweden	62	60	1,100
Other countries	340	530	3,300
World total (rounded)	4,700	5,200	89,000

However, some part of the lead produced comes from different secondary resources viz. lead scrap including lead acetate batteries, cable coverings, sheets, etc. Solder product wastes and dross may also be recovered for its small lead content. Nowadays, every piece of electronic equipment, especially computers, has its electronic components mounted by soldering. After end use of these equipment, popularly known as e-waste, they are characterized to be hazardous and the toxicity is principally due to the presence of lead metal in solder [38]. Consequently, there has been a growing attention for lead recovery from the secondaries/ wastes resources that are being incessantly generated due to the escalation of industrial production culminating from a high consumer demand for the technologically advanced gadgets.

Nickel: It is silvery-white, ductile, malleable and hard metal. It is good conductor of heat and electricity. It is use in alloy steels, rechargeable batteries, catalysts and other chemicals, coinage, foundry products and plating. The uses of electroless nickel on printed circuit boards (PCBs) is for wear resistance and diffusion barrier characteristics on plug-in contacts and circuit conductors. The service life of the contacts is greatly enhanced when electroless nickel is plated onto the copper because the hardness of the nickel improves wear resistance [39]. The figures of nickel reserves and mine production are reported by the United States Geological Survey (USGS) in 2014 in Table 10 & 11. Nickel consumption by the country and industry is shown in Fig 3.

Table 10. Reserves of nickel in metric tonnes [40].

Countries	Metric Tonnes
United States	160,000
Australia	18,000,000
Brazil	8,400,000
Canada	3,300,000
China	3,000,000
Colombia	1,100,000
Cuba	5,500,000
Dominican Republic	970,000
Indonesia	3,900,000
Madagascar	1,600,000
New Caledonia	12,000,000
Philippines	1,100,000
Russia	6,100,000
South Africa	3,700,000
Other countries	5,100,000
World total (rounded)	74,000,000

Table 11. Mine Production (metric tonnes) of nickel [40].

Country	2012	2013
Australia	246,000	240,000
Brazil	139,000	149,000
Canada	205,000	225,000
China	93,300	95,000
Colombia	84,000	75,000
Cuba	68,200	66,000
Dominican	15,200	12,500
Indonesia	228,000	440,000
Madagascar	8,250	26,000
New Caledonia	132,000	145,000
Philippines	424,000	440,000
Russia	255,000	250,000
South Africa	45,900	48,000
Other Countries	273,000	274,000
World total (rounded)	2,220,000	2.490,000

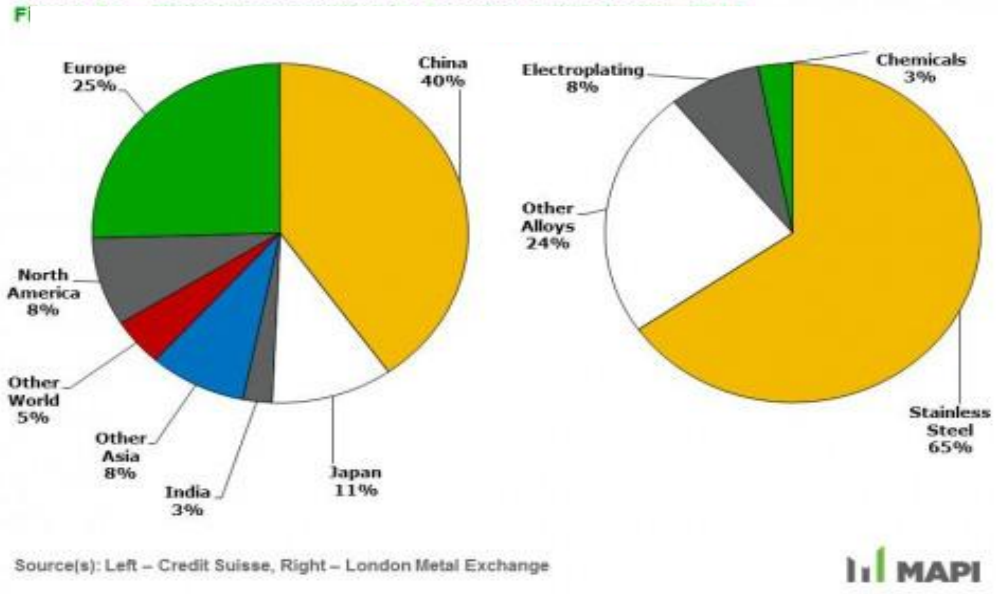


Fig. 3. Nickel consumption by the country and industry.

Literature review on process for metals recovery/recycling

Among the E-waste available, computers are the most idiosyncratic as far as further utilization is concerned. The electronic components of computers are also mounted by soldering onto a fiber-based epoxy PCBs by tracks of copper on that board. These complex assemblies embody copious materials like polymers, glass fiber, solder (an alloy of Pb and Sn) and also incorporate a noteworthy quantity of metals viz. Pb, Sn, Cu, Ni, etc, some of which are lethal to life and all of which are valuable resources. These PCBs contains harmful materials and caused pollution when disposed to surroundings. The key to saving the environment from these hazards lies in the detoxification of perilous soldering material present and so the recovery of these metals from electronic waste is necessary, both from an economic point of view as well as to conserve the natural resources. These materials could be processed either by pyrometallurgical or hydrometallurgical method after the pre-treatment process. Among these, the hydrometallurgical processing of complex concentrates represents an ecologically attractive alternative with respect to classical pyrometallurgical technologies which requires high energy and evolves toxic gases, thus not measured as an appropriate route. But hydrometallurgy involves the use of aqueous chemicals and much lower temperatures to separate metal through selective dissolution from their waste and is genial to the environment in comparison to other available recycling processes [41]. The recovery of metals by hydrometallurgical processes is efficient as compared to pyrometallurgical processes because of environmental protection and cost effectiveness. Even low metal containing materials can be treated on a small scale through this process [42]. Usually, physical beneficiation followed by hydro/pyrometallurgical processes is employed for the recovery of valuable metallic components from PCBs as metal recuperation is very complicated due to the heterogeneity of the materials present in it. In beneficiation procedure, PCBs segregated from e-waste is comminuted to smaller particle size followed by liberation as well as severance of metallic and non-metallic components. However, pyrolysis is one of the thermal pre-treatment processes, which is carried out in the absence of oxygen. During pyrolysis, dismantled component of spent PCBs are treated in an oxygen free atmosphere which decompose the organic part to low molecular

weight products of liquids or gases that can be used as fuel. The pyrolysis process is more proficient as both char and metallic constituents are obtained which could be recycled.

Various authors have studied the process such as pyrolysis, mechanical beneficiation, hydrometallurgical techniques etc. for the recovery of metals from waste PCBs. In general, direct leaching of metallic fractions coated or encapsulated with resin and ceramics rarely accomplish effective extraction of valuable metals from PCBs, and therefore pretreatment of PCBs such as beneficiation, pyrolysis is necessary. Literature review on the recovery of metals from waste PCBs by different processes such as physical beneficiation, pyrolysis, hydrometallurgical route etc. are discussed below:

3.1. Physical beneficiation of waste printed circuit boards (WPCBs)

Physical beneficiation is the process for the separating the metal fraction and non-metal fraction from waste PCBs includes crushing, shape separation, magnetic separation, electric conductivity-based separation, density-based separation and electrostatic separation [43]. A crushing stage is vital for an easier management of waste PCBs. Shape separation techniques have been predominantly developed to control properties of particles. Magnetic separators, in particular, low intensity drum separators are widely used for the recovery of ferromagnetic metals from non-ferrous metals and other non-magnetic wastes. Electric conductivity-based separation separates materials of different electric conductivity (or resistivity). Many authors have studied the physical beneficiation techniques to process waste PCBs for concentrating the metallic values as they can be segregated easily. Earlier, efforts [44-46] were made to beneficiate the ground PCBs. Lee et al. 1997 recovered copper, tin, and lead from waste PCBs by shape separation, magnetic and electrostatic separation [44]. Eswaraiah et al. 2008 carried out the classification of metals and plastic from PCBs by air separation [46]. Shape separation by tilted plate and sieves is the most fundamental technique that has been used in recycling industry [47]. An inclined conveyor and inclined vibrating plate were used as a particle shape separator to recover copper from electric cable of waste, printed circuit board scrap and waste television and personal computers [48]. Electrostatic separation has been predominantly used for the recovery of Cu and Al from electric wires and cables. Gravity concentration, separates materials of different specific gravity by their relative movement

in response to the gravitational force and one or more other forces, the latter often being the resistance to motion offered by a fluid, such as water or air [49].

To recover lead from these soldering materials, different processing steps such as physical techniques followed by chemical processes were attempted by different authors to recover metallic values [50-51]. A novel physical separation process for eco-friendly recycling of rare and valuable metals from end-of-life DVD-PCBs have been also reported [52]. The froth flotation for beneficiation of PCB fines was exploited to disperse them by reverse flotation technique [53]. Effective separation of the materials based on the differences on their physical characteristics features was the key for evolving a mechanical recycling system.

A disassembly stage is always essential to remove dangerous components. Crushing and separation are then key points for improving successful further treatments. Physical recycling is a promising method without environmental pollution and with reasonable equipment invests and diversified potential applications of products. Nevertheless separation between the metallic and non metallic fraction from waste PCBs needs to be improved.

3.2. Pyrolysis of waste printed circuit boards (WPCBs)

Pyrolysis of PCBs leads to the formation of gases, oils, and chars which can be used as chemical feed stocks or fuels. Pyrolysis degrades the organic part of the waste PCBs, making the process of separating the organic, metallic and glass fibre fractions of PCBs sample easier and recycling of each fraction more feasible. Furthermore, if the temperature is high enough, the pyrolysis process would melt the solder used to attach the electrical components to the PCBs.

Several authors have studied the pyrolysis of WPCBs for recovery of metals. Vacuum pyrolysis was mostly used to recover solder and helped separation of metals and glass fibres from PCB scraps. Vacuum pyrolysis reduces organic vapour residence time in the reactor and lowers decomposition temperature, thereby reducing the occurrence and intensity of secondary reactions.

Zhou et al. 2010 described the vacuum pyrolysis and vacuum centrifugal separation for recovery of metals from waste PCBs. Here authors are adopted, a two-step process

consisting of vacuum pyrolysis and vacuum centrifugal separation to treat waste printed circuit boards (WPCBs). Initially, waste printed circuit boards were pyrolysed under vacuum condition at 600°C for 30 min in a lab-scale reactor. The results of vacuum pyrolysis showed that the WPCBs (the base plates of which was made from cellulose paper reinforced phenolic resin) pyrolysed to form an average of 67.97 wt.% residue, 27.73 wt.% oil and 4.30 wt.% gas and pyrolysis of the other type of WPCBs (the base plates of which was made from glass fiber reinforced epoxy resin) led to an average mass balance of 72.20 wt.% residue, 21.45 wt.% oil and 6.35 wt.% gas. The outcomes of vacuum centrifugal separation showed that the separation of solder was complete when the pyrolysis residue was heated at 400°C with 1200 rpm speed of the rotating drum for 10 min [4]. Vacuum pyrolysis of the WPCBs at 550°C and mechanical processing for recycling waste PCBs was reported in which 74.7 wt.% residues, 15.0 wt.% oils, and 10.3 wt.% gases were obtained after the treatment [3].

Another process for the recovery of metals from waste PCBs was also reported by the researchers. Here the thermal pretreatment was carried out for the separation of the non metallic parts. The PCB pieces were heated into an electrical furnace at 500°C for a period of 1 h. This treatment was done in both air and nitrogen atmosphere. During the heating, a loss on ignition of approximately 22% took place. This process was very important for the further treatment, as it resulted in the removal of non-metallic parts of the samples, resulting in a more effective dissolution [50].

Thermal treatment of WPCBs in air and nitrogen atmosphere was also reported by researchers [54]. From this work it is observed that the pyrolysis behavior can be divided into three stages where the first stage is up to temperature of 296°C where no loss in the weight of the PCB scrap was observed. The second stage was between 296-500°C where rapid decomposition of the PCB scrap took place. And finally the third stage was observed above 500°C where the rate of decomposition became almost constant. The amount of plastic removal increases with the rise in temperature. Temperature of around 500°C and duration of about 50 min are adequate for the effective removal of volatile compounds of PCB. After the thermal treatment, 99% Cu was recovered from waste PCBs (pyrolysed PCBs) in nitric acid.

Recovery of metals after thermal treatment of WPCBs within the temperature range of 300-900°C during 15, 30 and 60 min was also reported. Both original and thermally pretreated samples were leached in 1M HCl at 80°C. The weight losses in the range of 5 to 35% were achieved. The increase of burning temperature caused the copper extraction into solution up to 98%, on the other hand copper extraction into solution from non-burned samples was up to 6%. [55].

Researchers also investigated a new process of "centrifugal separation and vacuum pyrolysis" for the combined recycling of solder and organic materials from WPCBs. The results of centrifugal separation showed that the separation of solder from WPCBs was complete when WPCBs were heated at 240°C with 1400 rpm speed of the rotating drum for 6 min intermittently. The outcome of vacuum pyrolysis at 600°C for 30 min indicated that the WPCBs without solder pyrolysed to form an average of 69.5 wt% residue, 27.8 wt% oil and 2.7 wt% gas and pyrolysis of the other type of WPCBs without solder led to an average mass balance of 75.7 wt% residue, 20.0 wt% oil and 4.3 wt% gas [56].

Thermogravimetric Analysis (TGA) is an analytical experimental method used for the determination of materials thermal stability and its fraction of volatile components by observing the differences in weight in correlation with temperature and time. The experiments are carried out normally in air atmosphere or in an inert atmosphere of helium (He), nitrogen (N) or argon (Ar) and the weight differences are recorded in a fixed heating rate.

Molto et al. 2008 [57] studied the decomposition of electronic waste, using TG-DTA (thermo-gravimetry-differential thermal analysis), in atmospheres containing nitrogen and oxygen. There were three stages of decomposition. In the first stage, up to 277°C, there mass loss was significant (0.15%/°C). Above 377°C, the rate of mass loss was low (0.013%/°C). TG was used by Li et al. 2010 to study the decomposition of E-waste in nitrogen and air atmospheres. There was rapid (0.21%/°C) mass loss between 300°C and 400°C [58]. There was no mass loss below 300°C. A maximum mass loss of 25% was observed in these atmospheres. Guo et al. 2010 reported rapid mass loss (0.245%/°C) in the decomposition of E-waste in a fluidized bed-TG system, in nitrogen atmosphere, at 280- 390°C. A maximum mass loss of about 32% was recorded. There were two stages of mass loss. For the first stage, the activation energy was estimated to be 90.49 kJ/mol and

for the second stage, it was estimated to be 137.80 kJ/mol, with pre-exponential factors of 3.95×10^{6} and 8.6×10^{10}, respectively [59]. Zhan and Qiu, 2011 [60] studied the pyrolysis of e-waste under vacuum and in nitrogen atmosphere. Their studies showed that maximum loss of mass occurred at 320°C. The activation energy for pyrolysis depended on the heating rate. This was accompanied by an increase in the pre-exponential factor with increase in heating rate. The estimation of the activation energy and the pre-exponential factor by these authors was debatable since the estimation of activation energy uses a linear expression where the intercept is also a complex function of the heating rate, activation energy and temperature. Zhan and Qiu, 2011 [61] studied the thermal decomposition of waste PCBs in nitrogen, argon and vacuum in the temperature range 300-400°C using TG-DTA. They reported activation energies 256, 212 and 186.2 kJ/mol respectively, for the decomposition in the three environment referred above. The reported pre-exponential factors were 6.5×10^{20}, 8.9×10^{17} and 2.2×10^{5}, respectively.

As discussed here, thermal decomposition of E-waste has been studied by several investigators in air and nitrogen atmospheres under TG-DTA where the temperature increases continuously with time. It is not possible to evaluate the decomposition processes under these conditions since the nature of the experimentation masks the relative merits of the various processes. Decomposition in air will destroy the organic chemicals which can be recycled if collected as vapor and condensed. Also, oxidation in air is likely to emit gases detrimental to the environment. The vapors can be collected through pyrolysis in a non-reactive environment. Heating in nitrogen is not favorable since nitrogen reacts with organic chemicals. Pyrolysis in an inert atmosphere such as argon can produce clean vapors of the organic chemicals present in the PCBs without posing any hazard to the environment and enable profitable recycling. It will be possible to carry out the pyrolysis at temperatures lower than that required for decomposition in air. This can result in reduction of the cost of energy required for the process. A reduction in the temperature of pyrolysis and the time of holding will make the process more economical.

3.3. Literature review on hydrometallurgical processing for recovery/recycling of metals

Hydrometallurgy process is a recycling method which include leaching, solvent-extraction, electrowinning, etc. processes for metals recovery. Leaching is the process of extracting a soluble constituent from a solid by means of a solvent, for electronic wastes leaching involve acid and/or ammonical treatment due to the fact that acid leaching is a feasible approach for removing of base metals so as to free the surface of precious metals. The solutions are then subjected to separation and purification procedures such as precipitation of impurities, solvent extraction, electrowinning, cementation to isolate and concentrate the metals of interest.

3.3.1. Literature review on leaching of metals

In hydrometallurgical waste processing, leaching is widely used for the selective dissolution of the desired metal leaving impurities in the residue which could be safely disposed without disturbing environment. The process is gaining importance in the metallurgical laboratory/industries for the recovery of metallic value. This is also evident from the treatment of complex wastes generated in the different countries for the recovery of metals using different leachant. A number of publications and review paper for the recovery of metals from wastes have appeared in the literature review which is discussed (below) in the thesis. Studies on hydrometallurgical processing of waste and secondaries, the studies have been carried out using different lixiviant such as nitric acid, sulphuric acid, hydrochloric acid, ammonia etc. The leaching was more effective in hot condition with both acid and ammoniacal solution.

3.3.1.1. Leaching in nitric acid medium

Leaching of waste PCBs for recovery of metal in the presence of high oxidising agents are extensively used. Nitric acid is a good oxidising agent for recovery of metals from WPCBs [62-76]. Several authors reported nitric acid leaching of WPCBs for recovery of metals.

Kumar et al. 2012 described the leaching behavior of metals in nitric acid from 2 to 4 mm waste printed circuit boards (WPCBs) containing 22.0% ± 1.1 Cu, 6.7% ± 0.2 Ca, 0.68%

± 0.02 Sn, 0.59 ± 0.01 % Pb, 2.71% ± 0.08 Al, 0.22% ± 0.01 Fe, etc. 98.3% Cu was extracted from printed circuit boards in 3M HNO_3 using 25 g/L pulp density at 60°C for 5 h with agitation speed of 800 rpm was reported. At the same experimental conditions using 100 g/L pulp density, the concentration of Cu in the leachate was 21.12 g/L (96%), and the concentrations of Pb, Al, Fe and Ca were 0.52 g/L, 0.91 g/L, 0.13 g/L, 1.70 g/L, respectively. The solid precipitates obtained in the leach liquors of PCBs included stannic oxide and calcium aluminum oxide in nitric acid [62]. Further, Yoo et al. 2012 developed the hydrometallurgical process to separate and recover the metals such as Sn, Ag and Cu from waste Pb-free solder based on nitric acid leaching, followed by the separation of Ag and Cu through AgCl precipitation or cementation. Nitric acid dissolved Cu and Ag from the waste material while converting tin to stannic oxide (SnO_2), which is very sparingly soluble in the HNO_3 solution. From Pb-free solder, > 99% Ag and Cu were recovered in 2M HNO_3 at 75°C using 100 g/L pulp density with stirring 400 rpm in 120 min. The addition of NaCl or Cu powder was used to separate Ag from Cu in the solution. The addition of 2M of NaCl or 125 g/L of Cu powder to the leaching solution at 30°C led to the successful recovery of Ag [63]. Jha et al. 2010 also reported the leaching studies for the recovery/ recycling of metals from PCBs containing Cu, Ni, Fe, Pb and Sn using various acids such as H_2SO_4, HCl and HNO_3. While sulfuric acid was not a suitable leachant for the dissolution of metals from PCBs, hydrochloric acid selectively dissolved tin. 99.99% Cu, Fe, Ni and 36.7% Pb were dissolved in 6M HNO_3 using pulp density 100 g/L and 90°C. The kinetic studies were also carried out with 2M and 4M HNO_3 at 90°C showed "Ash diffusion control dense constant size-spherical particles" model [64]. Complete recovery of copper from mechanically pre-treated PCBs in 1N HNO_3 was also reported [65]. Efforts were also made to recover 92.7% Cu from printed circuit boards in 3N HCl+1N HNO_3 at 120 min [66]. Oliveira et al. 2009 also compared the leaching behaviour in several leachant (sulfuric, hydrochloric and nitric acids, at 2M H^+ concentration) of the major metals present in WPCBs at temperatures 25ºC and 90ºC and 4 hours of reaction time. Sulfuric acid leaching was not very promising concerning metals dissolution being only effective for iron. Hydrochloric acid allowed the leaching up to 60% of tin and about 50% of lead, as well as the iron. Nitric acid was the most efficient leachant due to its oxidizing properties. Recoveries of 90% or more for copper,

iron, nickel and zinc were achieved at the higher temperature. Lead was also dissolved (up to 80%), as well as silver (more than 70%) [67]. Another process reported by Chaurasia et al. 2013 for the extraction of Cu & Sn from solder of PCBs in nitric acid. Authors also noticed that, nitric acid is a strong oxidizing agent has selective dissolution properties for copper, tin and lead. Moreover, it is cheap and the possibility of its regeneration makes it preferable to HCl which may form unwanted precipitates. With copper and lead, it forms soluble nitrates as given below [68]:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO \quad (1)$$

$$Pb + 2HNO_3 = Pb(NO_3)_2 + H_2 \quad (2)$$

99% Cu was recovered from enriched ground PCBs (obtained after beneficiation by air separator) in 3.5M HNO_3 at 50°C using 120 g/L pulp density in 1 h time was also reported [69]. Thermal treated PCBs (under air and nitrogen atmosphere at 500°C for 1 h) also were used for copper recovery in different acid such as HNO_3, HCl, H_2SO_4. It observed that nitric acid was good leachant for copper recovery [50, 54]. The reactions of metals present in PCBs by aqueous nitric acid solution were expressed as follows [63, 69]:

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2 \quad (3)$$

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO \quad (4)$$

$$3Pb + 8HNO_3 = 3Pb(NO_3) + 4H_2O + 2NO \quad (5)$$

$$Ni + 4HNO_3 = Ni(NO_3)_2 + 2H_2O + 2NO_2 \quad (6)$$

$$3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 4H_2O + 2NO \quad (7)$$

Further, mechanically pre-treated PCBs was also used for copper extraction in different acid such as 2.18N H_2SO_4, 3N HCL, 1N HNO_3 and combination of those acidic solutions at different proportions in which nitric acid was proved to be a good leachant. The dissolution of spherical copper particles in nitric acid were reported by the researchers [70]. Another process for electro kinetic recovery of Cd, Cr, As, Ni, Zn and Mn from waste printed circuit boards in different assisting agents (HNO_3, HCl, citric acid) was reported [71]. Physical process and nitric acid leaching to recover lead from PCBs were also reported [51]. It was also obtained that, the electrostatic separation process was employed to enrich metallic constituents such as copper and lead for subsequent metal recovery [72]. Attempts were also being made to use lead free solder materials but it

requires high soldering temperatures and creates more stress on board level components during the manufacturing processes [73]. About 89% of lead recovery from waste PCBs using supercritical water oxidation combined with electro kinetic process was investigated by researchers [74]. Further, the lead dissolution was found 80% with 2M HNO3, but sulfuric acid was found not effective for the same [75]. The efforts were also made to develop a lab scale process for lead leaching from waste PCBs using a combination of leaching, electrochemical ion exchange and electro-deposition [76].

3.3.1.2. Leaching in sulfuric acid medium

Acid leaching in presence of an oxidant is extensively used for the recovery of metals from waste PCBs. Several researchers reported the recovery of metals such as Cu, Pb, Ni etc. from the waste PCBs in sulphuric acid with oxidising agent.

Peres et al. 2012 reported the recovery of metals in sulfuric acid from washed PCBs powder which was collected from the bottom of the washing flask. Cu & Sn were recovered from this sample in 2.18N H_2SO_4 at 60±2ºC temperature (measured by a mercury thermometer, -10ºC/110ºC) and leach liquor obtained was 2.8 g/L of Cu and 2.0 g/L Sn [77]. Further, the recovery of metals (Cu, Fe, Ni, Ag and Pd) from waste PCBs in H_2SO_4–$CuSO_4$–NaCl solutions at temperature (20-80°C) in 120 min was reported. At a Cl^-/ Cu^{2+} ratio of 21 and 80 °C, the complete extraction of copper as well as 90% Fe, Ni and Ag, and 58% Pd were achieved from WPCB sample (1% w/v). Increasing the solids ratio (1-15 w/v) had a negative effect on the dissolution of metals with no copper extraction at ≥10% w/v [78]. Another processes for leaching of the nonmagnetic component of waste PCBs (obtained after electrostatic separation) using 2M H_2SO_4+0.2M H_2O_2 at 85°C for 12 h resulted in greater than 95% extraction of Cu, Fe, Zn, Ni, and Al was also reported [79]. Jha et al. 2011 also reported the hydrometallurgical process for recovery of metals from organic swelled PCBs. Authors also compared this leaching studies with crushed PCBs for recovery of copper using sulfuric acid in presence of hydrogen peroxide under atmospheric pressure condition. The leaching of PCBs in 6M sulfuric acid at 90°C using a pulp density of 100 g/L under atmospheric condition resulted in the dissolution of a minor amount of copper due to the presence of plastic coating on the surface of metallic layers. On the other hand, when the liberated metal

sheets from organic swelled PCBs were treated with 2M sulfuric acid with 15% hydrogen peroxide in an autoclave under oxygen atmosphere, 97.01% copper was recovered with an increase in hydrogen peroxide concentration from 5 to 15% (v/v) keeping constant pulp density 30 g/L [80]. Further, Yang et al. 2011 reported the leaching of copper from shredded particles of waste printed circuit boards (PCBs) in 15% sulfuric acid solution using 30% hydrogen peroxide as an oxidant at 23°C for 3h with solid/liquid ratio of 1/10. Additionally, leaching temperature and initial copper ion concentration were insignificant effect on the leaching recovery of copper. The effect of different particle size of shredded waste PCBs on leaching of copper was investigated under the optimum leaching condition. It was also noticed that the shredding pieces of waste PCBs <1 mm size were efficient and suitable for copper leaching.

$$Cu + H_2O_2 + H_2SO_4 = CuSO_4 + 2H_2O \quad (8)$$

Then the leaching solution was concentrated to crystallize $CuSO_4 \cdot 5H_2O$ and the reused for the next cycles [81]. Gharabaghi et al. 2013 developed the dissolution kinetics of nickel in sulphuric acid. Around 96% of nickel was extracted from the sample (hazardous waste) of particle size −250 μm in 8% (v/v) sulphuric acid concentration using solid/liquid of 0.10 at 30 min leaching time. From the results it was observed that with the increase in the leaching time, temperature, sulphuric acid concentration, decrease in solid/liquid ratio and particle size, improved the leaching rate of nickel. The experimental data were best fitted by a diffusion-controlled model indicated that diffusion through the product layer was the rate-controlling step during the leaching and the activation energy was 9.06 kJ/mol. After leaching, gypsum was formed which reduce the leaching rate [82].

3.3.1.3. Leaching in hydrochloric acid medium

Hydrochloric acid is also used in hydrometallurgical processing of waste printed circuit boards containing copper, lead, nickel etc. The chlorinated water or chlorine gas and oxidizing agent were employed for dissolution of metals as its chloride. Several authors have reported the leaching of waste PCBs in hydrochloric acid as discussed below. Havlik et al. 2010 reported the recovery of copper and tin in hydrochloric acid. 98% copper and almost tin recovery in 1M HCl at 80ºC from thermal pre-treated PCBs was

obtained. Copper is leached significantly in the oxidative environment only, but HCl is a non-oxidizing acid, and hence there should be no significant reactions between Cu and HCl.

$$Cu + 2HCl\,(aq) = CuCl_2 + H_2\,(g) \quad (9)$$

$$2Cu + 2HCl\,(aq) = 2CuCl_2 + H_2\,(g) \quad (10)$$

During the leaching the oxygen from the surrounding atmosphere gets into the solution, which acts as an oxidizing agent according to:

$$4Cu + 4HCl\,(aq) + O_2\,(aq) = 4CuCl\,(aq) + 2H_2O \quad (11)$$

which may result in a partial transfer of copper into the solution. During the burning, copper is released from the composite and is oxidized. The copper oxides, in contrast to pure copper, are leached relatively well in the non-oxidizing environment of hydrochloric acid. The copper recovery from the pyrolysed samples increased during the leaching, but it is probably caused by the release of copper from the composite and the increase of the reaction interface area as well as by the presence of the atmospheric oxygen [55]. Another work was also carried out for recovery of metals such as copper, zinc, lead and tin from waste PCBs using electro-generated chlorine in hydrochloric acid solution. The generation of cuprous ions in combined reactor decreased the leaching efficiency due to the change of electrode reactions. In the separate reactor, leaching up to 71% copper along with 98% Zn, 96% Sn and 96% Pb was achieved using 2.0 mol/L HCl solution at a current density of 714 A/m^2, 50°C temperature and 400 rpm in 240 min. Higher rates of copper leaching were obtained with 3.0 mol/L HCl which dissolved CuCl more readily [83-84]**.** Leaching behavior of the major metals present in printed circuit boards in different leachant (2M H_2SO_4, HCl, & HNO_3) at 90ºC for 4 h were studied by researchers [67]. Chaurasia et al. 2013 also studied the recycling of tin and copper in hydrochloric acid and nitric acid [68]. 92.7% Cu was recovered from beneficiated PCBs in 3N HCl +1N HNO_3 was also studied [66]. Further, almost complete recovery of copper and tin from mechanical-physical pretreated PCBs in 1M and 2M HCl at 80ºC was also studied **[**85].

3.3.1.4. <u>Leaching in other medium</u>

Ammonical/ammonium hydroxide/ammonium carbonate and ammonium sulfate were used for the metals recovery from the wastes. Several researcher also reported the leaching of PCBs in ammonium or other solutions. Wang et al. 2011 reported the leaching of PCBs at 55°C for 150 minutes using 4M NH_4OH and 1M $(NH_4)_2CO_3$ as leaching solution, with 700 rpm stirring speed and 0.2 MPa oxygen. With this method, Zn, Cu and Ni could be effectively recovered from printed circuit boards by 100%, more than 99% and more than 64%, respectively [86]. 96.7% of copper was recovered from waste printed circuit boards at a temperature of 35°C for a leaching duration of 2 h with ammonium sulfate and ammonia concentration of 2M at a solid: liquid ratio of 1:10 g/l [87]. 98% Cu, Fe, Ni recovered from waste printed circuit boards (WPCBs) in cupric chloride solutions ($HCl–CuCl_2–NaCl$) at 80ºC for 120 min was studied [88]. 89% Pb was recovered from the residual solid after (zinc extraction from zinc plant residue) in 200 g/L NaCl at 25°C in 10 min using pulp density 20 g/L were reported [89].

Since these waste PCBs or other materials bear many metals, during the leaching step, other metals were also leached simultaneously with the metal/s of interest. Therefore, the leach liquor had to be further treated to recover the acid and valuable metals and/or to eliminate the less interesting ones. Besides the conventional method of metal separation i.e. precipitation, recent technologies include ion exchange, membrane separation, solvent extraction and selective adsorption. Among them, solvent extraction is widely used in hydrometallurgical plants for the purification, separation or concentration of metals from aqueous media as well as mineral processing and feasibility due to its inherent simplicity [90]. The solvent-extraction process is more effective for the purification and recovery of metals from the complex and the low metallic containing solution. The purified solution is used to recover metal by electrowinnig or crystallization. The quality of metal obtained by solvent-extraction process is of very high purity as compared to conventional processes.

The inorganic components are hydrometallurgically treated by leaching in acid that generates a huge amount of acidic effluents, which if disposed to the environment causes harmful diseases as well as ecological imbalance. So, due to that extraction acid from the acidic leach solution is necessary. Therefore, several researchers were studied for the

extraction of acid using different extractants. Literature review on extraction of acid by solvent-extraction route as given below:

3.3.2. Literature review on solvent extraction of mineral acid and metals from leach solution

3.3.2.1. Extraction of mineral acid from the leach solution

A survey of literature has shown that solvent extraction is one of the most effective methods for the recovery of mineral acids from solutions [91-96]. Eyal et al. 1991 studied the extraction behavior of mineral acids such as H_2SO_4, HCl and HNO_3 with TEHA, TCA and N, N-dioctyl aniline in various diluent systems and reported that diluent and modifier provide a strong tool for an efficient reversible extraction of acids [97].

3.3.2.1.1. Extraction of nitric acid

Some authors have reported the extraction of nitric acid from different organics. Shin et al. 2009 developed a process to recover nitric acid from the waste stream of wafer industry using solvent extraction technique Complete extraction of nitric acid from the waste stream of wafer industry (containing 260 g/L CH_3COOH, 460 g/L HNO_3, 113 g/L HF and 19.6 g/L Si) by solvent extraction technique using TBP at O/A ratio 3/1 in four stage was reported. Results showed that nitric acid extract in four stages using O/A ratio 3/1 resulting the concentration of pure HNO_3 recovered is 235 g/L with a purity of 99.8% [98]**.** Efforts were also made to extract nitric acid with octyl (phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO), resulting complete extraction of nitric acid with 1:1 stoichiometry at 25°C [99]. Another process reported by Bell et al. 2012 for the extraction of nitric acid into tridentate diglycolamide ligand, TODGA [100]. Further, recovery and reuse of nitric acid from effluents containing free nitric acid in absence and presence of metal nitrates was reported. Resulting 69-76% nitric acid may be extracted by single stage extraction with dilute TBP [101].

3.3.2.1.2. Extraction of sulfuric acid

Authors already demonstrated that the binary extractant system comprising a strong basic amine and a strong acid, such as Aliquat 336/dinonyl naphthalene sulphonic acid, exhibited efficient and reversible extraction towards H_2SO_4 mineral acid [102-104].

Agrawal et al. 2007 reported the extraction of sulfuric acid from waste pickle liquor of a steel industry by Alamine 336 resulting 90% H_2SO_4 extraction in three counter-current stages at the A:O ratio 1:2 phase ratio. Stripping of loaded acid was done with distilled water at 60°C [91]. Agrawal et al. 2008 also reported the recovery of both sulfuric acid and zinc from the spent zinc bleed stream (SZBS) generated during zinc electrowinning in the refineries using tris-(2-ethylhexyl) amine (TEHA) dissolved in kerosene resulting 90% H_2SO_4 extraction in three counter-current stages at the A:O of 1:2. Loaded acid was stripped with hot distilled water at 60°C. McCabe Thiele plot shows that at O/A of 1: 2.11, the loaded acid was stripped in three stages. Hence TEHA is a prospective reagent for the extraction of sulphuric acid from the industrial waste streams such as spent zinc bleed stream of a zinc electroplating industry leaving behind zinc which could be used for the preparation of pure zinc oxide [92]. Three extractants for the recovery of sulfuric acid from acidic waste solutions were also tested including TEHA, Alamine 336 and Cyanex 923, among which, TEHA performed best in terms of acid extraction and stripping. McCabe-Thiele diagram showed that the 98% sulfuric acid extract in three stages using O/A ratio of 2 at 22°C by 50% TEHA used as an extractant, 40% octanol and 10% Shellsol A150 used as diluent and modifier [105]. Another process developed by Ntengwe et al. 2010 to remove sulfuric acid from electrowin solutions using Alamine 336 in isodecanol-shell sol 2325 solvent mixture was also reported. The alamine336-isodecanol-shellsoll 2325 system was found to be effective in recovering H_2SO_4 from industrial effluents at increasing concentrations of alamine with efficiencies reaching 99% at lower values (2.5:1) of organic/aqueous ratios. 52% acid was obtained when loaded organic was stripped with distilled water at aqueous/organic ratio of 15:1, 99% when stripped with sodium carbonate at aqueous/organic ratio of 5:1 [106]. Further, Haghshenas et al. 2009 also reported the comparison studied between TEHA and Cyanex 923 on the separation and recovery of sulfuric acid from aqueous solution. The results showed that each 1 mol of sulfuric acid was extracted by 1 mol of Cyanex 923; while each 1 mol of TEHA could extract 2 mol of sulfuric acid. Based on McCabe–Thiele

plots, the number of required stages for sulfuric acid extraction by TEHA is 4; while under the same operating conditions, these stages increase to 5. On the other hand, TEHA with fewer stages could extract more H_2SO_4 as compared to Cyanex 923. Generally, it seems that the recovery of sulfuric acid from aqueous media using TEHA is more feasible than Cyanex 923 [107]. Moreover, Tait et al. 1993 reported the other work which a mixture of Alamine 336 and D2EHPA showed higher extraction ability towards H_2SO_4 than other tested binary systems involving cationic extractants (D2EHPA, PC 88A and Cyanex 302) with amine based extractants like Aliquat 336, Adogen 283 and JMT [108]. The most recent review concerning studies on the recovery of acids was done with the waste stream of steel and electroplating industries, pickle liquor and spent bleed streams [93].

3.3.2.1.3. Extraction of hydrochloric acid

Several authors have studied the extraction of hydrochloric acid from the solution using different organic as an attractant. Scibona et al. 1966 investigated the extraction behavior of HCl, HBr and HI with diverse amines and the affinity constant values for acid-amine reaction was discussed in terms of electrostatic and ion-water interactions in the organic and aqueous phases respectively [109]. Further, Banda et al. 2013 compared the Amine extractants, such as TOA, Alamine 336, Alamine 308 and TEHA for extraction and stripping behavior of HCl. The extracted HCl was easily stripped from loaded TEHA phase when compared with the other tested tertiary amine system. Solvent extraction reaction of HCl by TEHA was determined from the extraction data. Unlike TOA and Alamine 336, adding cationic extractant to TEHA had negligible effect on the extraction and stripping of HCl. The result showed that 3 stages were necessary for maximum extraction of HCl to the organic phase at an O/A phase ratio of 4.8 using 1.5M TEHA as an extractant [110]. Efforts were also made to extract 95% HCl with TEHA and by stripping with water was also reported [111].

Solvent-extraction process is used for the selective extraction and purification of different metals from the aqueous leach solution. Different organic extractant are used for selective extraction of metals from different types of solution leaving other constituents in the

aqueous raffinate. So, literature review for extraction of metals using organic as an extractant from different media is given below:

3.3.2.2. Solvent-extraction of metals from leach solution

Solvent-extraction process is used for the selective extraction and purification of different metals from the aqueous leach solution. Different organic extractant are used for selective extraction of metals from different types of solution leaving other constituents in the aqueous raffinate. Sometimes impurities are extracted to purify the solution depending on the nature of the constituents present in the solution. Depending on the lixiviants used for the dissolution of metallic values, nitrate, sulfate or chloride containing leach solution generated. The extraction and separation of metals depend on the type of the leach solution and accordingly literature review has been made:

3.3.2.2.1. Extraction of metals from nitrate media

Being a high oxidizing agent, nitric acid leaching is better for metal recovery from the wastes. The development of new organic solvents has also considerably simplified the separation and recovery of metals and minimized the processing cost. Some processes are also in commercial use in both ferrous and non-ferrous metallurgical industries using solvent-extraction route. In non-ferrous metal industries, solvent-extraction process is in use for extraction of copper, nickel etc. The importance of the process has recently been highlighted in the production of metals. Widespread studies have been carried out on the extraction and separation of metals from nitrate solution using different extractants. Different extractant have been used for the extraction of desired metal or sometimes impurities are extracted to get desired pure product. As such only a few studies were reported by the researchers on the extraction of copper from nitric acid leach liquor of PCBs.

Le et al. 2011 reported the selective recovery of copper from the enriched ground PCBs using leaching and solvent extraction techniques. The metal-enriched ground sample was acquired from the beneficiation of the sized PCBs in a laboratory scale column type air separator contained mainly 49.3% Cu, 3.83% Fe, 1.51% Ni, 5.45% Sn, 4.71% Pb, and 1.85% Zn. This sample was leached in nitric acid containing 42.11 g/L Cu, 2.12 g/L Fe,

4.02 g/L Pb, 1.58 g/L Zn, and 0.4 g/L Ni. Further studies were made by using 50% LIX 984N, copper was selectively extracted from nitrate leach liquor of enriched ground printed circuit board using A/O ratio 1:1.5 at pH 1.5 in three stages. The stripping of copper from the loaded organic with sulfuric acid produced copper sulfate solution [69]. Further, Zhang et al. 2010 developed the solvent extraction flow chart for the separation of Cu, Ni and Fe using LK-C2 (LIX 984) as extractant from nitrate solution of waste PCBs. Copper was extracted using 15% LK-C2 in kerosene at two stages at initial pH of 2.60 and the extraction percentage was 99.98%. Fe and Ni were extracted using 20% LK-C2 in kerosene at two stages at initial pH of 3.0 and 10.0 and the extraction percentages are 96.14 and 99.35% respectively [112]. Recently, Lazarova reported that LIX 984 N: a 1:1 mixture of LIX 860 N-I (5-nonyl salicylaldoxime) and LIX84-I (2-hydroxy-5-nonylacetophenone-oxime) performed effectively in Cu–HNO_3 system at lower pH because of synergistic effect of the salicylaldoxime and low degradation of aldoximes it performed similar to that of LIX 860 N-I [113-115]. Another work for extraction of copper from leach liquor of sphalerite concentrate by using organic 10% Acorga M5640 in which 2.5% isotridecanol as modifier is also reported [116].

3.3.2.2.2. Extraction of metals from sulfate media

Sulfuric acid is commonly used for the leaching of different wastes, ores etc. in various metallurgical industries. The leach liquor thus obtained contains metals which could be recovered by solvent extraction process using organic extractant. The process is also used on commercial scale in the recovery of metals from the sulfate leach liquor of wastes. Many authors have reported the extraction of metals such as copper, nickel etc. from sulfate media. Kumar et al. 2009 Selective extraction of Cu after iron precipitation from sulfate leach liquor of e-waste by 10% LIX 84 using O/A ratio 1 at pH above 2.0 in single stages and Cd, Zn, Ni extraction by using D2EHPA (di(2-ethylhexyl) phosphoric acid) was reported. The extraction of copper by the organic solvent [RH] may be represented as [117].

$$Cu^{2+}_{aq} + 2RH = [CuR_2]_{org} + 2H^{+}_{aq} \quad (12)$$

Further, 97% Cu was extracted in three stages from the leach liquor of e-waste containing 1.98g/L Cu at pH 1.91 in presence of impurities (0.1 g/L of Cd, Zn and Ni) in continuous

mode in mixer settler unit maintaining flow rate 4.0 L/h by using 5% LIX 84 diluted in kerosene at A/O ratio of 1. Loaded organic was completely stripped with 10% sulfuric acid in two stages [118]. Agrawal et al. 2010 reported the extraction and separation of copper from metal rich concentrate (obtained from the beneficiation circuit) by leaching (in sulphuric acid) and solvent extraction routes. The sulphate leach liquor this obtained had 23.98 g/l Cu, 0.26 g/l Ni, 0.003 g/l Co, 1.7 g/l Zn, 0.0035 g/l Cd, 0.9 g/l Fe. This solution was further subjected to solvent extraction for separation and recovery of Cu selectively from the leach solution. Cu was completely extracted in three stages from sulfate leach liquor of beneficiated circuit by using 25% LIX 84IC at O/A ratio 2:1 at pH 1.7. Cu was stripped from loaded organic phase by H_2SO_4 [119]. Another process for copper extraction from sulfate leach liquor of copper from converter slag by using 10% MOC 45 diluted kerosene at A/O 1:2 in two stages was studied by researchers [120]. Solvent extraction of copper from leach liquor of a low grade chalcopyrite in two stages by using 1.5% LIX 984N-C at O/A ratio 1:2 at pH 1.85 was also reported [121]. Further, 95% Cu was selectively extracted (after iron removal by precipitation with $CaCO_3$) by using LIX 984 from a solution containing metals such as Cu, Co, Zn Fe was studied [122].

Another process of selective extraction of copper from sulfate solution containing Cu, Cd, Zn & Ni by using LIX 84 at pH 2 at O/A ratio 1/1 was reported [123]. By using 10% Acorga M5640 in which 2.5% isotridecanol presence as modifier at pH 1.35, copper separated from zinc leach liquor obtained by acidic ferric sulphate leaching of an industrial sphalerite concentrate was also investigated by researchers [124]. Efforts were made for extraction of Cu by using LIX 84 and Co, Ni by using Na-Cyanex 272 from the leach liquor of copper concentrate [125]. Separation of Cu and Ni from their sulfate solution using LIX 664N in kerosene in which complete extraction of Cu with 40% LIX 664N using O/A ratio 2:1 at pH 2 and 80% Ni extraction with 30% LIX 664N using O/A ratio 2:1 at pH 9 was further studied [126]. Extraction of copper from sulfate leach liquors of synthetic Cu–Ni–Co–Fe matte using oxime based extractants such as LIX 84 and LIX 973N in kerosene was studied. Results showed that the extraction isotherm data with 40 vol.% LIX extractants (barren of copper) at unit phase ratio indicated 3 stages of extraction with LIX 84 and 2 stages of extraction with LIX 973N were necessary to

achieve >95–99% copper extraction. The co-extraction of Ni, Co and Fe was <2 mg/L [127]. Agrawal et al. 2008 studied solvent extraction for the separation of copper and nickel from their sulfate solution in which 99.9% Cu was extracted with 20% LIX 84 at pH 2.5, using 5% Cyanex 272 and 98.06% Cu was extracted at pH 4.85. In both the cases nickel was left in the raffinate [92]. 80% copper was extracted from sulfate leach liquor of smelter slag by using LIX 984 in which kerosene shellsol D70 as diluent was also reported [32]. Nam et al. 2004 developed a process for recovery of copper, nickel, cobalt from the matte of the polymetallic sea nodules following pressure leaching-solvent extraction route [128]. Reddy and Priya, 2005 developed a process for extraction and separation of Cu(II), Ni(II) and Zn(II) using LIX84I as an extractant from sulfate solution [129]. Copper was extracted from the mixed sulfate solution in presence of other metallic constituents using LIX 622 at pH 2 and unit phase ratio [130]. The studies have been also made for separation of copper and zinc from the leach solution obtained in the treatment of a complex sulfide concentrate using LIX64N [131-132]. The solvent extractions of the cations such as Cu(II), Fe(III), Ga(III), Ni(II), Co(II), In(II), Zn(II) and Pb(II) with LIX 984N have been explained by Miguel et al. 1997 [133]. Amores et al. 1997 also reported the application of MOC 45 for copper extraction from sulphate solutions [134]. Calligaro et al.1983 also studied the extraction of copper, nickel, cobalt, zinc and iron from solutions using LIX 64N in kerosene [135].

3.3.2.2.3. Extraction of metals from chloride media

The chloride metallurgy has potential due to a better leaching characteristics of chlorine and hydrochloric acid, development of newer material of construction to tackle the corrosivity and volatility of the lixiviants etc. Widespread studies have been carried out on the extraction and separation of metals from chloride solution using different extractants. As the extraction of metals depends on the nature of the extractable metal species present in the aqueous phase, different extractant have been used for the extraction of desired metal or sometimes impurities are extracted to get desired pure product. Several authors studied the extraction of metals from chloride leach solution. Extraction of copper from chloride leach liquor of copper sulfide concentrate and chalcopyrite by four LIX reagents (LIX84-I, LIX612N-LV, XI-04003 and LIX984N)

were used as extractants while kerosene was used as a diluent. At a pH below 0.5, the copper extraction increased quickly with increasing pH value while at a pH above 0.5, it increased only slightly with increasing pH value. The copper extraction in organic solution was virtually not affected by the impurities. The iron extraction in organic solution increased with decreasing A/O ratio from 2:1 to 1:8 as the copper extraction decreased. Conversely, the Cu/Fe ratio in organic solution increased as copper extraction increased [136-137]. In continuation to above, Devi et al. 2014 reported the extraction of copper (II) from chloride solution using 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime) (10% LIX®973 NS-LV) in kerosene. In presence of Fe(III), highest separation factor of 25.13 was obtained from 0.005M HCl using 10% (v/v) LIX 973NS-LV in kerosene, but it increased to 83.2% when 0.5M Na_2SO_4 was present along with Cu and Fe(III). The separation factor was 58.07 from the 0.005M HCl using 10%(v/v) LIX 973NS-LV in kerosene when both Fe(II) and Fe(III) were also present [138]. Sarangi et al. 1999 reported for **e**xtraction of nickel and cobalt from 1M chloride solutions using the sodium salt of Cyanex 272 as extractant diluted with kerosene with tri-*n*-butyl phosphate (TBP) employed as a phase modifier [139]. Separation of Ni and Co from solutions in the presence of metals such as Cu, Zn, Mn, etc. was also reported [140]. The separation of Cu(II), Fe(III) and Zn(II) from mixed sulphate/chloride leach using TBP, LIX 841 and Cyanex 923 in kerosene was reported by researchers [141]. Further, Belkhouch et al. 2005 observed in the extraction of Cu(II) over Ni(II) by using mixtures of D2EHPA and TBP in heptane [142]. Zhu et al. investigated a synergistic solvent extraction system for separating copper from iron in high chloride concentration using Versatic 10 and LIX 63 to separate copper from iron in high chloride concentration solutions and transfer copper into sulphate solutions [143]. Another process reported by Pradhan et al. 2014 for the separation of iron over copper with a shaking time of only 30 s with 0.1M Cyanex 921 and from 2M HCl. The separation is possible at 27°C with 0.1 M Cyanex 921 from 2M HCl solution. The separation of copper and iron was also feasible from 5 mol/L HCl using 0.02 mol/L Cyanex 921 [144].

3.3.2.2.4. <u>Extraction of metals from other media</u>

In order to recover the metallic values from waste resources, different researchers have reported various hydrometallurgical processes. Liang et al. 2013 reported the optimizing mixed culture of two acidophiles to improve copper recovery from printed circuit boards (PCBs) [145]. Giannopoulou et al. 2007 also reported the recovery of copper and nickel from acidic polymetallic aqueous solutions [146]. Additionally, Gameiro et al. 2010 investigated copper extraction from ammoniacal medium in a pulsed sieve-plate column with LIX 84-I using Shellsol D- 70 as diluents with efficiencies of copper removal in the range of 90.5–99.5% [147]. Another work reported by Chellammal et al. 2010 the electrolytic recovery of dilute copper from a mixed industrial effluent of high strength COD [148]. With the treatment of leach liquor of PCBs (obtained after leaching in ammonium sulfate and ammonia concentration) for solvent extraction of copper with 50% LIX 84 in kerosene, 3 min period of equilibration at pH of 10, 99.6% copper was recovered from the leached solution **[**87]. The non-dispersive solvent extraction (NDSX) of copper from aqueous ammoniacal/ammonium carbonate medium with LIX 973N using a micro porous hydrophobic polypropylene hollow fiber contactor was also reported by researcher **[**149] Xie et al. 2009 reported **t**he recovery of copper and cyanide from waste cyanide solution with the guanidine extractant (LIX 7950) and the modified amine extractant (LIX 7820). Temperature had a significant effect on copper extraction. Both the distribution coefficient and the stoichiometric extraction constant of $Cu(CN)_3^{2-}$ with LIX 7950 decreased when the temperature was increased from 25°C to 45°C .The extraction process is exothermic with the enthalpy change of the reaction (ΔH°) of -190 kJ/mol [150]. Parija et al. 2000 further studied the separation of nickel and copper from ammoniacal solutions through co-extraction and selective stripping using LIX84 as the extractant [151].

The enriched metallic fraction obtained was leached in acidic/ alkaline solution to dissolve the desired components leaving gangue as the residue. The metal was then recovered following precipitation, cementation, ion exchange, solvent extraction, electrolysis, etc. Out of the various hydrometallurgical processes, cementation is one of the techniques found to be feasible to achieve a high degree of metal removal within a fairly reasonable contact time. High process efficiency, complete detoxification of heavy metals and recovery of most metals in pure metallic form are few advantages that make it

viable and thus employed on commercial scale for extraction and separation of various non-ferrous metals from leach solutions of low grade ores/ secondaries.

3.3.3. Literature review on lead Cementation

The precipitation of a metal from a solution by means of another metal is called cementation. The reaction is an electrochemical reduction process, as in:

$$Me_A^{2+} + Me_B \longrightarrow Me_A + Me_B^{2+} \quad (13)$$

Where Me_A has a low oxidation potential than Me_B.

In cementation, a more reactive metal dissolves in a solution to precipitate a less reactive metal from the solution.

The removal of lead ions from different kinds of solutions by cementation has been studied by a number of researchers. Authors were reported that the Pb cementation from different solutions by using different metals (Ni, Zn, Fe and Al) which have high oxidation potential [152-159]. Ni, Zn, Fe and Al are placed high in the electrochemical series (greater oxidation potential) while Pb is placed towards the bottom (low oxidation potential).

The recovery of lead using ammoniacal leaching to dissolve lead sulfate found in used battery wastes was investigated. About 86% of metallic lead was recovered at 100°C in 180 min via cementation, using Ni powder as the reductant [152]. Farahmand et al. 2009 studied the cementation of lead with aluminium powder from the brine-leaching filtrate of lead-bearing zinc plant residues (ZPRs). Lead cementation with aluminum powder were studied in which aluminum powder quantity-1.5 times of stoichiometric value, time-90 min, aluminum powder fraction with a particle size −125+88 μm and temperature-70°C resulting high degree of lead removal (~95%) from the solution within a fairly reasonable contact time. The overall cell reaction for the cementation of lead by aluminum could be stated as [153]:

$$3Pb^{2+} + 2Al = 2Al^{3+} + 3Pb \quad (14)$$

Cementation of lead from brine leaching solution by aluminum powder was studied, resulting maximum lead recovery when using Al:Pb of 1.5. Cementation with Aluminum was fast and economical. Authors also observed that temperature has no more effect on cementation recovery [154]. Volpe et al. 2009 reported metallic lead recovery from lead-

acid battery paste by urea acetate dissolution and cementation on iron under optimum conditions time of 4h, agitation speed 400 rpm at temperature 50°C in nitrogen atmosphere. Under the operating conditions, up to 99.7% of lead acid battery paste, mainly composed of $PbSO_4$, PbO_2 and $PbO{\cdot}PbSO_4$ species was converted to metallic lead [155]. Raghavan et al. 2000 described the hydrometallurgical process of metals extraction from solutions of salts of lead generated at the zinc plant. In their research, the residual lead sulphate was treated with sodium chloride solutions after that it was filtered. Then the operation of cementing by using waste aluminum was followed [156]. At an initial concentration of 4.5 g/L lead ions a 97.1% extraction efficiency was obtained. The solution of salts was obtained through the leaching of zinc residue. For a lead content of 7.79 g/L, extraction efficiency was 92.7%. In 2000, researchers [157] studied the removal of lead ions from acidic aqueous solutions by cementation on iron rotating disc. Lead salt solutions were prepared using reagents of lead nitrate and the pH (pH-2) value had been controlled by adding H_2SO_4 and HCl. Cementation reaction showed a diffusion activation energy of 9.6 kJ/mol (25-80°C). Cementation efficiency was 73% at an initial concentration of lead ions of 70 mg/L after 180 min of cementation. Also in 2000, Shin and others [158] recovered lead as lead sponge in a solution with a concentration of 1.0% g HCl containing Pb^{2+} and Cl^- by cementing using pure aluminium or magnesium rod as reducer. Abdollahi et al. 2006 also reported in 2006 extraction of zinc and lead from residues produced by zinc- Iranian producing plants using the salts solubilizer method. Research were conducted for the extraction of zinc using H_2SO_4 at 700°C from solubilized residue. The solid residue that was left after the extraction of zinc was further used for lead recovery using NaCl by leaching process. Lead in solution, after filtering, was cemented with aluminium plating. Cementing efficiency for a 16.36 g/L lead was almost 97- 98% [159].

3.3.4. Literature review on copper electrowinning

Electrowinning is the electro-deposition of metals from their ores that have been put in solution via a process commonly referred to as leaching, solvent extraction. In electrowinning, a current is passed from an inert anode through a liquid leach solution containing the metal so that the metal is extracted as it is deposited in an electroplating process onto the cathode. Electrowinning process is extensively used in the production of copper.

Several authors studied on electrowining of copper from sulfate solution. Panda et al. 2001 reported the electrowinning of copper from sulfate electrolyte (contains copper, 20 g/L; sulfuric acid, 30 g/L; sulfur dioxide, 4.1 g/L) using current density 150 A/m^2 at temperature 50°C, obtained smooth, bright and compact deposits with better surface morphology, maximum current efficiency and minimum power consumption [156]. Viswanath et al. 2011 also reported the electrowinning of copper powder from copper sulfate solution in presence of glycerol (10-15%) and sulphuric acid (0.5 to 1.0 N) using current strength approx 0.5 A. After electrowinning, the produced copper powder contained more of square, hexagonal, cubical and spherical shape particles & less weakly bonded dendrite particles [161]. Copper sulfate and sulfuric acid are strong electrolyte and therefore they dissociated completely. The water molecule dissociates as:

$$CuSO_4 = Cu^{2+} + SO_2^{2-} \quad (15)$$

$$H_2SO_4 = 2H^+ + SO_4^{2-} \quad (16)$$

$$4H_2O \rightleftharpoons 4H^+ + 4OH^- \quad (17)$$

Reaction at cathode

$$Cu^{2+} + 2e = Cu \quad (18)$$

$$2H^+ + 2e = H_2 \quad (19)$$

The net cathodic reaction is

$$Cu^{2+} + 2H^+ + 4e = Cu + H_2 \quad (20)$$

Reaction at anode

$$4OH^- = 2O + 2H_2O + 4e \quad (21)$$

$$2O = O_2 \quad (22)$$

The net cell reaction is:

$$Cu^{2+} + 2H^+ + 4H_2O = Cu + H_2 + O_2 + 2H_2O \quad (23)$$

Another process was reported by Pedro et al. 2014 to optimized parameters such as current density (2600 A/m^2), pulse bed time (60 s), add concentration (100 mg/L) for copper electrowinning from synthetic copper sulfate solution using a pulsed bed electrode obtained 100% current efficiency and 1.7 KWh/kg energy consumption. These values are better than those found for flat plate electrodes [162]. In continuation to above, Veglio et al. 2003 also reported for recovery of valuable metals (94-99 % of the initial content of Cu and Ni) at the cathode from electronic and galvanic industrial wastes by leaching and electrowinning techniques. Energy consumption was 2.13 and 4.43 kWh/kg for the electrowinning of copper and nickel metal respectively. Metal deposits were adherent to cathode, being of good morphology, exceptional quality and purity [163].

Researchers were also reported that acid mist generated during final stages of hydrometallurgical metal refining process including the electrowinning of copper. During electrowinning of copper, a direct electrical current is passed between an anode and a cathode that are submersed in a copper-rich solution. At the inert anode, water molecules are electrolysed and oxygen bubbles are produced on the surface of the anode. These oxygen bubbles grow and ultimately detach from the surface and rise in the bulk of the solution. These bubbles burst at the free surface of the solution and produce highly acidic droplets; of which the fine ones becomes airborne and form an acid mist throughout the tank house of the electrowinning plant. Acid mist is highly corrosive and results in the corrosion of cathode plates and anode's hanger bar. It also poses a serious health hazard and causes extreme discomfort to the skin, eyes, etc [164].

Effort were also made to obtained copper metal sheet as against twice that amount for conventional practice [165]. Furthermore Bharucha et al. 1982 succeeded in designing a novel graphite anode for use in copper electrowinning [166]. A mixture of air and 12–15% SO_2 was sparged through a porous graphite anode. 92% Cu was recovered from acid mine drainage by electrowinning technique and the specific energy consumption was approximately 7 kWh/kg of deposited copper was further reported [167].

3.4. Conclusions

Several recycle technologies were reviewed in this thesis. From the review, it could be said that, PCBs recycling process usually included different processes such as physical beneficiation, pyrolysis, hydrometallurgical. Physical beneficiation involved a preliminary step where size reduction of the waste was performed followed by a step where metallic and non-metallic fractions were separated and collected for further management. Materials were also recovered by pyrolysis process, while metal fraction could be treated by hydrometallurgical route.

- After the literature review, it was observed that the pyrolysis of waste PCBs was not carried out in low temperature under different atmosphere such as vaccum, nitrogen, air etc.
- TG-DTA studies have been reported in the literature on the pyrolysis of WPCBs in an inert atmosphere. But, these studies have used very minute quantities of E-waste, about a few milligrams. In industrial operation, size reduction to such fine levels will not be cost-effective because of a large amount of energy required for comminution. The kinetics of mass transfer between the gas and solid phases will be different in the two regimes, on milligram scale and on industrial scale. The results obtained from TG-DTA could be reproduced on a large scale of pyrolysis.
- Investigations must be carried out on large sample sizes (in terms of mass) to understand the fundamental features of the pyrolysis under inert atmosphere in order to optimize the process and exploit it on commercial scale.
- In order to optimize the process conditions with respect to temperature and time of holding, systematic studies have to be carried out in the laboratory to compare the pyrolysis in inert gas with respect to that in air, using samples of large mass. There is little information available in literature on investigations of this kind.
- Various efforts have been made to break the encapsulation by using organic swelling, physical beneficiation and pyrolysis. Physical beneficiation and organic swelling process are energy and cost intensive respectively. However, pyrolysis is low energy consuming technique and produces marketable product LD-oil (low-density oil). After pyrolysis of PCBs, it becomes brittle and easy to liberate and make leaching reaction faster even with low acid concentration. This novel

technique separates each and every layer which enables the acid to leach out metals almost completely.

- Based on the review made on the leaching process of WPCBs containing copper, lead, nickel etc., the following points may be highlighted. These materials used for recovery of metals or sometimes disposed off as landfill. In order to recover metals, the hydrometallurgical processes have been considered which are more eco-friendly and produced residues suitable for safe disposal as metals could be selectively dissolved in suitable lixiviants. The different lixiviants viz. sulphuric acid, nitric acid, hydrochloric acid and other medium have been used on bench scale/pilot scale. It is observed that for the recovery of metals (Cu, Ni & Pb) nitric acid is good leachant due to its oxidizing properties as compare to sulfuric acid and hydrochloric acid. In nitric acid, metals were recovered by atmospheric leaching. But in case of sulfuric acid metals (Cu, Ni & Pb) were recovered by pressure leaching and presence of oxidizing agent also such as hydrogen peroxide etc. The leach solution so obtained during leaching could be used for metal recovery by solvent-extraction, ion-exchange, cementation processes. The metal or salt could be produced be produced from purified solution by electrowinning or crystallization.
- Many of the authors have reported for extraction of acid from leach solution. For extraction of sulfuric acid using TEHA, Alamine 336, D2EHPA, PC 88A, Cyanex 302, Cyanex 923 by solvent extraction techniques were reported. Extraction of nitric acid using TBP, TODGA, CMPO etc. from leach solution were reported. Extraction of hydrochloric acid were reported from leach solution using TOA, Alamine 336, Alamine 308 and TEHA organics as an extractant. Depending on the concentration of acid present in the aqueous feed solution, suitable organic solvent could be used for the selective extraction of acid.
- Most of the authors have reported for extraction of copper and nickel from sulphate and chloride leach liquor in which it is observed that LIX reagents (84, 84-IC, 984, 664 etc.) were used as an extractant. Few studies were reported for the extraction of copper and nickel from nitrate leach liquor in which most of the authors have reported for the extraction of copper and nickel from leach liquor

using LIX 984 organic respectively. Extraction of copper and nickel from other medium such as ammonical medium etc. were also reported. Depending on the concentration, acidity and constituents present in the aqueous feed solution, suitable organic solvent could be used for the selective extraction and separation of metals (copper & nickel). The solvent-extraction of metal has potential to treat the complex nitrate, sulfate and chloride leach solution obtained from materials WPCBs or others.

- Recovery of lead from leach solution by cementation process using Ni, Al and iron disc were reported. Authors have reported the copper electrowinning from sulfate solution at different parameters such as concentration, cathode current density, time, temperature etc.

After literature review, it is noticed that combined process of pyrolysis-physical beneficiation-leaching-solvent extraction-electrowinning-cementation for the recovery of metals from waste PCBs is not reported yet. Present thesis work reports a novel process flow sheet comprises of pyro-hydro hybrid metallurgical process for the recovery of metals such as copper, lead and nickel from pyrolysed PCBs. The systematic scientific studies have been carried out in this thesis work for the recovery of metals from the pyrolysed PCBs left after pyrolysis. The developed process is cleaner and environmental with zero waste generation concepts and has potential to be commercialized after validation on pilot scale trials.

EXPERIMETAL STUDIES

CHAPTER -4

PYROLYSIS (PRE-TREATMENT) OF WASTE PRINTED CIRCUIT BOARDS (WPCBS)

\

CHAPTER-4

PRE-TREATMENT (PYROLYSIS) OF WASTE PRINTED CIRCUIT BOARDS (WPCBS)

4.1. Introduction

PCBs, especially of computers are the most idiosyncratic for further utilization as it incorporate noteworthy quantity of metals viz. Pb, Fe, Cu, Ni, etc, some of which are lethal to life and all of which are valuable resources. But their heterogeneous mixture makes the recycling of these scraps/wastes difficult. Waste PCBs are removed from electronic devices during the dismantling phase and recovery of metals from waste printed circuit board (PCB) may contribute to reduce the environmental impacts caused by the extraction of high-valued and/or highly toxic materials from nature. The PCBs encapsulated with epoxy resin hinders the leaching reaction due to restrain of surface contact [1]. Various efforts have been made to break the encapsulation by using organic swelling, physical beneficiation and pyrolysis [2-4]. Physical beneficiation and organic swelling process are energy and cost intensive respectively. However, treatment of PCBs after pyrolysis is comparatively low acid consuming technique. After pyrolysis, plastic and other volatile compounds are liberated easily from PCBs and thus, make leaching reaction faster even with low acid concentration.

The process and reactor design used in industrial pyrolysis operations are far from optimal. Controlled pyrolysis under suitable atmospheres can help in efficient recovery of the metals and organic chemicals that can be recycled. An oxidising atmosphere can lead to the oxidation of the metals in the WPCBs which can influence the economics of the subsequent recovery of the metals using hydrometallurgical routes. Practically no attempt has been made by investigators to understand the early stages of pyrolysis during which the oxidation reactions can be prominent though considerable literature is available on the recovery and the nature of organic chemicals produced. The influence of the flow of inert gas during pyrolysis on the recovery of volatile organic chemicals is yet to be explored though this phenomenon it has a large potential to enhance the rate of recovery and reduce the energy consumption in the process. It is crucial to study the pyrolysis of waste under an inert atmosphere and compare it with burning in air (a process extensively used

in industrial treatment of E-waste to evaluate the effectiveness of the process of pyrolysis under inert atmosphere.

TG-DTA studies have been reported in literature on the pyrolysis of WPCBs in inert atmosphere. But, these studies have used very minute quantities of E-waste, about a few milligrams. In industrial operation, size reduction to such fine levels will not be cost-effective because of the large amount of energy required for comminution. The kinetics of mass transfer between the gas and solid phases will be different in the two regimes, on milligram scale and on industrial scale. The results obtained from TG-DTA cannot be reproduced on larger scale of pyrolysis. Investigations must be carried out on large amount (in terms of mass) to understand the fundamental features of the pyrolysis under inert atmosphere in order to optimize the process and exploit it on commercial scale.

Therefore, in the present study, TGA (in milligram) was used to understand the nature of mass change during the early stages of pyrolysis under different atmospheres. Experiments were carried out to evaluate the process of pyrolysis under argon with large amount, about 5 grams, and compare it with burning in air. The large amount will help in predicting the performance of the process under real conditions with a high level of confidence. The studies show that pyrolysis under flowing inert gas enhances the efficiency of pyrolysis significantly. The results of the study are discussed in the sections that follow:

4.2. Experimental study

Thermo-gravimetry apparatus (Linseis STA PT 1600, Germany) was used for TGA of waste printed circuit boards (PCBs). About 30 mg of sample of size approx 0.002-0.003 m (2-3 mm) taken in an alumina crucible was used in each run. The temperature of the furnace was set at 673K (400°C) and heating rate of 10K/min (10°C/min) was employed. The desired atmosphere was maintained in the TGA chamber by passing oxygen, air or argon through the chamber. Printed circuit boards were collected from discarded computers. The major components of the PCBs were copper, epoxy resin and glass fibre. Minor electronic components of the PCBs such as batteries, capacitors etc. were removed by IR heating. The chemical analysis of the processed waste printed circuit boards (WPCBs) is given in Table 1.

Table 1 Chemical analysis of depopulated WPCBs.

Metals	Mass (%)
Cu	28.22
Ni	0.23
Fe	0.66
Al	2.10
Pb	1.45
Sn	----
Sb	0.032
Cr	0.012
W	0.379
Si	0.33
Mo	0.054
C	17.4
Ca	1.47
LOI	22.91
Others	Balance

For pyrolysis of WPCBs (about 5 g) on laboratory-scale, the depopulated PCBs were crushed into small pieces in scutter crusher, mills etc. and were further reduced to size using a manual cutter. Experiments under isothermal conditions were carried out in a tubular furnace. About 5 g of the WPCBs was taken in a quartz capsule measuring 0.03 m (30 mm) length and 0.02 m (20 mm) diameter with two perforations each about 0.007 m (7 mm) size on the cylindrical surface along the same line. These served as ports for charging the capsule with the electronic waste for pyrolysis. The temperature of the capsule was measured using a K-type thermocouple placed adjacent to the capsule. The initial and final mass of the experimental samples were measured correct to 0.1 mg using an analytical balance. Temperature was measured within an error limit of ±2 K. Argon from a cylinder was passed through the furnace when pyrolysis was carried out under argon atmosphere. A schematic of the apparatus used in the experiments is given in Fig. 1.

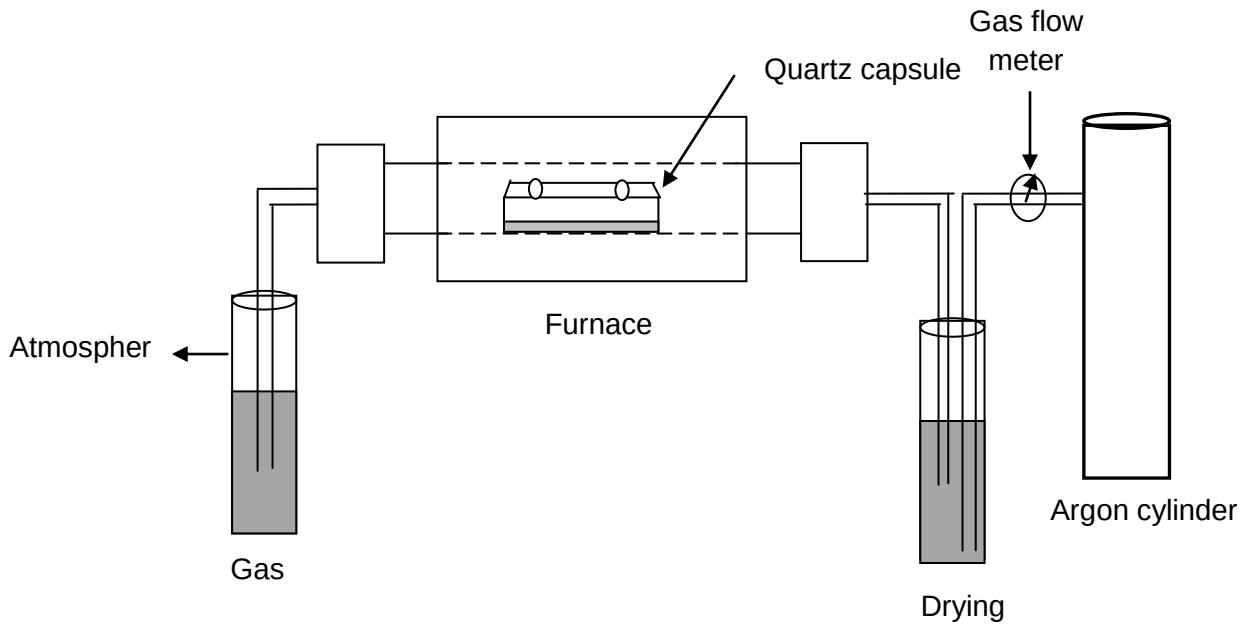


Fig. 1 Experimental apparatus for pyrolysis under argon atmosphere.

The capsule was maintained at the desired temperature for the required period of time. When thermal decomposition was carried out under air, the two ends of the furnace were kept open to atmosphere. At the end of the holding period, the capsule was drawn quickly out of the furnace and cooled in air. The mass of the sample along with that of the capsule was recorded at the beginning and at the end of the experiment. The change in mass of the sample, as a percentage of the initial mass of the sample was used for estimating the degree of pyrolysis under various conditions.

4.3. Results and discussion

4.3.1. Thermo-gravimetry studies

The result presented in Fig. 2 gives the mass change observed in the TGA runs under different atmospheres. In the case of argon atmosphere, there was a continuous decrease in the mass of the sample. This indicates that volatile matter is being removed from the sample during all stages of heating. There was no gain in mass since the atmosphere was inert. In the case of air and oxygen atmospheres, there was an increase in the mass of the sample during the early stages of heating in TG-DTA furnace, until the temperature reached about 523K (250°C). After this temperature, there was a rapid drop (about 0.5%/K) in the mass of the sample. A similar rapid decrease in the mass (0.93%/K) was observed when argon was used as the chamber atmosphere, also. It was found that the

maximum mass loss in the case of samples heated in oxidizing atmospheres was less than obtained when heated in argon, after taking into consideration the gain in mass due to oxidation in the case of the two oxidising atmospheres. The mass loss was occurring in the case of the sample heated in air is about 30% less than that recorded for the sample heated in argon, taking into consideration the maximum mass loss recorded at the end of the rapid mass loss period (around 573K (300°C)). This limit would represent the recovery of organic compounds as volatile matter during pyrolysis. The experiments show that 30% less of volatile organics would be collected during heating in air compared to pyrolysis in argon atmosphere.

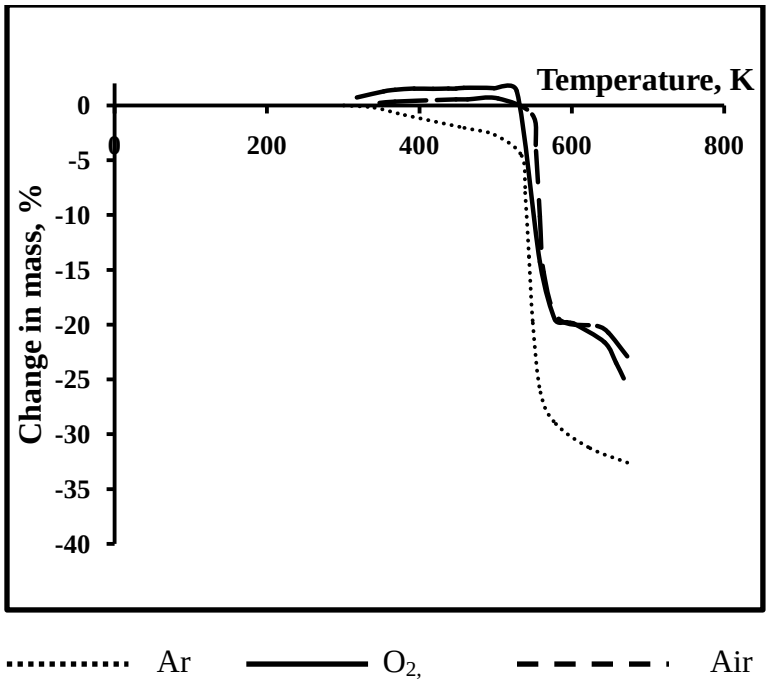


Fig. 2 Thermo-gravimetry of WPCBs heated in argon, oxygen and air [Sample (WPCBs) -30 mg].

To further illustrate the nature of pyrolysis under different atmospheres, the percentage change in mass of the sample under argon atmosphere and under oxidising atmospheres are shown as function of temperature in Fig. 3 & 4, respectively. The mass change occurring until the period when the mass loss was rapid is represented in the two figures.

It is seen from Fig. 2 that the rapid mass loss occurs at about 523K (250°C) in all the samples, irrespective of the atmosphere. This temperature slightly shifts to higher values

in the case of the oxidizing atmospheres compared to argon atmosphere. It was seen that the mass decreases continuously in the case of argon atmosphere. In the case of the oxidising atmospheres, there was a gain in mass until the mass loss period starts. The change in mass with temperature is strikingly similar in the case of the two oxidizing atmospheres. In the case of heating in oxygen, the mass change exhibits an initial linear region where the mass change is approximately linear with respect to temperature. This was followed by a region where the gain in mass is constant, in the temperature range 373-448K (100-175°C). This was a region where the gain in the mass of the sample due to oxidation is compensated by a loss in mass due to the release of a volatile substance. Through an extrapolation of the linear region in mass change to higher temperatures (up to 548 K (275°C)), the total mass loss due to the release of the volatile matter can be estimated. The estimated mass loss was about 1%. The additional volatile matter being released in the temperature range 373-448K (100-175°C) is moisture adsorbed in the WPCBs. It may be noted that the WPCBs were reported to contain about 0.5-0.9 mass% moisture [58, 168]. The mass gain increases again in the temperature ranges 448-473K (175-200°C) after which the mass gain decreases. The temperature at the end of this period was close to the boiling point of phenol (454.7K) [169] which was known to be the predominant component of the volatile organic matter present in WPCBs [170]. The mass gain in the sample decreases with the onset of the boiling of phenol and the rapid removal of the vapours of this compound. A similar behavior is exhibited by the sample heated in air. Figure 2 also contains a TGA profile for a case where there was no gain in mass on heating. In this case, it is apparent that the pieces of WPCB placed in the TGA apparatus contained no metallic component that could be oxidized. However, as discussed in the following sections, the oxidation of metal did not in fluence the mass loss due to the removal of volatile matter. It is noted that the total change in mass of the sample was the same as in the case of the sample where there was an initial gain in mass, after accounting for the mass gain in the early stages of heating.

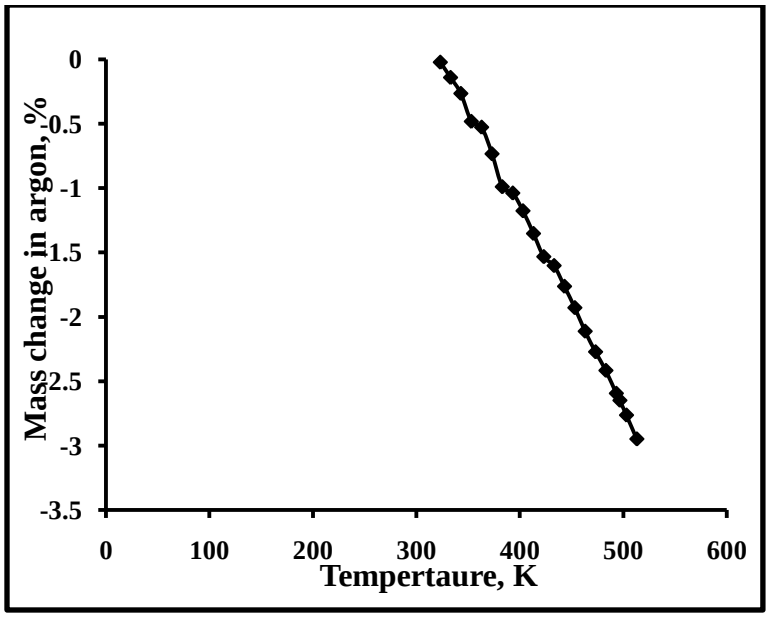


Fig. 3 Percentage mass change in argon atmosphere [Sample (WPCBs) -30 mg].

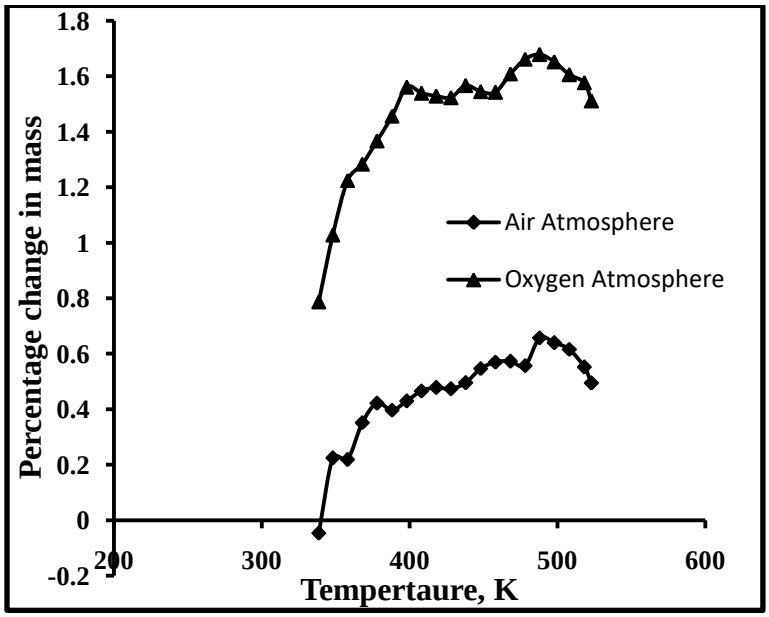


Fig. 4 Percentage mass change in oxidising atmospheres [Sample (WPCBs) -30 mg].

Assuming that the rate of removal of volatile organic matter from the WPCBs in the oxidizing atmospheres would be the same as that observed in argon atmosphere, the effective gain in the mass of the sample heated in the oxidizing atmospheres was estimated after accounting for the mass loss due to the removal of volatile organic matter.

The effective mass change was expressed as a percentage of the original mass as a function of temperature in Fig. 5. It was found that the rate of oxidation follows a linear law which was common for the oxidation of metals during the first few minutes of oxidation at low temperatures [171]. The vapourisation of volatile matter from the WPCB followed a logarithmic law [58] in the temperature range 373-493K (100-220°C) as demonstrated in Fig. 6. From this figure, the activation energy and pre-exponential factors were estimated to be 25.27 kJ/mol and 1.13×10^{3} sec^{-1} respectively. Percentage change in mass using different heating rate in argon atmosphere was shown in the Fig. 7. From the figure, it noticed that mass loss was higher when using heating rate 10K/min (10°C/min) as compare to 5K/min (5°C/min) under argon atmosphere.

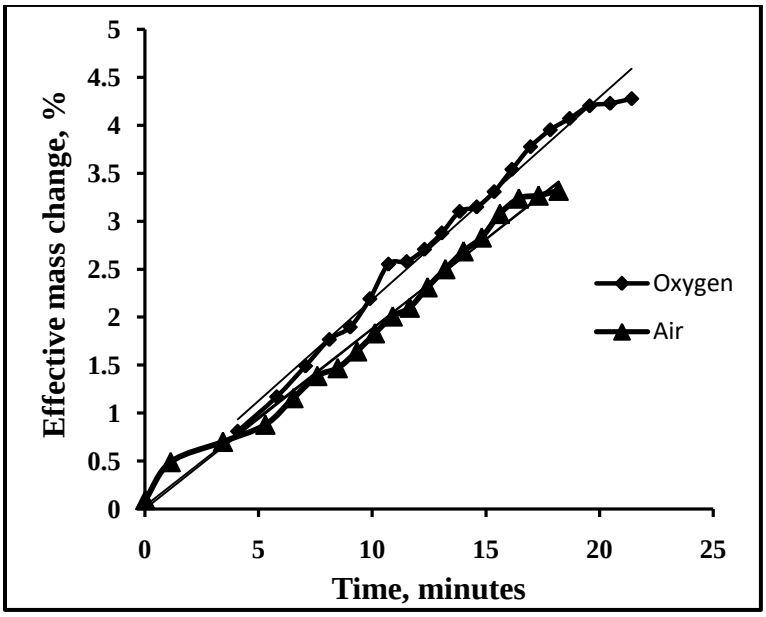


Fig. 5 Kinetics of oxidation of metals in WPCBs [Sample (WPCBs) -30 mg].

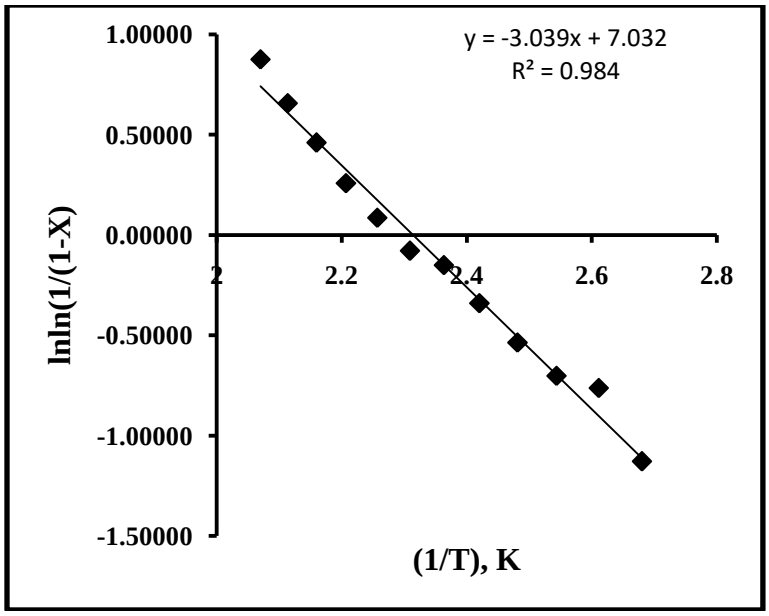


Fig. 6 Kinetics of vapourization of volatile matter in WPCBs [Sample (WPCBs) -30 mg].

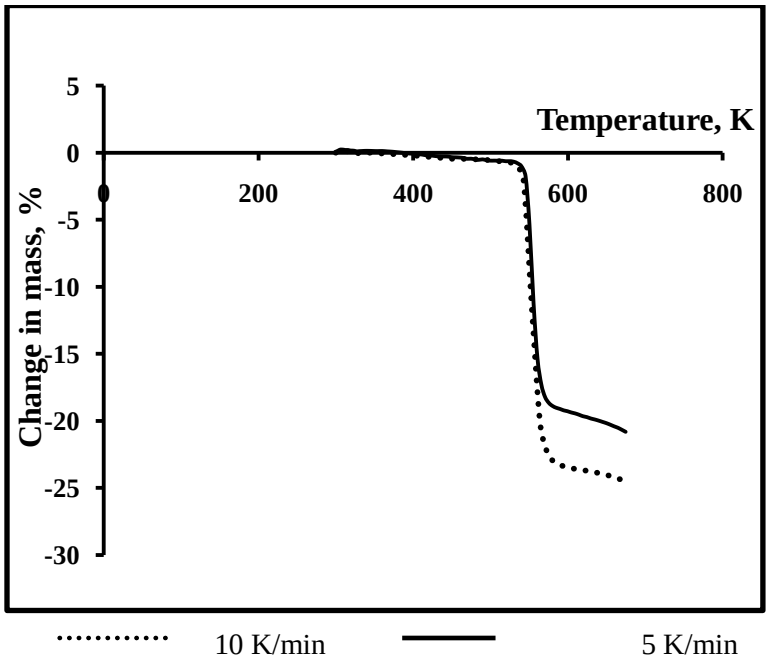


Fig. 7 Thermo-gravimetry of WPCBs at different heating rates.

4.3.2. Pyrolysis on laboratory-scale

Table 2 documents the mass loss in air and argon atmospheres when the thermal decomposition was carried out in a tubular furnace as discussed above. Thermo-gravimetry studies showed that there was a threshold temperature at which a rapid loss in

mass of the sample started. The zone of rapid mass loss was completed within 30K of the threshold temperature, during non-isothermal heating. After the completion of the rapid mass loss, there was practically no change in the mass of the sample on further heating. A major objective of the experimental studies on the laboratory-scale sample was to estimate the threshold temperature for the rapid mass loss on large amount of sample. It was found that significant mass loss occurred in air only when the temperature was above 623K (350°C). This is contrary to the observations under TG where it was found that mass loss started at 583K (310°C) and the process was complete at 623K (350°C). In argon atmosphere, significant mass loss was occurred at 548K (275°C). This temperature was closer to the temperature of the start of mass loss in argon atmosphere in TG experiments. In both cases, that of heating in air and argon, the total mass loss recorded after 4 minutes of holding at the temperature of pyrolysis was less than that recorded in TG experiments. This time interval corresponds to the time interval for which the sample was held in the temperature regime of maximum mass loss in the TG experiments. It is obvious that large mass of the WPCBs pieces and the closer packing of these have retarded the kinetics of mass transfer of vapors released from the particles during heating. The continuous flow of argon has helped in removing the vapors rapidly from the surface of the particles leading to a faster rate of pyrolysis at a lower temperature.

Table 2 Pyrolysis of WPCBs in tubular furnace.

S.No.	Atmosphere	Mass of WPCBs (initial), g	Temp. (K)	Holding Time (minutes)	Change in mass (%)
1	Air	9.99	548	4	1.1
2	Air	4.956	579	4	2.3
3	Air	10.0	600	4	2.26
4	Air	4.741	627	6	20
5	Air	10	668	11	22.66
6	Air	15	573	11	18.2
7	Air	10.5	733	4	23.8
8	Argon	5.352	548	4	20.43
9	Argon	4.94	596	4	22.1
10	Argon	5.033	598	4	21.76
11	Argon	15	573	4	18.5

The data presented in Table 2 were representative data of a number of experiments carried out to establish that the threshold temperature is influenced by the flow of inert gas through the furnace tube. When, about, 5 g of sample was heated in air at 579K (306°C), the total mass loss was 2.3%. For the same amount of sample, a mass loss of 20.43% was recorded at 548K (275°C), when the sample was heated in a flowing stream of argon. A similar level of mass loss could be obtained when heating in air at 627K (354°C) when heated for 6 minutes. These data help to illustrate that heating in a flowing stream of argon would reduce the pyrolysis temperature and enhance the rate of pyrolysis also. On increasing the sample amount to about 10 g, a mass loss of about 20% similar to that obtained for a 5 g sample at 627K (354°C) could be obtained only at a temperature of 668K (395°C) and 11 minutes of holding. When the temperature was increased to 733K (460°C), similar mass loss was registered after a holding time of 4 minutes. When, 15 g sample was heated in argon atmosphere at 573K (300°C), the total mass loss was 18.5%. A similar level of mass loss could be obtained when heating in air at 573K (300°C), when heated for 11 minutes.

A heat transfer analysis was carried out to estimate the temperature of the WPCB pieces introduced into the furnace. This was necessary since the time of holding the sample was short, about 4 minutes, on average and the temperature of the furnace was also low, about 600K (327°C), on average. Heisler charts [172] were used for estimating the temperature of the WPCB pieces in contact with the furnace tube maintained at a given temperature, after a given period of contact time. The thermo-physical properties of quartz (which was the material holding the WPCB pieces) such as thermal diffusivity (1.4×10^{-6} m^2/sec) and thermal conductivity (1.4 W/m°C) were obtained from published sources [173-174]. Fourier number and Biot number were estimated from these properties and the thickness of the quartz capsule, taken to be 2 mm. From these dimensionless numbers and the Heisler's charts, the ratio (T_0-T_∞/T_i-T_∞) was inferred. Here, T_0 is the temperature of the inner surface of the quartz capsule after a time interval of "t" seconds; T_∞ is the temperature of the furnace and T_i is the initial temperature of the quartz capsule. For a furnace temperature of 573K, it was found that the inner surface of the capsule reached a temperature of 553K (280°C) within 60 seconds. This is above the boiling point of phenol as discussed above. The heat transfer restrictions present in the case of laboratory-

scale experiments would explain why a higher threshold temperature was required in this case to remove the volatile matter compared to the TG experiments. Flow of argon would enhance heat transfer in addition to removing the vapours from the reaction site contributing to a more efficient pyrolysis compared to heating in still air.

4.3.3. Mathematical model-mass transfer

The rate of mass transfer from the WPCBs (consequently, the rate of mass loss) was modeled. Several investigators [4, 60, 170 and 175] have shown that phenol and derivatives of phenol were the major organic compounds released during the pyrolysis of PCBs. The rate of removal of phenol from the WPCBs would be controlled by the kinetics of the following processes:

(a) rate of evaporation of phenol from the surface
(b) transport of the vapours of phenol away from the surface of the WPCB.

Experiments using the TG apparatus have established that the rate of mass loss from the WPCBs was quite rapid after a threshold temperature was reached.

Experiments reported in literature have shown that the thermal decomposition of epoxy resins which form the organic base of the WPCBs is controlled by the kinetics of mass transfer [176]. It has been discussed also above that heat transfer was rapid in the system and was not the rate-controlling step. Volatile compounds were formed during the decomposition of the resin which was the major component of the PCB. The vapours released at the surface of the pieces have to diffuse through the surrounding atmosphere before being removed completely from the reaction site. Apart from the low diffusivity of the vapour, close packing of the WPCB pieces can hinder the transport of the vapour away from the reaction site. This step was expected to be slower than the rate of evaporation and, therefore, rate-controlling. As a corollary, it can be expected that a flowing stream of gas can help in sweeping the vapours away from the reaction site and help in accelerating the process of removal of the organic compound from the WPCB pieces. Therefore, the mathematical model of mass transfer from the surface of the PCBs was modeled on the following premises:

(1) Phenol was the organic compound produced during the process of pyrolysis.

(2) Vapors of phenol were produced at saturation level at the surface of the pieces of WPCBs heated in the capsules. (boiling point of phenol is 454.7K (181.7°C).

(3) These vapors were removed from the surface by the flowing stream of gas.

The flux of vapour transferred per unit time per unit area of cross-section from the surface of the particles is given by

$$J = k_m(C^0 - C^b) \quad (24)$$

Where, J is the flux, k_m, the mass transfer coefficient, C^0, the concentration of the vapor at the surface of the particle and C^b, the concentration in the bulk of the flowing gas stream. The concentration of vapor at the surface was estimated using standard procedure [177]. The concentration in the bulk was assumed to be zero. The mass transfer coefficient is related to the Sherwood number through the following expression [177]:

$$Sh = k_m.D/L \quad (25)$$

Where Sh is the Sherwood number; D, the diffusivity of phenol and L, the characteristic length of the system from which mass transfer occurs. The diffusivity of phenol in air was taken to be 0.00082 m^2/s [178]. This was assumed to be valid for diffusion through argon also. The pieces of WPCBs placed in the quartz capsule formed a monolayer about 0.002 m (0.2 cm) in thickness. Hence, the characteristic length of the system was taken to be 0.002 m (0.2 cm). The capsule was filled to about 11% of the volume, by the pieces of WPCB. The Sherwood number can be estimated from the Reynold's number and the Schmidt number through the following expression [179]:

$$Sh = 0.664\ Re^{1/2} Sc^{1/3} \quad (26)$$

Where Re is the Reynold's number and Sc, the Schmidt number. The Reynold's number and the Schmidt number are given by the following expressions [180]:

$$Re = (d_0.U_{av}.\rho)/(\eta) \quad (27)$$

Where d_0 is the characteristic length of the system; U_{av}, the superficial velocity of the gas stream; ρ, the density of the vapour and η, the viscosity. The viscosity was estimated using standard procedure [180].

$$U_{av} = Q/A \quad (28)$$

Q (m^3/s) is the flow rate of the stream of argon gas and A, the cross-sectional area of the furnace tube through which the gas flows. The diameter of this tube was measured to be 0.06 m (6 cm).

$$Sc = (\eta/\rho.D) \quad (29)$$

"D" is the diffusivity of phenol in air. From expressions 1-6 above, the mass transfer coefficient was estimated. Following this, the flux was computed from expression (1). The system was assumed to be represented by a flat plate whose length was equal to the length of the quartz capsule in which the material was taken, i.e. 0.03 m (3 cm).

From this, the surface area over which the vapor is removed was estimated. The total amount of vapor removed in a period of 4 minutes was then estimated. The quantity of vapor removed will depend upon the flow rate of the inert gas. Fig. 8 represents the mass of vapor removed as a function of flow rate of gas. There is good agreement between the value predicted by the model and that observed experimentally. For example, the flow rate of argon during the experiments was measured to be 4×10^{-4} m^3/minute. The mass transferred from the surface predicted by the model, at this flow rate is 1.77 g. This is in good agreement with that observed (Table 2).

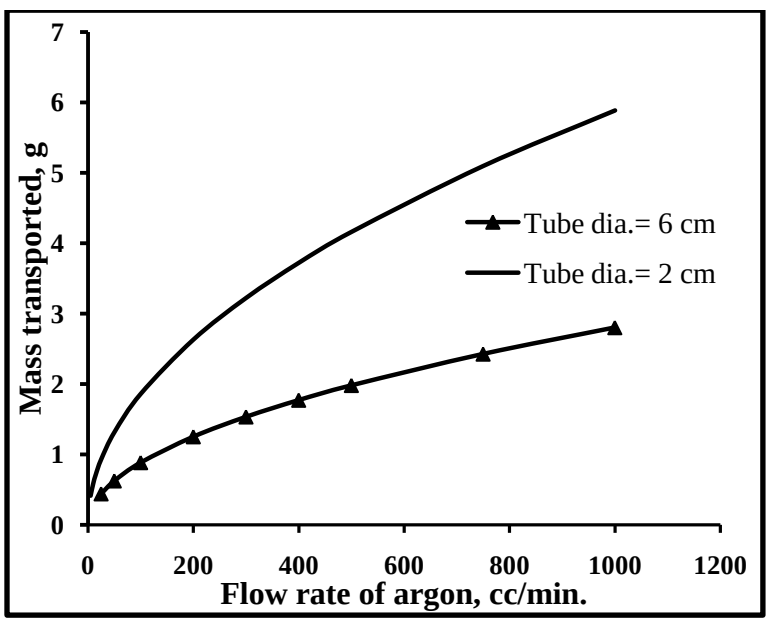


Fig. 8 Influence of gas flow rate and system geometry on rate of pyrolysis [Sample (WPCBs) -5 g].

Similarly, it can be inferred from Fig. 8 that as the flow rate approached 0 litres/minute, the mass of vapor removed will decrease to less than 0.2 g. This is also in good agreement with the observed mass loss in air where there was no flow of gas and the experiments were carried out in still air. The model has assumed mass transfer to occur

from the surface of a flat plate. This an approximation of the system where the mass transfer occurs from the surface of a large number of small pieces packed in a thin bed. Also, the velocity of the gas stream inside the quartz capsule was taken to be the same as in the furnace tube. However, the velocity of gas in the quartz capsule will be less than that in the furnace tube. These approximations lead to a higher estimated value for mass transfer. The model shows that the rate of pyrolysis will increase rapidly with increase in the flow rate of the inert gas. The model can be used for devising methods for enhancing the rate of pyrolysis. For example, Fig. 8 also shows the amount of vapour removed when the cross-sectional area of the furnace tube was changed to 0.02 m. There is significant increase in the rate of mass loss for the same flow rate of argon. It would be appreciated that this model considers transfer of organic vapour from the surface of the WPCB pieces by a flowing stream of inert gas. It is assumed that the vapour does not react with the stream of gas and no new species are formed. As discussed in this section on the modeling of mass transfer in the system, it was estimated that the flux of vapour transferred from the surface of the WPCB pieces was 2×10^{-3} $kg.cm^{-2}.s^{-1}$. Hence, it could be inferred that the process was controlled by the kinetics of mass transfer of vapour from the surface of the WPCB pieces. Pyrolysis of WPCBs was also performed in vacuum atmosphere in order to compare it with the same process done in argon atmosphere.

4.3.4. Vacuum pyrolysis of waste printed circuit boards (WPCBs)

Depopulated PCBs were crushed and subjected to pyrolysis under vacuum atmosphere. During pyrolysis the hazardous gases were liberated, which get condensed in full proof system. Low density oil was generated and prevents the environment with hazardous effect. Experiments were carried out at different temperature in order to observe the mass loss due to the decomposition of the organic content. Capsule containing almost 15 g crushed PCBs were placed in a temperature controlled furnace fitted with a drying tube, vacuum pump and a gas collector. The furnace containing the sample was allowed to reach the desired temperature which required ~1 hr time and then left for few min. After pyrolysis, the solid residue of PCBs, termed here as poly-cracked PCBs, were collected from the furnace and its loss in mass percentage was calculated from the solid yields using the formula as below:

$$\text{Mass Loss (wt\%)} = [(X_{bp}-X_{ap})/ X_{bp}] \times 100 \quad (30)$$

Where, X_{bp} is the weight of PCBs sample before pyrolysis and X_{ap} is the weight of PCBs sample after pyrolysis. To investigate the effect of temperature on weight loss of PCBs, studies were conducted at various temperatures ranging from 523 to 873K (250°C to 600°C). It was observed that at a particular time of 4 min (after reaching the desired temperature), 5.60 and 14.63 wt% of PCB is lost at 523K (250°C) and 573K (300°C), respectively. However, higher temperatures do not have much influence on the amount of substances removed from the sample. The process is very fast and for each temperature almost similar weight loss was observed after conducting three repeated set of experiments under same conditions (Table 3). Thus, weight loss of ~15% was taken to be optimum for pyrolysis of PCBs at 573K (300°C) for 4 min.

Table 3 Effect of temperature on vacuum pyrolysis of waste printed circuit boards (WPCBs) for 4 min.

Temperature (K)	**Exp-1 (weight %)**	**Exp-II (weight %)**	**Exp-III (weight %)**	**Average (weight %)**
523	5.59	5.62	5.65	5.6
573	14.67	14.63	14.61	14.63
673	15.1	15.07	14.81	14.9
873	20.29	20.38	20.39	20.4

When 15 g of sample was heated in vacuum atmosphere at 573K (300°C), the total mass loss estimated was 15% approximately. When the same quantity of sample was heated in argon atmosphere at 573K (300°C), the total mass loss reported was 18.5%. So the total mass loss was higher in argon compared to that in vacuum atmosphere. The pyrolysed sample obtained under this condition was further physically beneficiated to obtain low and high metal concentrate for recovery of metals.

4.3.5. Characterisation of oil

Experiments were conducted in the laboratory to pyrolyse the WPCB under vacuum and in flowing stream of argon. About 10% of the mass of the WPCB could be recovered as oil in these experiments. The photograph of the oil (Fig. 9) which was characterized using FT-IR (Fig. 10) and found to contain radicals of O-H, C-C, C-H and C-O. The degree of

pyrolysis was not significantly enhanced on increasing the pyrolysis temperature from 300°C to 400°C. Recovery of oil and degree of pyrolysis were higher in argon stream compared to pyrolysis under vacuum. Computation of the energy requirement of the process showed that there is a huge potential for converting this process into a viable technology for the recovery of oil rich in phenol and its derivatives on industrial scale.

Fig. 9. Photograph of oil collected during pyrolysis.

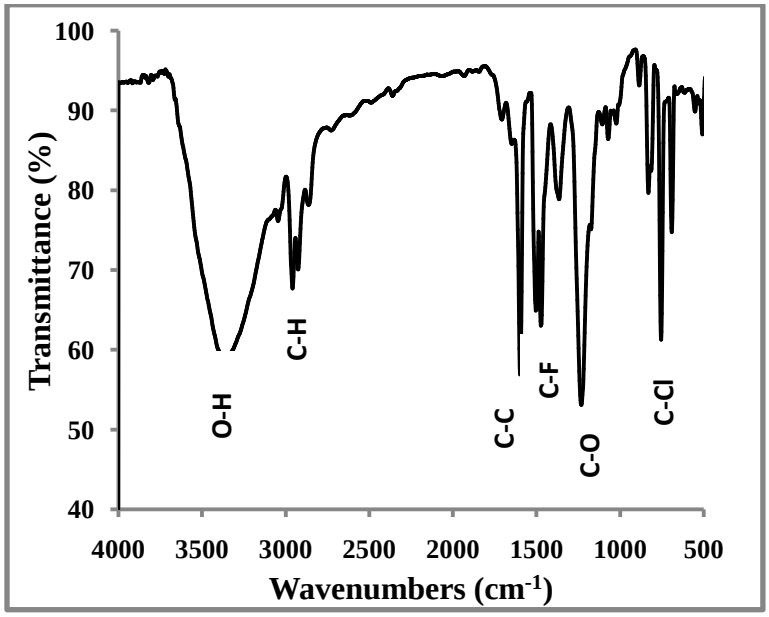


Fig. 10 FTIR of oil collected during pyrolysis.

4.4. Conclusion

When WPCBs was heated in an oxidising atmosphere such as air or oxygen, the metallic components in the WPCBs was oxidized. The kinetics of oxidation follows a linear law. The oxidation of metals can affect the subsequent recovery of metallic values after pyrolysis. The recovery of volatile organic chemicals was about 30% less when the

WPCBs were heated in air compared to the recovery in argon atmosphere. When the WPCBs were heated in a flowing stream of gas, the rate of pyrolysis increases significantly. At a flow rate of inert gas of 4×10^{-4} m^3/minute, it was found from experiments that the rate of pyrolysis is about 10 times faster than that in still atmosphere and the temperature of pyrolysis decreases by about 323K (50°C). In other side it was also observed that, the total mass loss was higher in argon atmosphere compared to heating in vacuum atmosphere. Material obtained after pyrolysis of WPCBs under argon and vacuum atmosphere was same but energy consumption was low in case of argon atmosphere. These factors will lead to significant saving in energy required for pyrolysis. The mass transfer has been modeled mathematically. There is good agreement between the predictions of the model and the experimental observations. The model can be successfully exploited to enhance the rate of pyrolysis. This can lead to more efficient operation of the process and a reduction in the cost of pyrolysis. This process demonstrated on laboratory scale is a viable one and can potentially be scaled up for industrial applications. The fumes was also generated during the pyrolysis get condensed to generate marketable LD-oil (low density oil). About 10% of the mass of the WPCB could be recovered as oil during experiments which were conducted in argon and vacuum atmosphere. The oil was characterized using FT-IR and found to contain radicals of O-H, C-C, C-H and C-O.

The pyrolysed PCBs sample obtained under this condition was used for the further set of experiment. These pyrolysed PCBs was initially beneficiated to separate low and high metal concentrate which was further proceed for recovery of metals by hydrometallurgical techniques.

CHAPTER-5

LEACHING OF METALS FROM DIIFERENT METALLIC FRACTIONS (LOW AND HIGH METAL CONCENTRATE) OF POLY-CRACKED (PYROLYSED) PCBs

CHAPTER-5

LEACHING OF METALS FROM LOW AND HIGH METAL CONCENTRATE OF POLY-CRACKED (PYROLYSED) PCBs

5.1. Introduction

Leaching is the removal of a soluble fraction, in the form of a solution, from an insoluble, usually permeable, solid phase with which it is associated. Leaching agents can include water, acid, bases and salt solutions. Oxidation-reduction reactions may also be involved [41]. In metal processing industries leaching has been extensively used to remove metals as soluble salts and is also referred to as a hydrometallurgical process [42]. Pre-treatment processes such as pyrolysis, crushing and grinding are often used on the solid feed material prior to leaching, depending on the proportion of the soluble constituents, and its distribution in the bulk solid. This is often done in order to increase the rate of leaching. When a material is being dissolved from the bulk solid to liquid, the rate of mass transfer from solid surface to the liquid is often the controlling factor.

This work reports a novel process flow sheet which consists of pyro-hydro hybrid metallurgical process for the recovery of metals from poly-cracked (pyrolysed) PCBs. Numerous systematic scientific studies were carried out for the recovery of metals from pyrolysed PCBs which were obtained after pyrolysis. The poly-cracked (pyrolysed) PCBs generated was physically beneficiated for separation of low and high metal concentrate and proceeded for hydrometallurgical treatment for recovery of metals. Various process parameters such as effect of time, temperature, pulp density, etc. were studied to optimize favorable conditions for dissolution of metals from the concentrate.

5.2. Experimental studies

5.2.1. Materials

Printed circuit boards were dismantled from obsolete computers and the small components such as batteries, capacitors, etc. populated on PCBs were removed by IR heating. This resulted in desoldering (by IR heating) of all the populated parts of PCBs. At this temperature, Sn present in solder material got melted due to its low melting point while other metals remained intact in the PCBs sheets. Negligible trace of precious metals such as Au, Ag etc. were expected to be present in depopulated boards. It mainly

contained Cu, Ni, Pb, etc. These depopulated sheets were crushed and processed for pyrolysis. Chemical composition of the pyrolysed PCBs is shown in Table 1. Poly-cracked (pyrolysed) PCBs obtained after pyrolysis were used for experimental purpose and it was comprised of metallic and non-metallic constituents. The poly-cracked PCBs was further beneficiated to separate the pyrolysed epoxies and metallic concentrates. Beneficiated PCBs were screen analyzed to separate low (-10 mesh size) and high (+10 mesh size) metal concentrate which were processed for recovery of metals by leaching process.

Table 1 Chemical composition of poly-cracked (pyrolysed) PCBs.

Metals	**Poly-cracked PCBs (%)**
Cu	39.85
Ni	0.22
Fe	2.58
Pb	0.05
Sn	---
Zn	3.27
LOI	12.44
Others	Balance

5.2.2. Methods

5.2.2.1. Physical beneficiation of poly-cracked (pyrolysed) PCBs

Initially, poly cracked (pyrolysed) PCBs were subjected to comminution using crusher machine (roll crusher and scutter crusher) and mills (ball mill and rod mill) for liberation of associated metals from epoxies/ polymer. Exploratory tests were performed to look into the possibility of effective separation of liberated metals by using scrubbing/washing. After the scrubbing, the sample was further processed for screened analysis to separate (low and high metal concentrate). The separated metallic components were further processed for selective recovery of the metallic constituents in purer form by hydrometallurgical processing.

5.2.2.2. Leaching studies

5.2.2.2.1. Pressure leaching

Leaching studies for the recovery of metals from the fraction of poly-cracked PCBs containing low metallic content (-10 mesh size) were carried out at elevated temperature using autoclave (Parr Instrument Company, USA) in presence of oxygen atmosphere with different sulfuric acid concentration. Samples were put along with the leachants in a particular ratio and heated to a desired temperature for different time interval. Mechanical agitation was also maintained to ignore the mass transfer effect on metal dissolution.

5.2.2.2.2. Atmospheric leaching

Recovery of metals from high metal concentrate (+10 mesh size) of poly-cracked (pyrolysed) PCBs in atmospheric leaching condition was first examined by different acids and then varying the concentration of acids, pulp density and temperature. The leaching of high metal concentrate of poly-cracked PCBs sample was carried out in a temperature controlled closed three necked Pyrex glass reactor fitted with condenser. The acidic leachant was poured in the reactor as per required experimental condition and then solution was heated on a hot plate. Once the desired temperature was attained, the crushed sample was added to the reactor and finally it was mixed using a magnetic stirrer. The metal content of pyrolysed PCBs was analyzed using ICP-OES (VISTA-MPX, CCD Simultaneous ICP-OES make in VARIAN, Australia). Samples taken at different interval were determined using atomic absorption spectrometer (AAS) (Perkin Elmer model, Analyst 200; USA).

5.3. Results and discussion

The poly-cracked (pyrolysed) PCBs obtained after pyrolysis was further put to physical beneficiation process to separate the metallic concentrate from the non-metallic part. Leaching study was carried out to dissolve the metals present in the charged material. Different acidic medium were primarily used to recover maximum amount of metals. Various other parameters were also studied for making this process a suitable route for metal recovery.

5.3.1. Physical beneficiation of the poly-cracked (pyrolysed) of PCBs

Poly-cracked PCBs collected after pyrolysis was now devoid of the organic content and left only with the metallic part, non-metallic part and epoxies. Poly-cracked PCBs contained ~49.02% metallic and ~50.04% non-metallic content. The poly-cracked (pyrolysed) PCBs was subjected to physical beneficiation for the separation of metallic from non-metallic fractions using crushers and mills. Further, the ground poly-cracked PCBs was scrubbed/washed with water without using any additives to enrich the metallic concentrate up to 97.8% and the grade metal enhanced by ~46% using scrubbing. Initially, this sample was pulped in a scrubbing tank followed by mixing of slurry at determined agitation speed. Hydrophobic nonmetallic materials containing plastics, resins, epoxies etc. floated on the surface and were removed continuously. The remaining sink material left at the bottom of the tank mostly contained dense metallic particles which were mixture of several valuable metals. Further, the scrubbed sample was further screened to separate low metal concentrate (-10 mesh i.e. <2 mm size) and high metal concentrate (+10 mesh i.e. >2 mm size). Chemical analysis of high metal concentrate (+10 mesh size) and low metal concentrate (-10 mesh size) of poly-cracked PCBs are shown in Table 2

.**Table 2** Chemical analysis of high metal concentrate (+10 mesh size) and low metal concentrate (-10 mesh size) of poly-cracked PCBs.

Metals	**Poly-cracked PCBs (+10 mesh size) (%)**	**Poly-cracked PCBs (-10 mesh size) (%)**
Cu	86.89	34.26
Fe	1.05	2.45
Ni	0.095	0.43
Pb	0.084	1.11
Zn	0.016	0.36
Others	Balance	Balance

5.3.2. Leaching studies

5.3.2.1. Pressure leaching of low metal concentrate (-10 mesh size) of poly-cracked (pyrolysed) PCBs in sulfuric acid

Rate of dissolution of metal was increased by leaching process at high temperature and pressure. Pressure leaching of poly-cracked PCBs (-10 mesh size i.e, <2mm size) was carried out in different concentration of H_2SO_4 in an autoclave applying 20 bar oxygen, pressure at 150°C for 90 min, keeping pulp density 100 g/L. Fig. 1 shows that percentage leaching of copper is increased from 67.3 to 99.9% with increase in sulfuric acid concentration from 1.0M to 2.4M. Under these experimental condition, 2.4M H_2SO_4 at 150°C using oxygen pressure of 20 bars and pulp density of 100 g/L for 90 min, other metals were also leach out in minor compositions. Leach liquor compositions are Cu-10.76 g/L, Ni-0.38 g/L, Fe-2.55 g/L and Pb-0.07 g/L. This leach liquor was subjected to solvent-extraction for recovery of acid and metals (chapter-6 in section 6.2).

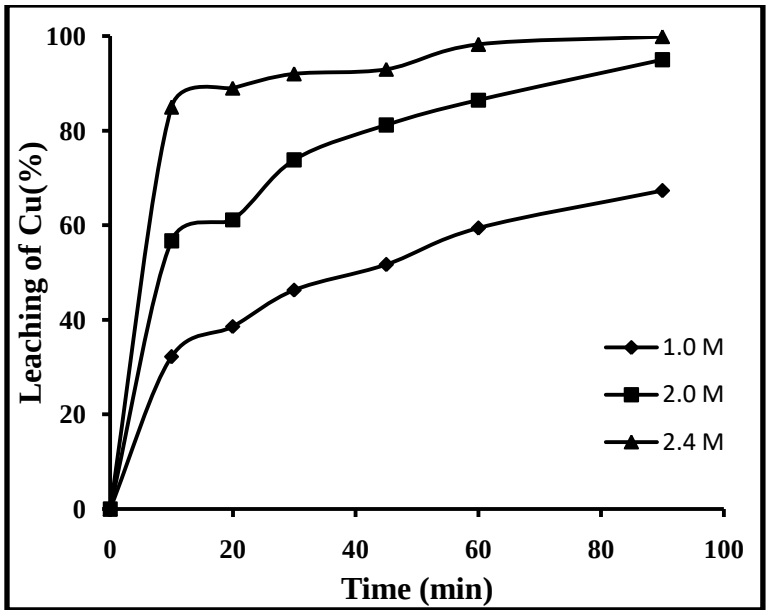


Fig. 1 Pressure leaching of low metal concentrate (-10 mesh size) of pyrolysed PCBs. [Experimental Conditions: Pressure =20 bar, Temperature = 150°C, Pulp Density = 100 g/L, Time= 90 min].

On the other side, pressure leaching of copper from crushed untreated PCBs (before pyrolysis) was also carried out with different concentration of sulfuric acid in an autoclave at 20 bar pressure using oxygen atmosphere, pulp density of 100 g/L, time 90 min and temperature 150°C. This was done for doing the comparison between pressure leaching of pyrolysed PCBs and untreated PCBs. It was noticed that the percentage recovery of copper metal was found to be only 0.18%, 0.38% and 0.41% with 1.0M, 2.0M and 2.4M H_2SO_4 respectively as shown in Fig. 2. This is due to the complex material of construction of PCBs, which make the separation of metals, plastics and

epoxy resins, a complicated task. These materials of PCBs were so compactly encapsulated that the acid was incapable to reach up to every layer of the metal sheet and leach them even at elevated temperature, pressure and acid concentration.

Various efforts were made to break the encapsulation by using organic swelling, physical beneficiation and pyrolysis [2-4]. Physical beneficiation and organic swelling process were energy and cost intensive respectively. However, treatment of PCBs after pyrolysis appeared to be comparatively low acid consuming technique. After pyrolysis, plastic and other volatile compounds were liberated easily from PCBs and thereby, made the leaching reaction faster even with low acid concentration.

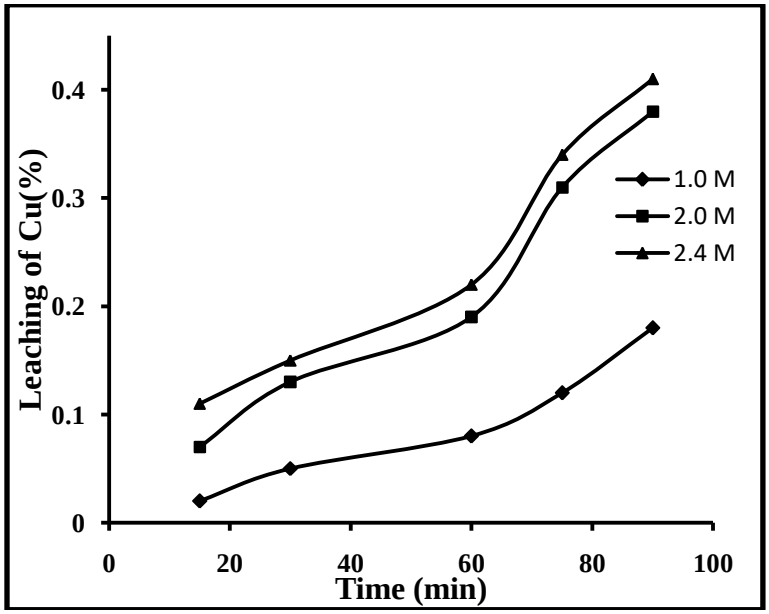


Fig. 2 Pressure leaching of crushed (-10 mesh size) untreated (before pyrolysis) PCBs. [Experimental Conditions: Temperature = 150°C, Pulp Density = 100 g/L, Time= 90 min].

5.3.2.1.2. Modeling of the rate of reaction

The kinetics for the pressure dissolution of copper from low metal concentrate (-10 mesh size, i.e <2mm size) of pyrolysed PCBs in sulfate media was calculated using all the standard equations of shrinking core models at 150°C, 20 bar pressure using 100 g/L and different concentration of sulfuric acid. All the standard equations of the shrinking core models were tested [181-184] for reaction kinetics. All the standard equations of the shrinking core models are X=Kct (film diffusion control dense constant size small particles), $1-(1-X)^{2/3}$=Kct (film diffusion control dense shrinking spheres), $1-(1-X)^{1/2}$=Kct (chemical reaction control dense constant size cylindrical particles), $1-(1-X)^{1/3}$=Kct

(chemical reaction control dense constant size or shrinking spheres), $1-3(1-X)^{2/3} + 2(1-X) = Kct$ (Ash diffusion control dense constant size spherical particles. where K_c is the reaction rate constant (min^{-1}), t is the time (min) and X is the fraction of metal reacted (% extraction/100).

The regression co-efficient R^2 was calculated for each model according to the following formula [185-18

$$\frac{\left(\sum_{i=1}^{i=N} (Y_i-\overline{Y})\,(Y_i°-\overline{Y°})\right)^2}{\sum_{i=1}^{i=N} (Y_i-\overline{Y})^2 \sum_{i=1}^{i=N} (Y_i°-\overline{Y°})^2} \qquad (31)$$

Where $Y_i°$ = experimental values, Y_i = calculated value, $\overline{Y°}$ = mean experimental value, $\overline{Y}$= mean calculated value.

The basis of selecting equation for a model is the highest value of R^2 i.e. the regression co-efficient of different shrinking core models. The highest value of R^2 is taken for selecting a model. The kinetics of the leaching of the low metal concentrate (-10 mesh size, <2mm size) of poly-cracked (pyrolysed) PCBs was studied from 10 to 90 min using 1M, 2M and 2.4M H_2SO_4 temperature. All the standard equations of shrinking core models were tested for reaction from the obtained experimental leaching data (Table 3). It was found that data fit with ash diffusion control dense constant size spherical particles; i.e. $K_ct = 1-3(1-X)^{2/3} + 2(1-X)$ for Cu. The selection of models was based on highest value of regression co-efficient (Table 4). The kinetic model presented in Fig. 3 is selected on the basis of regression coefficient i.e. higher the regression coefficient close to one the kinetic Kc values are almost constant.

Table 3 Calculated values of rate constant, Kct for the fraction of the reacted copper phase (X) of the low metal concentrate (-10 mesh size i.e. < 2mm) of poly-cracked (pyrolysed) PCBs for different models.

Model Kct=	**H_2SO_4 Conc^n.**	**Calculated values of Kct in different time in minutes**					
		10	20	30	45	60	90
X	**1M**	0.322	0.386	0.463	0.517	0.594	0.673
	2M	0.567	0.612	0.738	0.812	0.865	0.95
	2.4M	0.85	0.89	0.92	0.93	0.9823	0.999
$1-(1-X)^{1/2}$	**1M**	0.661	0.693	0.7315	0.7585	0.797	0.8365
	2M	0.7835	0.806	0.869	0.906	0.9325	0.975
	2.4M	0.925	0.945	0.96	0.965	0.99115	0.9995
$1-(1-X)^{1/3}$	**1M**	0.774	0.795333	0.821	0.839	0.864667	0.891
	2M	0.855667	0.870667	0.912667	0.937333	0.955	0.983333
	2.4M	0.95	0.963333	0.973333	0.976667	0.9941	0.999667
$1-(1-X)^{2/3}$	**1M**	0.846772	0.874335	0.903877	0.922237	0.945055	0.964357
	2M	0.937504	0.949819	0.977119	0.988219	0.993925	0.999167
	2.4M	0.9925	0.995967	0.997867	0.998367	0.999896	1
$1-3(1-X)^{2/3} + 2(1-X)$	**1M**	1.896316	1.851004	1.785631	1.732711	1.647164	1.547071
	2M	1.678511	1.625456	1.455356	1.340656	1.251775	1.0975
	2.4M	1.2775	1.2079	1.1536	1.1351	1.035087	1.001999

Table 4 Regression co-efficient, R^2 values for different shrinking core models for the kinetics of the leaching of the low metal concentrate (-10 mesh size i.e. < 2mm) of poly-cracked (pyrolysed) PCBs.

H_2SO_4 Conc^n.	**Regression coefficient, R^2 values for different models**					**Selected Models**
	X	**$1-(1-X)^{1/2}$**	**$1-(1-X)^{1/3}$**	**$1-(1-X)^{2/3}$**	**$1-3(1-x)^{2/3} + 2(1-x)$**	
1M	0.964	0.964	0.964	0.9182	0.9898	$1-3(1-X)^{2/3} + 2(1-X)$
2M	0.9284	0.9284	0.9284	0.79	0.9585	$1-3(1-X)^{2/3} + 2(1-X)$
2.4M	0.9147	0.9147	0.9147	0.7322	0.9231	$1-3(1-X)^{2/3} + 2(1-X)$

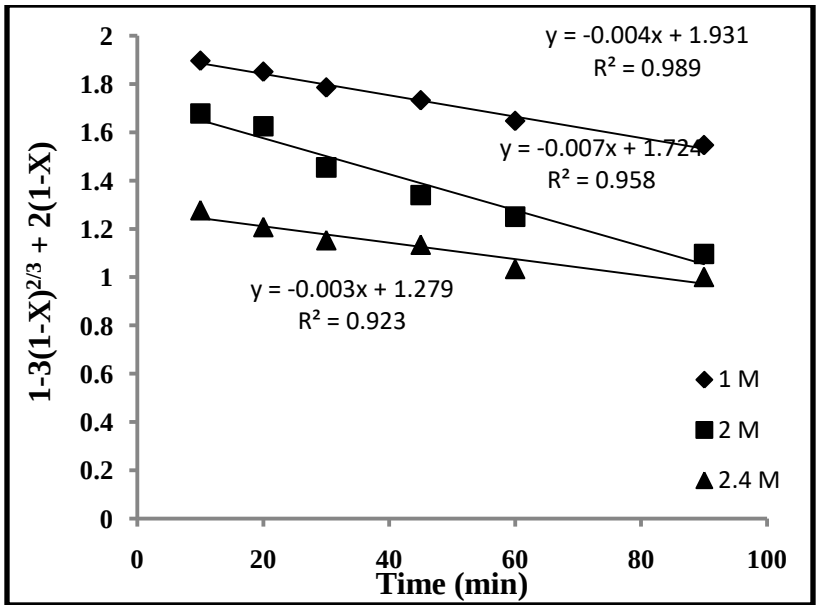


Fig. 3 Kinetics studies of copper metal leaching from pyrolysed (-10 mesh size) PCBs.

5.3.2.1.3. <u>EPMA-EDS studies</u>

EPMA study was also carried out using electron probe micro analyzer for microstructure of the leached residue obtained after leaching at optimized condition which showed good correlation with the mathematical result obtained, indicating heterogeneous distribution of particles in spherical form, as presented in Fig. 4. However, EDS studies shows the metals peaks for the residue left after leaching under optimized conditions, indicating only the presence of Al, Si , etc. (Fig. 4).

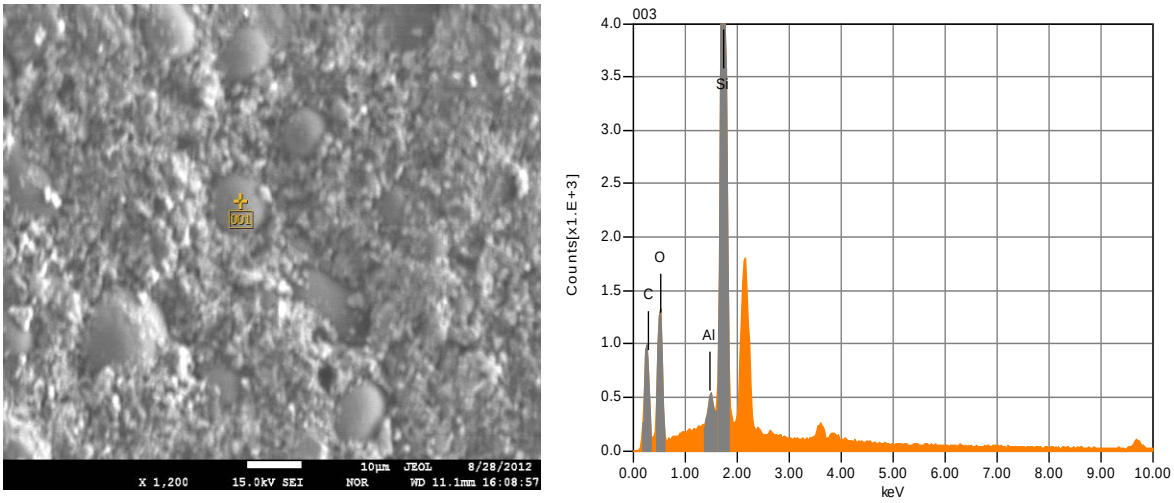


Fig. 4 EPMA and EDS of leached residue showing spherical particles.

5.3.2.2. Atmospheric leaching of high metal concentrate (+10 mesh size) of pyrolysed PCBs

Recovery of metals from the metallic concentrate obtained from pyrolysed PCBs, acid leaching studies were considered suitable. Different acidic solutions were initially used for the dissolution of maximum amount of metals. Various process parameters were studied as follows:

5.3.2.2.1. Selection of leachant

Chemical and physical character of the material to be leached, reagent cost and its ability to be regenerated were some of the factors which helped to select the effective leachant for the dissolution of metals. The performance of leaching agent for the effective dissolution and concentration of metals viz. Cu, Pb and Ni was investigated using different acid solutions such as sulfuric acid, hydrochloric acid and nitric acid in different time intervals. The results given in Fig. 5 indicate dissolution of metals from metallic concentrate in different acids with time, all experiments performed under same experimental condition. Fig. 5 shows the increase in time from 15 to 60 min, the percentage leaching of Cu, Pb and Ni were increased from 73.01 to 99.90%, 76.02 to 99.90% and 24.10 to 57.5% respectively using 4M HNO_3 at 90°C for 60 min maintaining under pulp density of 30 g/L. Following reaction takes place during the leaching procedure:

$$Cu_{(s)} + 5HNO_{3\,(aq)} \longrightarrow 2NO_{2\,(g)} + Cu\,(NO_3)_{2\,(aq)} + 2H_2O + H^+ \uparrow \quad (32)$$

$$Pb_{(S)} + 2HNO_{3\,(aq)} \longrightarrow Pb\,(NO_3)_{2\,(aq)} + H_2 \quad (33)$$

$$Ni_{(S)} + 4HNO_{3\,(aq)} \longrightarrow Ni\,(NO_3)_2 + 2NO_2 + H_2O \quad (34)$$

But the dissolution rate decreased with other two acids. It was found that Cu leaching increased from 1.75 to 2.95% and decreased from 0.19 to 0.07% during HCl and H_2SO_4 leaching respectively. This might be because of the hindrance provided by the formation of precipitates in case of sulphuric acid and hydrochloric acid. In case of HCl dissolution, we know that oxidation potential of Cu is lower than that of hydrogen, so it could not displace hydrogen from HCl. Copper was leached significantly only in the oxidative environment, however HCl is a non-oxidizing acid, and hence there should be no significant reactions between Cu and HCl [55]. However, there will be no reaction with

H_2SO_4 as the standard reduction potential of Cu is higher than H_2. Therefore Cu has a lesser tendency to give up electron than H. Hence Cu does not reduce H^+ ion given by dil. H_2SO_4 to H_2 and, therefore, Cu cannot react. Oxidizing agent (H_2O_2 or air) was also used in sulphuric acid for leaching of copper from waste PCBs. In case of Pb, HCl had less tendency for lead dissolution because formation of black precipitate of chloroplumbic acid [$H_2(PbCl_4)$] [1] and in case of H_2SO_4, $PbSO_4.H_2O$ is converted to α-PbO_2 [187]. The dissolution rate of Ni increased from 12.87 to 14.54% and 35.9 to 50% in 4M HCl and 4M H_2SO_4 respectively with increase in time from 15 to 60 min. In H_2SO_4 solution, passivation of nickel was supposed to occur in two stages and formed NiO [188].

Thus, HNO_3, a strong oxidizing reagent was found to be a positive leaching agent for Cu, Pb and Ni dissolution. Also, it had considerable advantage over acids like HCl, H_2SO_4, etc. which might provide hindrance due to the formation of precipitates. In addition, HNO_3 could be easy to regenerate and re-use attractive [76]. Leaching of metals with nitric acid in Pyrex reactor was a closed system experiment as condenser was attached with the reactor which condensed the nitrous oxide gas evolved at the time of experiment. So, nitrous oxide was not mixed with air and thereby not causing any hazard to environment.

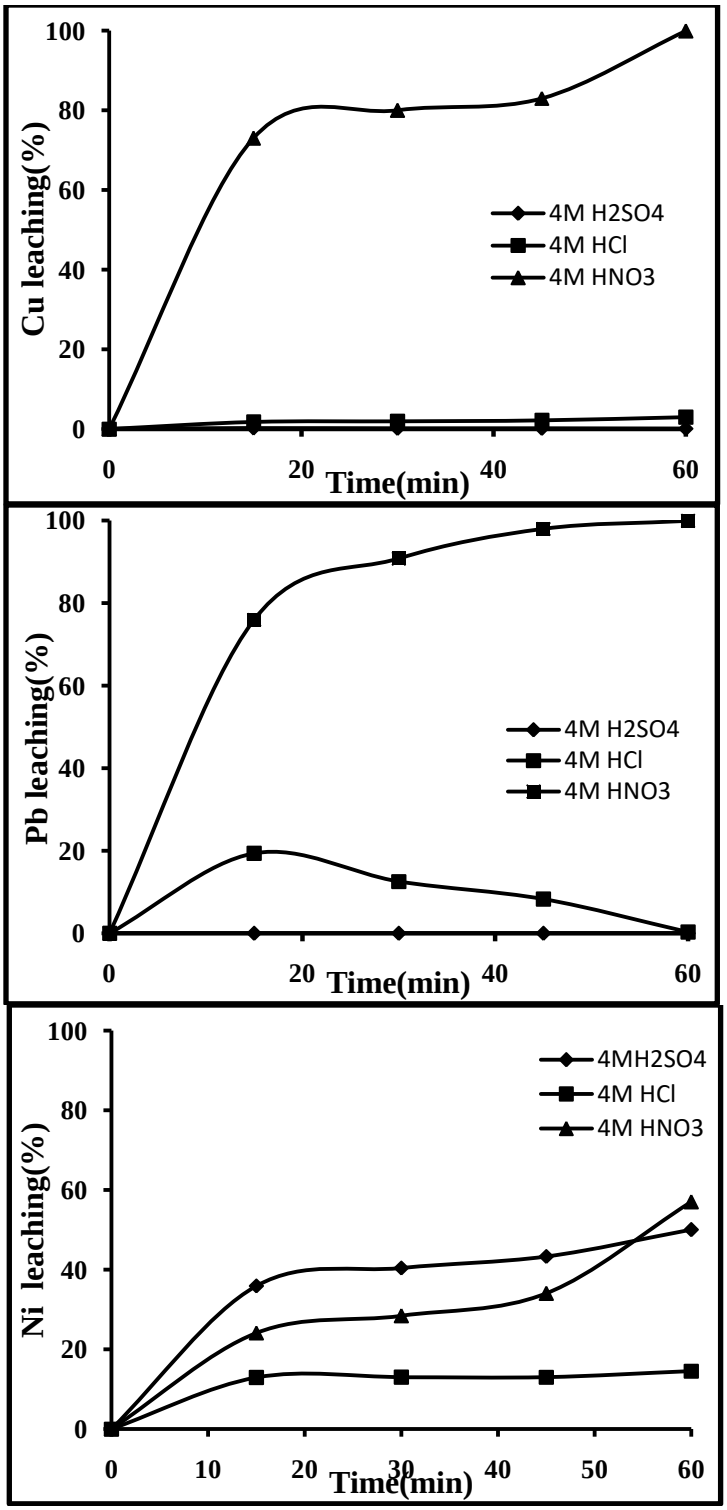


Fig. 5 Effect of different acids on recovery of Cu, Pb & Ni from poly-cracked PCBs. [Experimental Conditions: Pulp density-30 g/L, Temperature-90°C, Time-60 min, Stirring speed-250 rpm]

5.3.2.2.2. Effect of acid concentration

In general acid concentration has pronounced effect on metal extraction and is one of the important factors to be studied for optimizing the condition for metals dissolution. Various experiments were performed for metal extraction by altering HNO_3 concentration over a range of 1 to 4M keeping pulp density of 30 g/L in different time interval. The results presented in Fig. 6 indicates that at 90°C, Cu dissolution increases from 75.34 to 99% as acid concentration increases from 1 to 4M maintaining stirring speed 250 rpm for 60 min. Increase in leaching rate might be due to the increase in flux of H^+ ion across the particle boundaries, thus enhancing the rate of reaction.

99% Pb was leached with 2M HNO_3 in 15 min and with 4M HNO_3, leaching of lead increased from 76.0 to 99% in 60 min. When the acid concentration was less i.e. 2M HNO_3, it was observed that the lead dissolution occurred 99% within 15 min but in the case of 4M HNO_3 more time was required for 99% dissolution of lead. But this increasing dissolution rate of lead in HNO_3 solution was valid for a certain acid concentration only. This might be due to the formation of an adherent film of $Pb(NO_3)_2$ which was insoluble in HNO_3 and moreover it formed more protective film of PbO_2 at higher acid concentration [189]. The dissolution rate of nickel decreases from 99 to 57.5% with increase in acid concentration from 1 to 4M. According to the experimental results it might be possible that in the beginning of the passivation process on nickel $Ni(NO_3)_2 \cdot 4\ H_2O$ was formed and that changed to NiO_2 and then transformed slowly to NiO which might hinder the reaction [190]. The residue which was obtained after leaching will be further used for nickel extraction.

Leaching mechanism was further established by characterizing the leached residue by X-ray diffraction pattern. The residue obtained after metal leaching from metallic concentrate of pyrolysed PCBs with 4M HNO_3 at 90°C for 60 min, 30 g/L, 250 rpm. XRD was performed using Bruker AXS D8 instrument running at 0.2 sec/step shows various diffraction peaks which were analyzed for various phases. Fig. 7 shows the XRD peaks of the residue obtained after leaching for 15 min which indicated the presence of PbO_2, NiO. Fe_3O_4, Si_2N_2O as major and minor peaks of CuO. While the residue obtained after 60 min shows the peaks of SnO_2 and small peaks of Ni

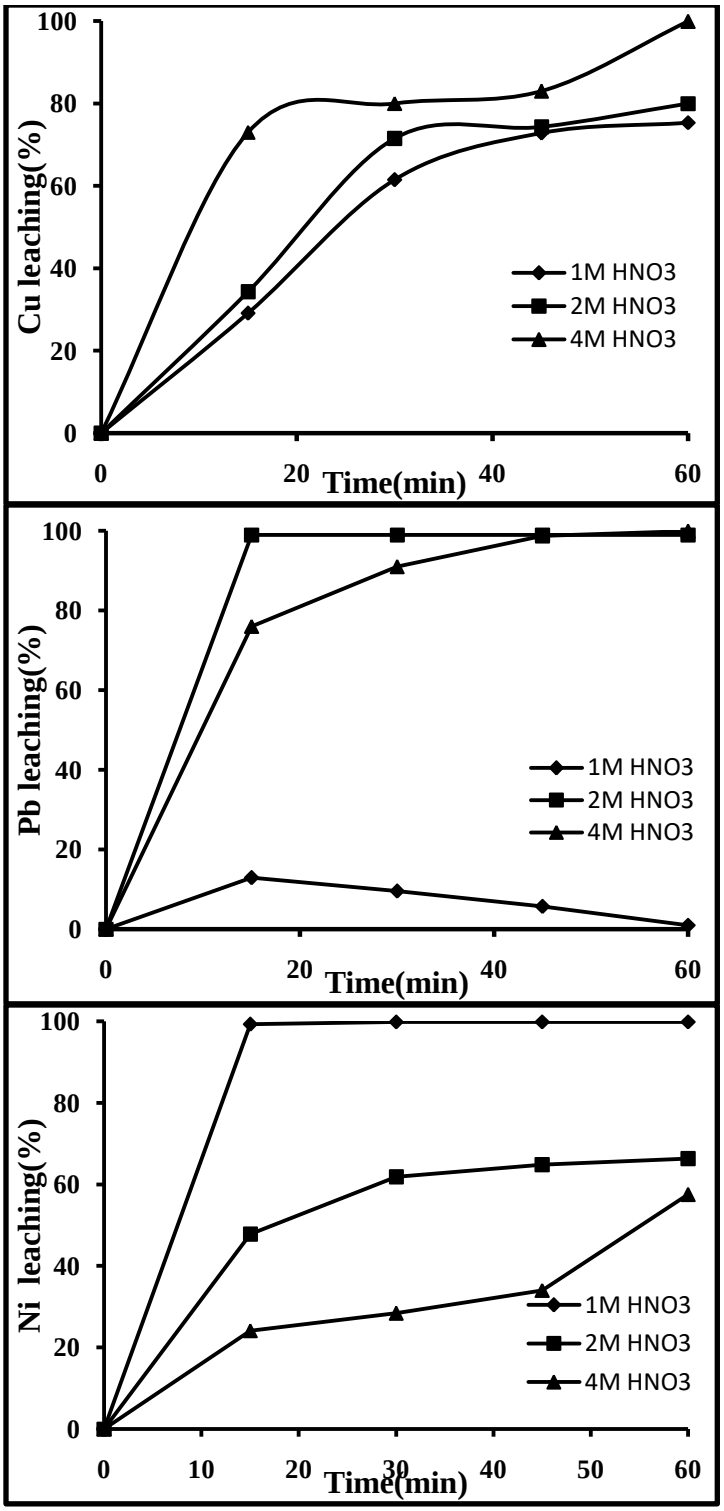


Fig. 6 Effect of nitric acids on recovery of Cu, Pb & Ni from poly-cracked PCBs. [Experimental Conditions: Acid- HNO_3, Pulp density-30 g/L, Temperature-90°C, Time-60 min, Stirring speed-250 rpm]

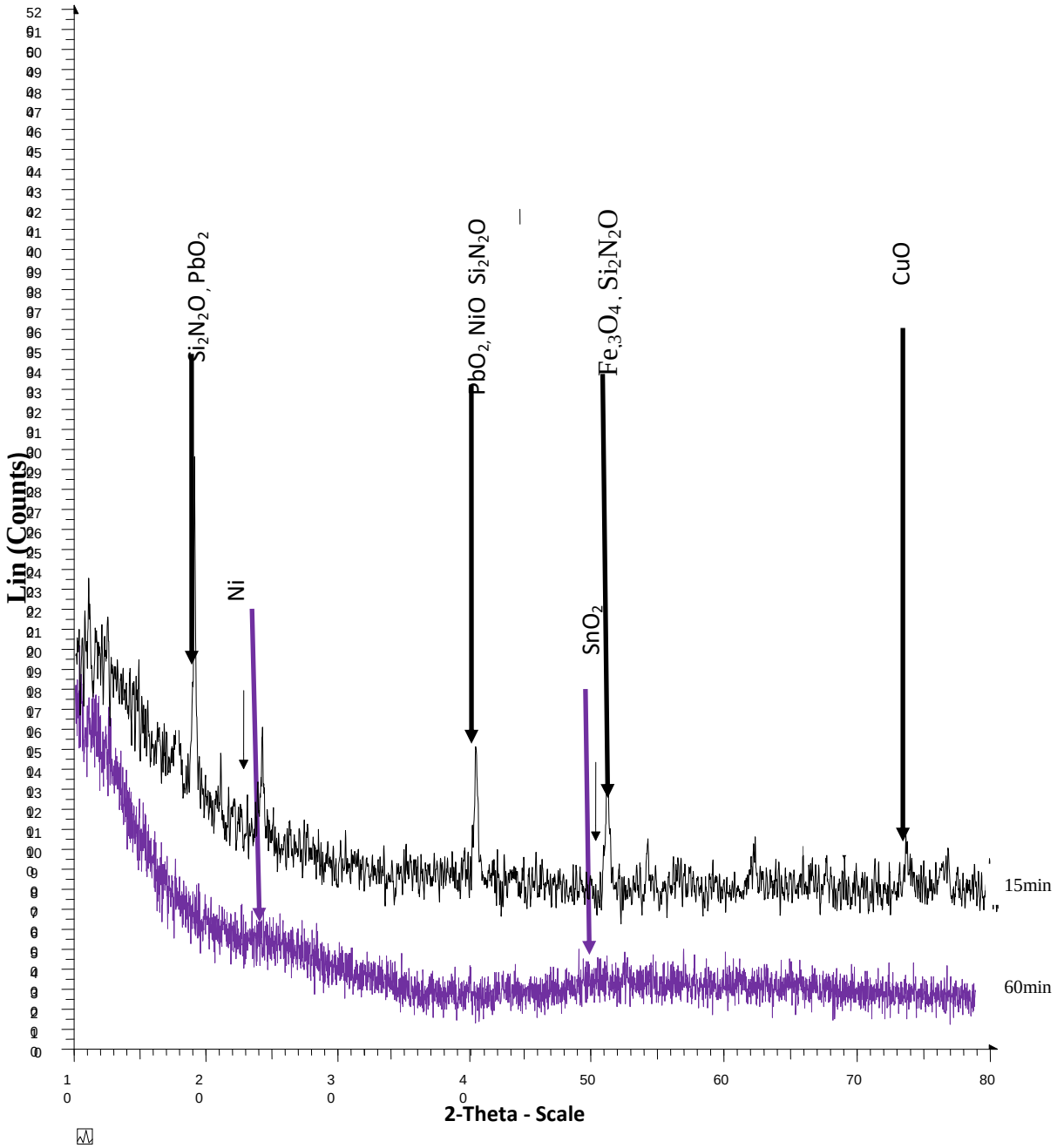


Fig. 7 XRD of the leached residues in different time interval.

5.3.2.2.3. Effect of pulp density

The effect of pulp density on metal dissolution were investigated by adding different amount (2.5, 7.5, 15 and 50 g) of metallic concentrate of pyrolysed PCBs in 500 ml of 4M HNO_3 solutions. Pulp density had significant effect on dissolution of metals with time. The percentage leaching of metals was found to be inversely proportional to pulp density as shown in Fig. 8. At the low pulp density the available surface area per unit volume of the solution was higher and therefore, the metal leaching was higher while increase in the pulp density decreased the available surface area per unit volume of the solution which caused decrease in percentage leaching of metals [191]. In case of Cu, it was observed that using 4M HNO_3 for 60 min, leaching rate first increased then it slightly decreased. Percentage leaching of Cu increased from 47.16 to 99% as pulp density increased from 5 to 30 g/L but it decreased to 62.5% at 100 g/L. In case of Pb, it was found that experiments performed with 5 and 15 g/L pulp density showed 99% Pb dissolved in 15 min only which remain unchanged up to 60 min. However, leaching percentage decreased to 78% as pulp density increased to 30 g/L in 15 min, but as time was increased to 60 min, 99% recovery was achieved. At 100 g/L, extraction decreased to almost 30.6% even after leaching for 60 min. A complete decline in the graph is shown for Ni dissolution where percentage leaching directly decreases from 99 to 22.1% with the increase in the pulp density.

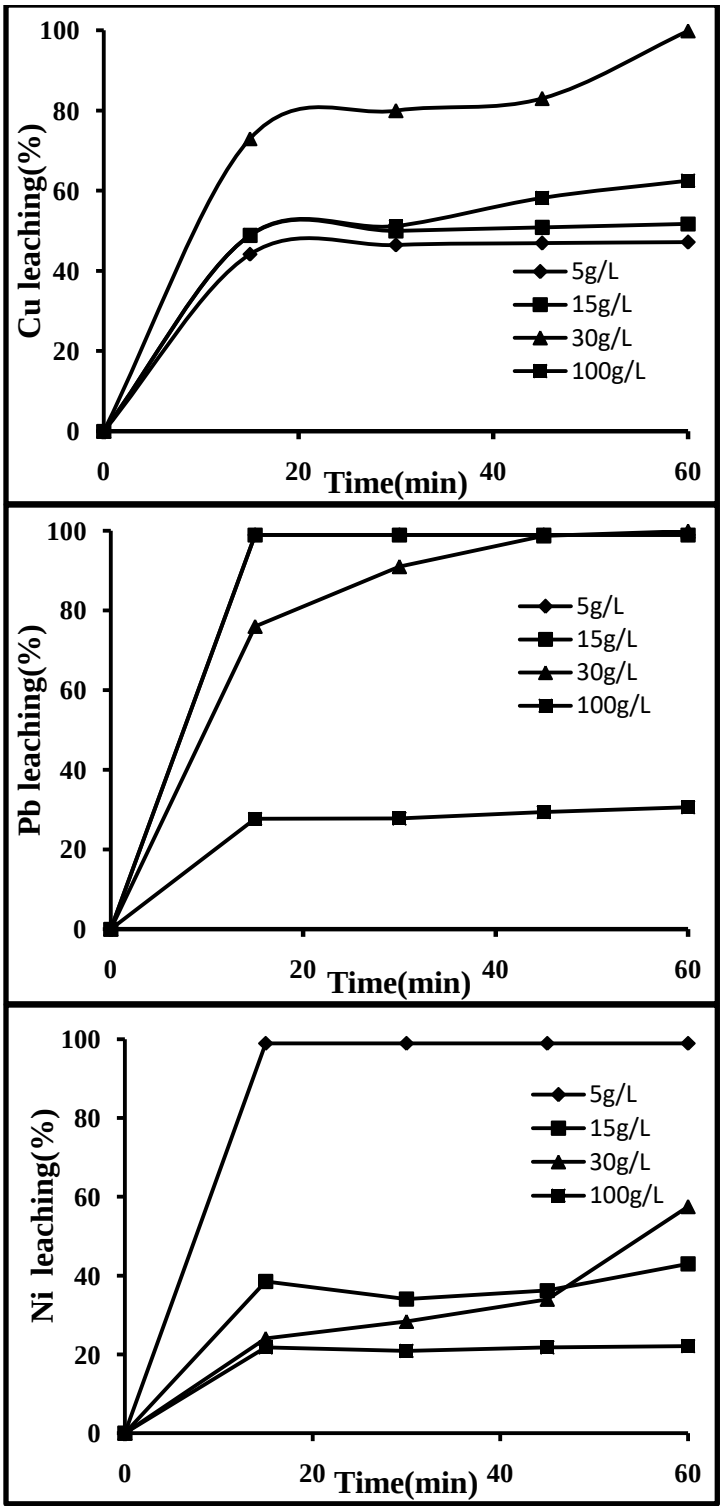


Fig. 8 Effect of pulp-density on recovery of Cu, Pb & Ni from poly-cracked PCBs. [Experimental Conditions: Acid- 4M HNO_3, Temperature-90°C, Time-60 min, Stirring speed-250 rpm]

5.3.2.2.4. Effect of temperature

To investigate the effect of temperature on metal dissolution, leaching experiments were carried out at varying temperature ranging from 30 to 90°C, for 60 min maintaining pulp density 30 g/L with stirring speed 250 rpm. The increase in solution temperature significantly intensified the reactive activity of HNO_3, which increased the rate of metal dissolution. The dissolution behavior of Cu using 4M HNO_3 for 60 min showed that the percentage leaching of Cu was increased from 47.02 to 59.8% at 30ºC, 54.51 to 63.85% at 60ºC and from 73 to 99% at 90ºC respectively as shown in Fig. 9. However, Percentage leaching of Pb was increased from 93 to 99% at 30ºC, 94 to 99% at 60ºC and 76 to 99% at 90ºC respectively. Percentage leaching of Ni was decreased from 99 to 57.5% with the increase in temperature from 30 to 90ºC due to formation of protective layer NiO which might hinder the reaction at high temperatures [190]. But apart from these conditions, 90ºC was selected to be optimized as maximum amount of Cu was recovered at this temperature.

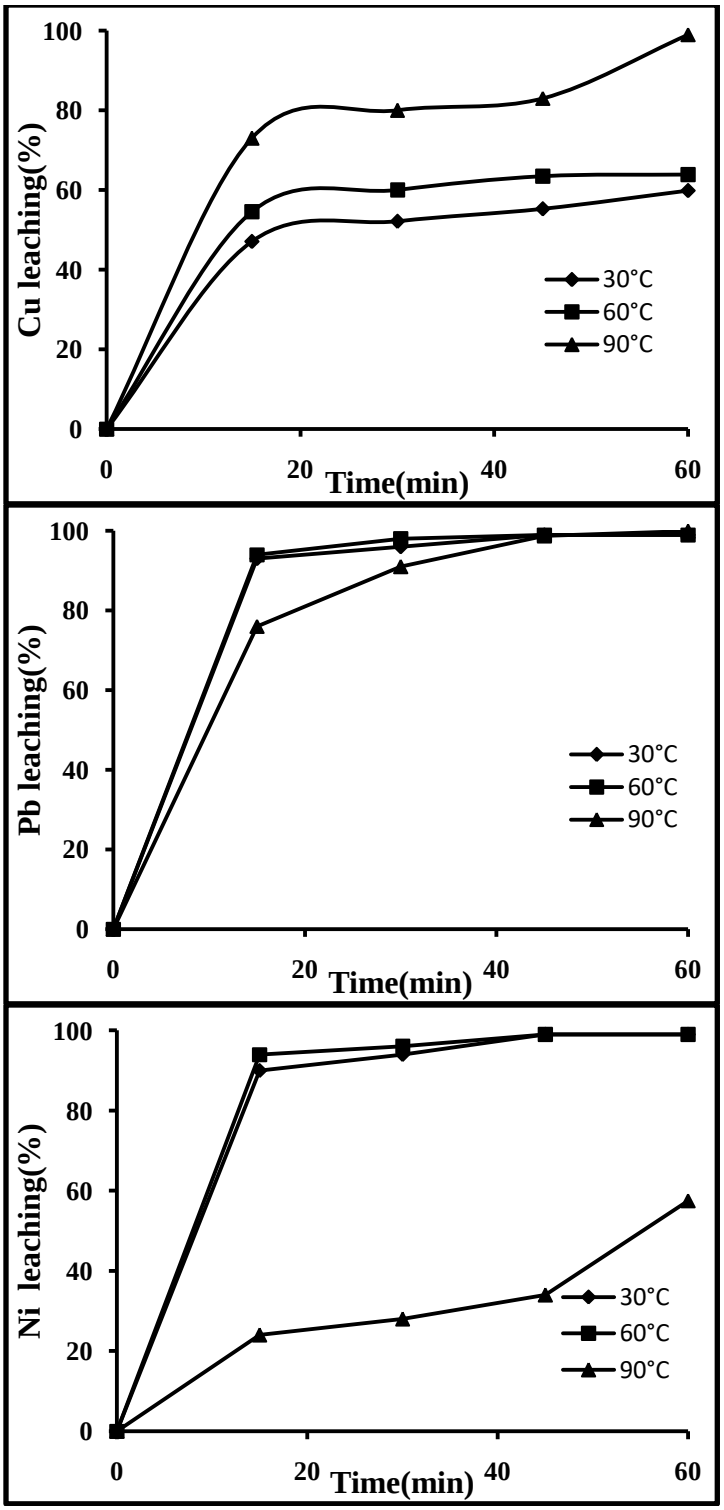


Fig. 9 Effect of temperature on recovery of Cu, Pb & Ni from poly-cracked PCBs. [Experimental Conditions: Acid- 4 M HNO_3, Pulp density-30 g/L, Time-60 min, Stirring speed-250 rpm]

5.3.2.2.5. Modeling of the rate of reaction

An effort has been made to study the kinetics of dissolution of metals (Cu, Pb & Ni) in the leaching of the WPCBs using shrinking core model. All the standard equations of the shrinking core models were tested [181-184] for reaction kinetics. All the standard equations of the shrinking core models are X=Kct (film diffusion control dense constant size small particles), $1-(1-X)^{2/3}$=Kct (film diffusion control dense shrinking spheres), $1-(1-X)^{1/2}$=Kct (chemical reaction control dense constant size cylindrical particles), $1-(1-X)^{1/3}$=Kct (chemical reaction control dense constant size or shrinking spheres), $1-3(1-X)^{2/3} + 2(1-X)$ = Kct (Ash diffusion control dense constant size spherical particles. where K_c is the reaction rate constant (min^{-1}), t is the time (min), and X is the fraction of metal reacted (% extraction/100).

The regression co-efficient R^2 was calculated for each model according to the following formula [185-186]

$$\frac{\left(\sum_{i=1}^{i=N} (Y_i-\overline{Y})\,(Y_i°-\overline{Y°})\right)^2}{\sum_{i=1}^{i=N} (Y_i-\overline{Y})^2 \sum_{i=1}^{i=N} (Y_i°-\overline{Y°})^2} \qquad (35)$$

Where $Y_i°$ = experimental values, Y_i = calculated value, $\overline{Y°}$ = mean experimental value, $\overline{Y}$= mean calculated value.

The basis of selecting equation for a model is the highest value of R^2 i.e. the regression co-efficient of different shrinking core models. The highest value of R^2 is taken for selecting a model. The kinetics of the leaching of the high metal concentrate (+10 mesh size, >2mm size) of poly-cracked (pyrolysed) PCBs was studied from 15 to 45 min using 30°C, 60°C and 90°C temperature. All the standard equations of shrinking core models were tested for reaction from the obtained experimental leaching data (Table. 5, 7, 9). It was found that data fit with ash diffusion control dense constant size spherical particles; i.e. $K_ct = 1-3(1-X)^{2/3} + 2(1-X)$ for Cu dissolution. Leaching kinetics for Pb dissolution was also calculated from the obtained experimental leaching data. It was found that data

fit with chemical reaction control dense constant size or shrinking spheres; i.e. $K_c t = 1-(1-X)^{1/3}$ for Pb dissolution. Similar for Ni dissolution, it was found that data fit with film diffusion control dense shrinking spheres i.e. $K_c t = 1-(1-X)^{2/3}$ for Ni dissolution. The selection of models based on highest value of regression co-efficient (Table 6, 8, 10). The kinetic models presented in Fig. 10 is selected on the basis of regression coefficient i.e. higher the regression coefficient close to one and almost constant kinetic Kc values.

Table 5 Calculated values of Kct for the fraction of the reacted copper of high metal concentrate (+10 mesh size, i.e. >2mm size) pyrolysed PCBs for different models.

Model, Kct=	Temperature (ºC)	15 min	30 min	45 min
X	**30**	0.4702	0.5212	0.5524
	60	0.5451	0.6	0.6344
	90	0.73	0.8	0.83
$1-(1-X)^{2/3}$	**30**	0.345251	0.387975	0.41486
	60	0.408515	0.457116	0.488706
	90	0.582257	0.658005	0.693122
$1-(1-X)^{1/2}$	**30**	0.272126	0.308046	0.330971
	60	0.325537	0.367544	0.395351
	90	0.480385	0.552786	0.587689
$1-(1-X)^{1/3}$	**30**	0.190835	0.217679	0.235055
	60	0.230919	0.263194	0.284952
	90	0.35367	0.415196	0.446034
$1-3(1-X)^{2/3} + 2(1-X)$	**30**	0.095354	0.121524	0.139779
	60	0.135344	0.171349	0.197318
	90	0.286771	0.374014	0.419366

Table 6 Regression co-efficient, R^2 values for different shrinking core model for the kinetics of the leaching of the copper metal from high metal concentrate of pyrolsed PCBs.

Temperature (ºC)	Regression co-efficient, R^2 values for different models					Selected model
	X	**$1-(1-X)^{2/3}$**	**$1-(1-X)^{1/2}$**	**$1-(1-X)^{1/3}$**	**$1-3(1-X)^{2/3} + 2(1-X)$**	
30	0.981	0.983	0.984	0.984	0.989	$1-3(1-X)^{2/3} + 2(1-X)$
60	0.982	0.985	0.986	0.987	0.991	$1-3(1-X)^{2/3} + 2(1-X)$
90	0.949	0.957	0.960	0.964	0.967	$1-3(1-X)^{2/3} + 2(1-X)$

Table 7 Calculated values of Kct for the fraction of the reacted lead of (high metal concentrate i.e. >2mm size)) pyrolysed PCBs for different models.

Model, Kct=	Temperature (ºC)	15 min	30 min	45 min
X	**30**	0.93	0.96	0.99
	60	0.94	0.98	0.99
	90	0.7602	0.91	0.987
$1-(1-X)^{2/3}$	**30**	0.998367	0.999467	0.999967
	60	0.9988	0.999867	0.999967
	90	0.98083	0.9973	0.999944
$1-(1-X)^{1/2}$	**30**	0.965	0.98	0.995
	60	0.97	0.99	0.995
	90	0.8801	0.955	0.9935
$1-(1-X)^{1/3}$	**30**	0.976667	0.986667	0.996667
	60	0.98	0.993333	0.996667
	90	0.92007	0.97	0.995667
$1-3(1-X)^{2/3} + 2(1-X)$	**30**	1.1351	1.0784	1.0199
	60	1.1164	1.0396	1.0199
	90	1.4221	1.1719	1.025831

Table 8 Regression co-efficient, R^2 values for different shrinking core model for the kinetics of the leaching of the lead metal from high metal concentrate of pyrolysed PCBs.

Temperature (ºC)	Regression co-efficient, R^2 values for different models					Selected model
	X	**$1-(1-X)^{2/3}$**	**$1-(1-X)^{1/2}$**	**$1-(1-X)^{1/3}$**	**$1-3(1-X)^{2/3}+2(1-X)$**	
30	0.998	0.955	1	1	0.999	$1-(1-X)^{1/3}$ or $1-(1-X)^{1/2}$
60	0.959	0.813	0.892	0.892	0.895	X
90	0.965	0.851	0.965	0.97	0.97	$1-(1-X)^{1/3}$ or $1-3(1-X)^{2/3} + 2(1-X)$

Table 9 Calculated values of Kct for the fraction of the reacted nickel of (high metal concentrate i.e. >2mm size)) pyrolysed PCBs for different models.

Model, Kct=	Temperature (ºC)	15 min	30 min	45 min
X	**30**	0.909	0.948	0.996
	60	0.94	0.96	0.997
	90	0.24	0.28	0.34
$1-(1-X)^{2/3}$	**30**	0.99724	0.999099	0.999995
	60	0.9988	0.999467	0.999997
	90	0.807467	0.8272	0.8548
$1-(1-X)^{1/2}$	**30**	0.9545	0.974	0.974
	60	0.97	0.98	0.9985
	90	0.62	0.64	0.67
$1-(1-X)^{1/3}$	**30**	0.969667	0.982667	0.998667
	60	0.98	0.986667	0.999
	90	0.746667	0.76	0.78
$1-3(1-X)^{2/3} + 2(1-X)$	**30**	1.173719	1.101296	1.007984
	60	1.1164	1.0784	1.005991
	90	1.9424	1.9216	1.8844

Table 10 Regression co-efficient, R^2 values for different shrinking core model for the kinetics of the leaching of the nickel metal from high metal concentrate of pyrolysed PCBs.

Temperature (ºC)	Regression co-efficient, R^2 values for different models					Selected model
	X	**$1-(1-X)^{2/3}$**	**$1-(1-X)^{1/2}$**	**$1-(1-X)^{1/3}$**	**$1-3(1-X)^{2/3}+2(1-X)$**	
30	0.996	0.960	0.996	0.996	0.994	X or $1-(1-X)^{1/2}$ or $1-(1-X)^{1/3}$
60	0.971	0.995	0.971	0.971	0.968	$1-(1-X)^{2/3}$
90	0.986	0.990	0.986	0.986	0.974	$1-(1-X)^{2/3}$

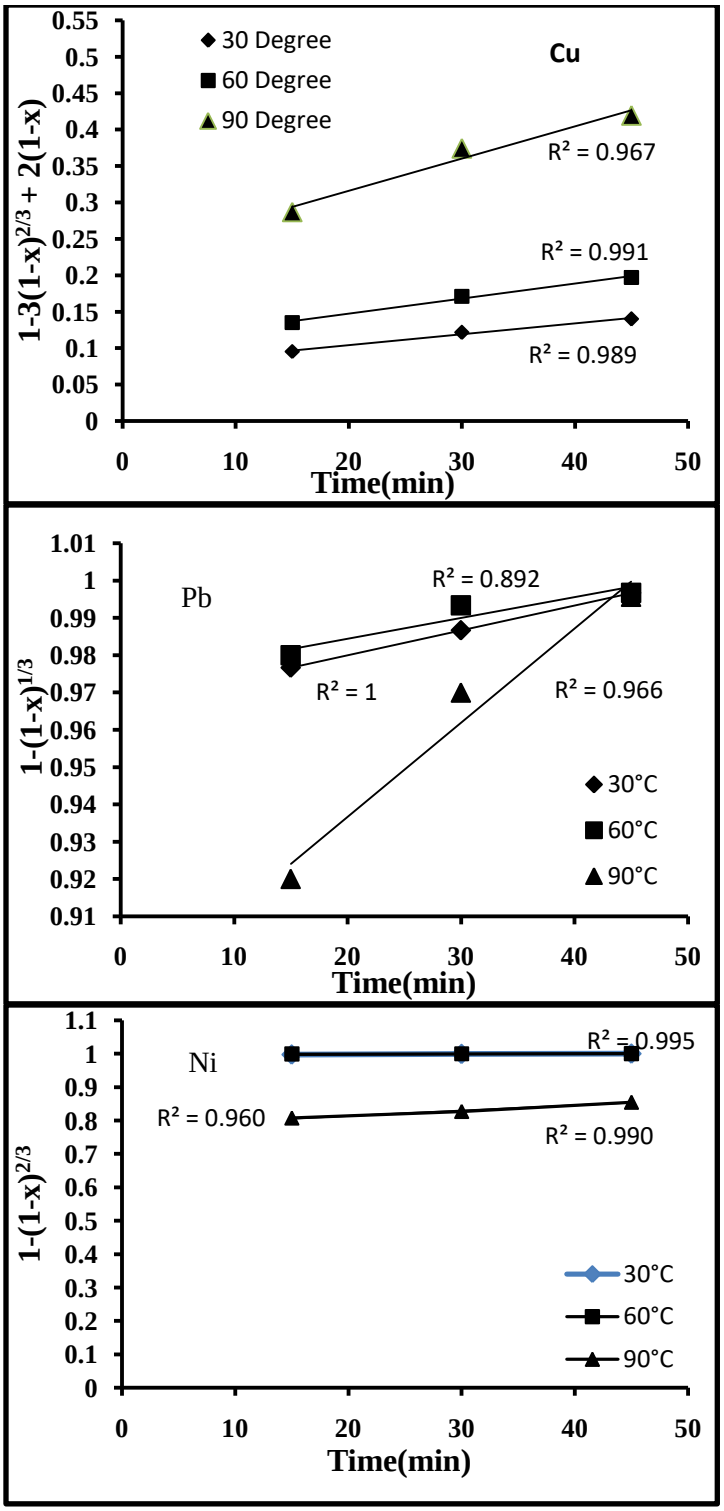


Fig. 10 Kinetics studies of Cu, Pb and Ni metals leaching from high metals concentrate of (>2mm size) pyrolysed PCBs.

5.3.2.2.6. EPMA-EDS studies

EPMA study was also carried out using electron probe micro analyzer for microstructure of the leached residue obtained after leaching at optimized condition which showed good correlation with the mathematical result, indicating heterogeneous distribution of particles in the form of spherical and constant size as shown in Fig. 11. However, EDS studies show the metals peaks for the residue left after leaching under optimized conditions, indicating only the presence of Ni, Sn, Si etc. and absence of Cu, Pb, etc. (Fig. 11).

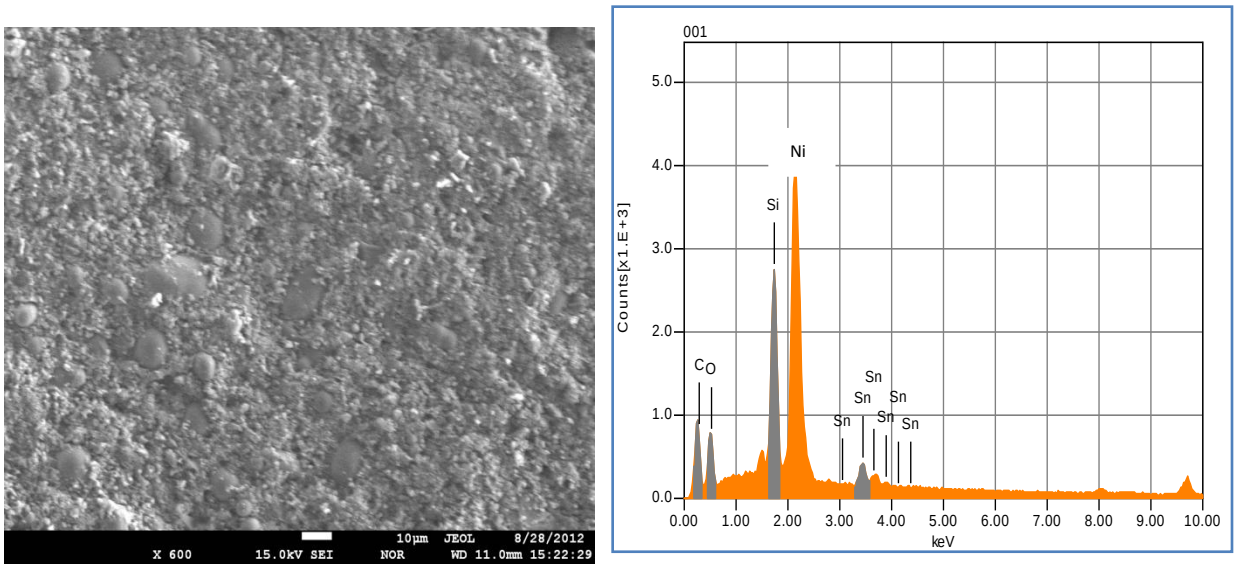


Fig. 11 EPMA and EDS of leached residue showing spherical particles.

Acidity of the leach liquor is 3.6M and composition of the metals in the leach liquor are 20.72 g/L Cu, 0.0156 g/L Ni, 0.058 g/L Fe & 0.0475 g/L Pb. Further, this leach liquor was processed for solvent extraction process for selective extraction of acid and metals (chapter-6 in section 6.3) present in the solution. Prior to Cu extraction, air sparging is essential to remove Fe content as its presence might reduce the efficiency of Cu metal sheet during the process of electrowinning.

5.4. Conclusions

- The poly-cracked (pyrolysed) PCBs were subjected to physical beneficiation for the separation of metallic from non-metallic fractions using scutter crusher and grinding mills. Further, the ground poly-cracked (pyrolysed) PCBs were scrubbed/washed with water without using any additives to enrich the metallic concentrate up to 97.8%. The scrubbed sample was further screened to separate low metal concentrate (-10 mesh i.e. <2 mm size) and high metal concentrate (+10 mesh i.e. >2 mm size).
- 99.9% copper was recovered from low metal concentrate (-10 mesh size) of poly-cracked (pyrolysed) PCBs by pressure leaching in an autoclave using 2.4M H_2SO_4 applying 20 bar oxygen pressure at 150°C for 90 min keeping pulp density 100 g/L.
- Kinetic studies showed that, the data fit most satisfactorily with with ash diffusion control dense constant size spherical particles; i.e. $K_ct = 1-3(1-X)^{2/3} + 2(1-X)$ for Cu dissolution. EPMA-EDS study was also validated with the results. Under the optimized experimental conditions, obtained leach liquor of low metal concentration of poly-cracked PCBs (pyrolysed) contained 2.2M H_2SO_4 (analyzed using titration method), Cu-10.76 g/L, Ni-0.38 g/L, Fe-2.55 g/L and Pb-0.07 g/L. Solvent extraction method was further carried out to selectively extract acid, Cu and Ni from this leach liquor which is discussed (chapter-6 in section 6.2).
- In 4M HNO_3 at 90°C for 60 min, pulp density of 30 g/L and maintaining stirring speed 250 rpm, 99% Cu, Fe, Pb and 57% Ni were recovered from +10 mesh size (> 2mm) of poly-cracked PCBs.
- Kinetic studies showed that, the data fit most satisfactorily with ash diffusion control dense constant size spherical particles model i.e. $K_ct = 1-3(1-X)^{2/3} + 2(1-X)$ for Cu dissolution, chemical reaction control dense constant size or shrinking spheres i.e. $K_ct = 1-(1-X)^{1/3}$ for Pb dissolution and & film diffusion control dense shrinking spheres i.e. $K_ct = 1-(1-X)^{2/3}$ for Ni dissolution. XRD and EPMA-EDS studies were also validated with the results obtained.
- Under the optimized experimental conditions, obtained leach liquor of high metal concentration of poly-cracked PCBs (pyrolysed) contains 3.6M HNO_3 (analyzed

using titration method), Cu-20.72 g/L, Ni-0.0156 g/L g/L, Fe-0.058 g/g/L and Pb-0.0475 g/L. Further, this leach liquor was processed for solvent extraction process for selective extraction of acid and metals (chapter-6 in section 6.3) present in the solution. Prior to Cu extraction, air sparging is essential to remove Fe content as its presence might reduce the efficiency of Cu metal sheet during the process of electrowinning.

Process flow-sheet is shown in Fig. 12 for recovery of metals from the waste printed circuit boards.

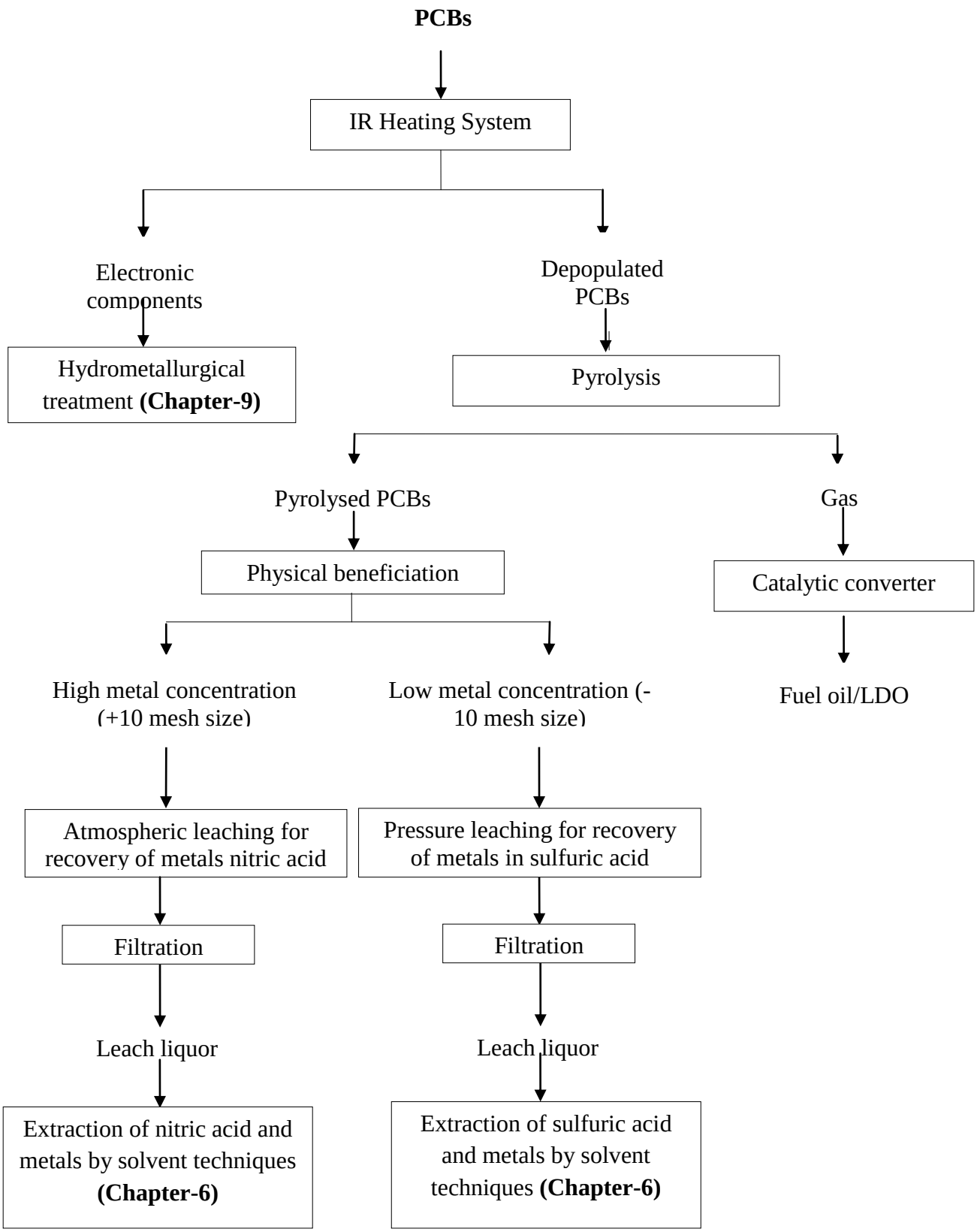


Fig. 12 Process flow sheet for recovery of metals from WPCBs.

CHAPTER-6

SOLVENT-EXTRACTION STUDIES

CHAPTER-6

SOLVENT-EXTRACTION

6.1. Introduction

Solvent extraction of metals is based on the use of an extracting agent which is soluble in an organic diluent but insoluble in aqueous solution. The process involves the transfer of the metal ion from the aqueous phase to the organic phase. The metal-organic compound is then "stripped" or transferred back to the aqueous phase, releasing the organic extractant which is returned to the extraction stage. By the same process, a more concentrated and pure solution is produced from which the metal salt is recovered.

The solvent-extraction studies have been carried out for recovery of metals from the leach liquor of pyrolysed printed circuit boards. Various process parameters viz. effect of pH, extractant concentration, O/A ratio, loading capacity etc. were studied to optimize favorable conditions for recovery of acid and pure metals solution.

6.2. Extraction of sulfuric acid and metals from Leach liquor-I (sulfate leach liquor of low metal concentrate (-10 mesh size) of poly-cracked (pyrolysed) PCBs)

6.2.0. Materials & methods

Leach liquor containing H_2SO_4-2.2M, Cu-10.76 g/L, Ni-0.38 g/L, Fe-2.55 g/L and Pb-0.07 g/L was generated by pressure leaching of low metal concentrate (-10 mesh size i.e, <2mm size) of pyrolysed PCBs in sulfuric acid. This leach liquor was subjected to solvent-extraction for recovery of acid and metals. The effect of various process parameters viz. time, pH, extractant concentration, O/A ratio were studied during solvent-extraction studies. The aqueous raffinate was analysed to know metals present. Organic reagent Tris (2-ethylhexyl) amine (TEHA) was (supplied by Sigma-Aldrich Chemie GmbH, Germany) used for acid extraction. 2-hydroxy-5-nonylacetophenone oxime, commercially known as LIX 84IC employed for extraction of copper and nickel was supplied by M/s Cognis Corporation, Ireland (Earlier M/s Henkel Inc., Tucson). Aqueous samples were prepared using distilled water. All other chemicals used were of analytical grade reagents.

6.2.1. Results & discussion

6.2.1.1. Solvent extraction of sulfuric acid

The acidic content of the leach liquor was found to be 2.2M, removal of which is essential prior to metal extraction from industrial point of view. The solvent Tris (2-ethylhexyl) amine (TEHA), was used for extraction of sulfuric acid from leach liquor of low metal concentrate poly-cracked (pyrolysed) PCBs to obtain acid free solution which can be later disposed of (after metal extraction) without affecting the environment. Different process parameters were studied for sulfuric acid extraction as given below.

6.2.1.1.1. Effect of extractant concentration on sulfuric acid extraction

Selective extraction of sulfuric acid from original leach liquor was carried out using different concentration of TEHA in the range of 10 to 70% (v/v) diluted in kerosene. The results presented in Fig. 1 show that extraction of H_2SO_4 increases from 8.62 to 56.56% as the extractant concentration increases from 10 to 70% (v/v) at O/A of 1/1 and mixing time of 5 min. 70% TEHA was taken to be optimum as higher concentration of TEHA is highly viscous and is very difficult to handle. Hence, higher concentration of TEHA is not preferred.

A plot of logD vs. log TEHA was also plotted as shown in Fig. 2, which have a slope value of 1.19 indicating the involvement of one mole of TEHA for the extraction of one mole of sulfuric acid from the leach liquor.

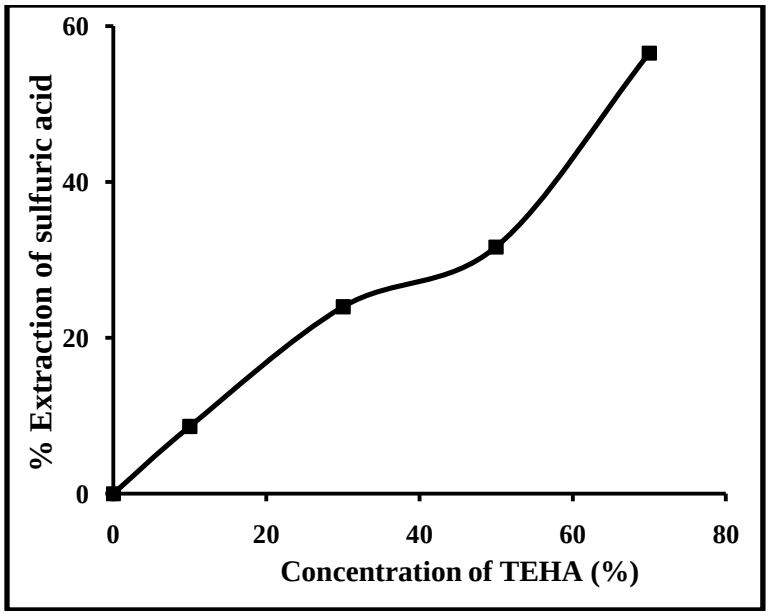


Fig. 1 Effect of extractant concentration on extraction of sulfuric acid.
[Experimental Conditions: Aq. Phase = 2.2M H_2SO_4, 10.76 g/L Cu, 0.38 g/L Ni, 0.07 g/L Pb & 2.55 g/L Fe, O/A ratio = 1/1, Time = 5 min]

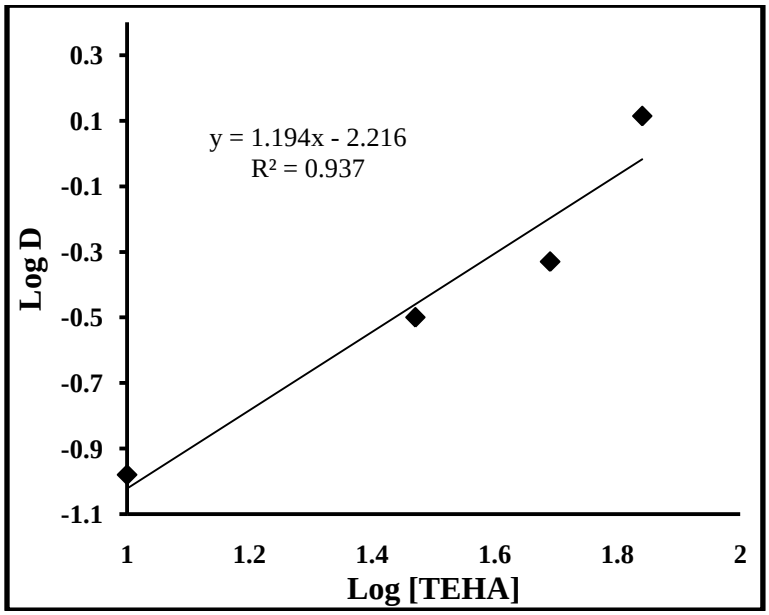


Fig. 2 Log D vs Log [TEHA].

6.2.1.1.2. <u>Effect of time and temperature on sulfuric acid extraction</u>

To optimize the contact time for H_2SO_4 extraction from original leached solution using 70% (v/v) TEHA diluted in kerosene, experiments were carried out at different time varying the range from 1 to 10 min maintaining O/A ratio 1/1. It was found that percentage extraction of H_2SO_4 increases from 37.56 to 56.56% as the contact time

increases from 1 to 5 min. Further increase in contact time shows negligible effect on acid extraction.

However, the effect of temperature on acid extraction was also noticed in order to reduce the viscosity of the extractant. But experiments done at different temperatures, ranging from 30 to 60°C, decreases the acid extraction from 55.7 to 46.6% (Fig. 3) as the loaded TEHA gets stripped back in the aqueous medium at higher temperature. Thus, 30°C was taken to be the optimized temperature for all the experiments.

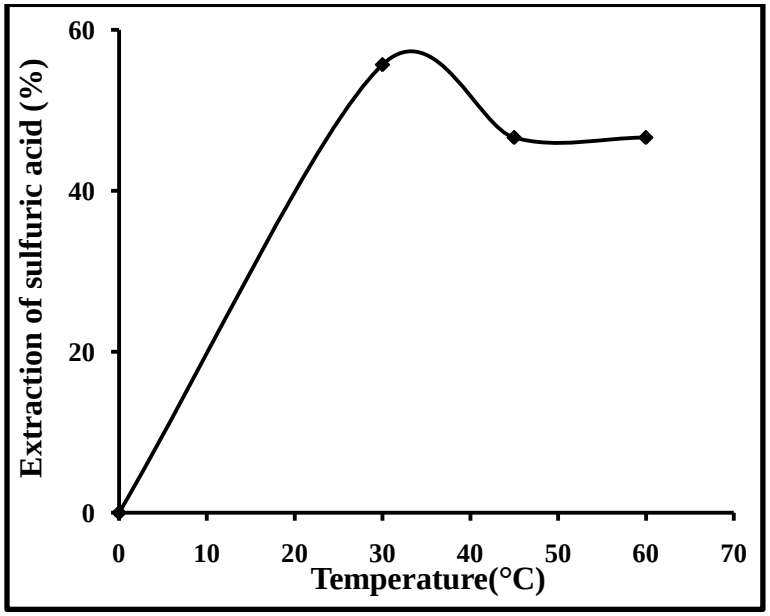


Fig. 3 Effect of temperature on extraction of sulfuric acid.
[Experimental Conditions: Aq. Phase = 2.2M H_2SO_4, 10.76 g/L Cu, 0.38 g/L Ni, 0.07 g/L Pb & 2.55 g/L Fe, Org. Phase = 70% TEHA, O/A ratio = 1/1, Time = 5 min]

6.2.1.1.3. <u>Effect of phase ratio (O/A) on sulfuric acid extraction</u>

The effect of O/A ratio on H_2SO_4 extraction was also studied from original leached solution containing 2.2M acid concentration. It was observed that H_2SO_4 extraction increases with the increase in O/A ratio. Maximum of 64.25% H_2SO_4 was extracted using 70% TEHA at O/A ratio 2/1 in 5 min of contact time as presented in Fig. 4. Further increase in phase ratio shows minor increase, thus, 2/1 ratio was taken to be optimum. In order to determine the number of stages required for complete acid recovery from leach liquor, Mc-Cabe Thiele plot was drawn using phase variation data (Fig. 5) which indicate that three stages are required for complete acid extraction at O/A ratio 2/1 with contact time of 5 min.

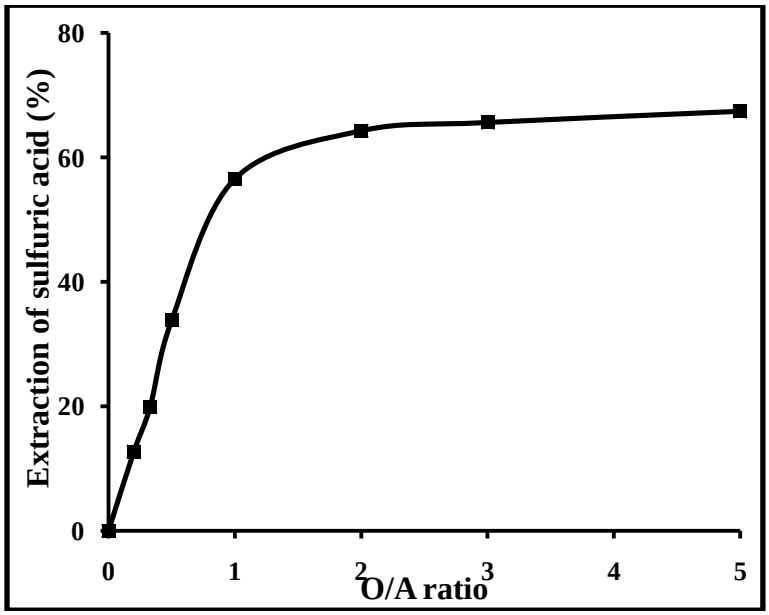


Fig. 4 Effect of O/A ratio on extraction of sulfuric acid.
[Experimental Conditions: Aq. Phase = 2.2M H_2SO_4, 10.76 g/L Cu, 0.38 g/L Ni, 0.07 g/L Pb & 2.55 g/L Fe, Org. Phase = 70% TEHA, Time = 5 min].

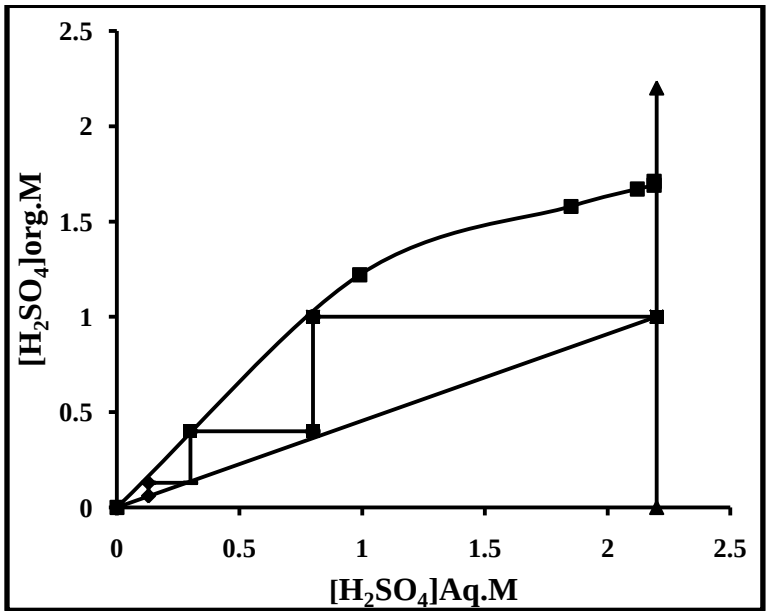


Fig. 5 Mc-Cabe Thiele plot for extraction of sulfuric acid.
[Experimental Conditions: Aq. Phase = 2.2M H_2SO_4, 10.76 g/L Cu, 0.38 g/L Ni, 0.07 g/L Pb & 2.55 g/L Fe, Org. Phase = 70% TEHA, O/A ratio = 2/1, Time = 5 min].

6.2.1.1.4. <u>Loading capacity of TEHA</u>

Loading capacity of the solvent being used was determined by repeated contact of 70% TEHA with leach liquor of pyrolysed PCBs at O/A ratio 1/1 for 5 min. In five contacts,

TEHA reagent got saturated and maximum loading capacity of the solvent was found to be 1.7M.

Stripping of the loaded TEHA was carried out using hot de-ionized water and was observed that complete stripping of H_2SO_4 takes place in three stages maintaining O/A ratio 1/1 and mixing time 10 min.

6.2.1.2. **Removal of iron**

Acid free original leached solution contains 2.55 g/L Fe along with 10.76 g/L Cu and other metals in minor amount. Prior to Cu extraction, air sparging is essential to remove Fe content as its presence might reduce the efficiency of Cu metal sheet during the process of electrowinning. For this, NaOH was added in the liquor to increase its pH up to 3.5 to 4.0 and heated at 80°C. Now Fe was removed from the aqueous solution by the process of air sparging which results in almost complete removal of iron by precipitating it as ferric hydroxide. The leach liquor left was analysed and found to contain negligible amount of Fe and was then again subjected to solvent extraction for selective recovery of Cu and Ni left in the leach liquor.

6.2.1.3. **Solvent extraction of copper**

6.2.1.3.1. Effect of contact time on copper extraction

10% (v/v) LIX 84IC diluted in kerosene was used to extract Cu from the acid and Fe free original leach liquor. Initially, effect of contact time on Cu extraction was studied which observed that increasing the contact time from 1 to 15 min, percentage extraction of Cu increases from 69.98 to 76.2%. However, in 5 min time almost 75% Cu was extracted so 5 min was taken to be optimum for further studies (Fig. 6). It was also found that along with Cu, minor amount of Ni was also co-extracted.

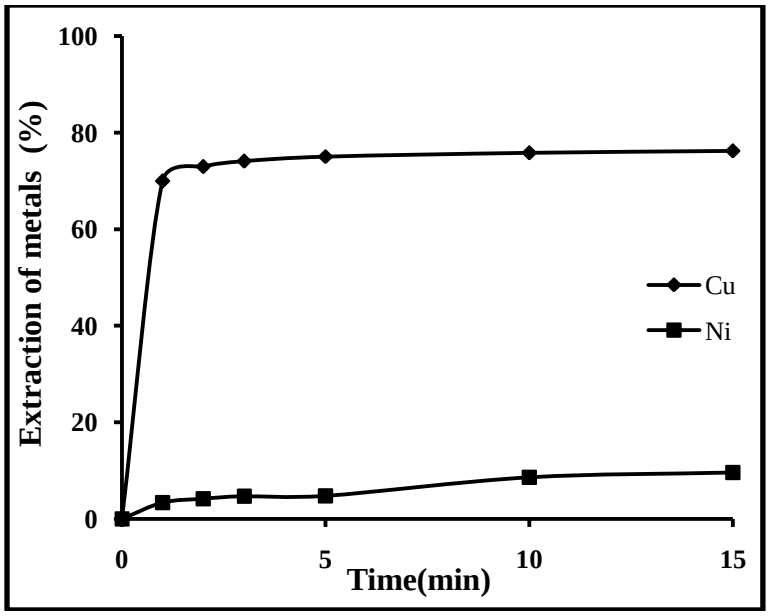


Fig. 6 Effect of time on extraction of Cu using 10% LIX 84IC.
[Experimental Conditions: Aq. Phase = 10.76 g/L Cu, 0.38 g/L Ni & 0.07 g/L Pb, Org. Phase = 10% LIX 84IC, O/A ratio = 1/1, Time = 5 min]

6.2.1.3.2. Effect of pH on copper extraction

The effect of pH was studied for the selective extraction of Cu from the original leach liquor containing 10.76 g/L Cu, 0.38 g/L Ni and 0.07g/L Pb. The extraction of Cu is mainly affected by the equilibrium pH, adjusted to a desired range. Using 10% LIX 84IC, Cu extraction increases from 32.90 to 90.51% and Ni from 0.55 to 11.03% with increase in pH from 0.69 to 3.04 as shown in Fig. 7 using O/A ratio 1/1 and maintaining equilibrium time of 5 min. It was observed that at pH 2.5, 89.3% Cu along with 5.07% Ni was extracted.

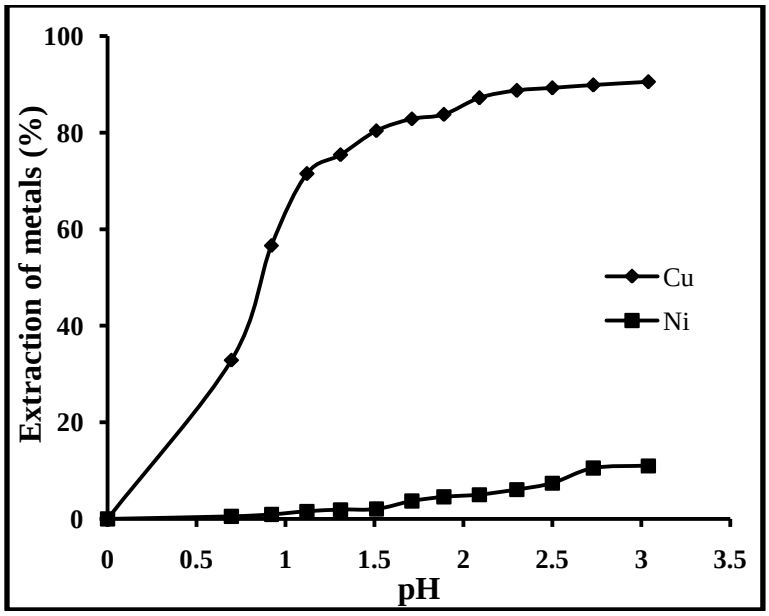


Fig. 7 Effect of pH on extraction of Cu using 10% LIX 84IC.
[Experimental Conditions: Aq. Phase = 10.76 g/L Cu, 0.38 g/L Ni & 0.07 g/L Pb, Org. Phase = 10% LIX 84IC, O/A ratio = 1/1, Time = 5 min].

6.2.1.3.3. Effect of extractant concentration on copper extraction

Extractant concentration plays an important role during metal extraction. Effect of different concentration of LIX 84IC varying from 5 to 20% was studied and found that Cu extraction increases from 71.06 to 98.5% with increase in extractant concentration from 5 to 20% as shown in Fig. 8. 10% LIX 84IC extracts about 89.97% Cu at equilibrium pH of 2.5 maintaining O/A ratio 1/1 and mixing time 5 min and thus, used for further studies. Along with Cu, 5.01% Ni was also co-extracted using 10% LIX 84IC.

A plot of Log D vs. Log LIX 84IC was also plotted as shown in Fig. 9 which have a slope value 2.045 indicating that 2 mole of extractant are associated with 1 mole of extracted metal species, thus, forming copper complex in the organic phase.

$$M^{2+}_{aq.} + 2[(HA)_2]_{org.} \leftrightarrow [MA_2.2HA]_{org.} + 2H^{+}_{aq.} \quad (36)$$

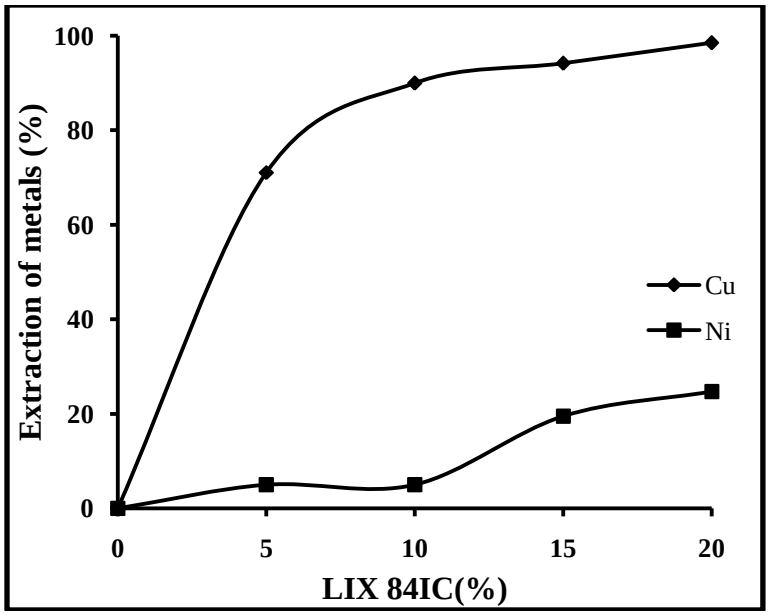


Fig. 8 Effect of extractant concentrations on extraction of Cu.
[Experimental Conditions: Aq. Phase = 10.76 g/L Cu, 0.38 g/L Ni & 0.07 g/L Pb, Org. Phase = 10% LIX 84IC, O/A ratio = 1/1, Time = 5 min, pH= 2.5].

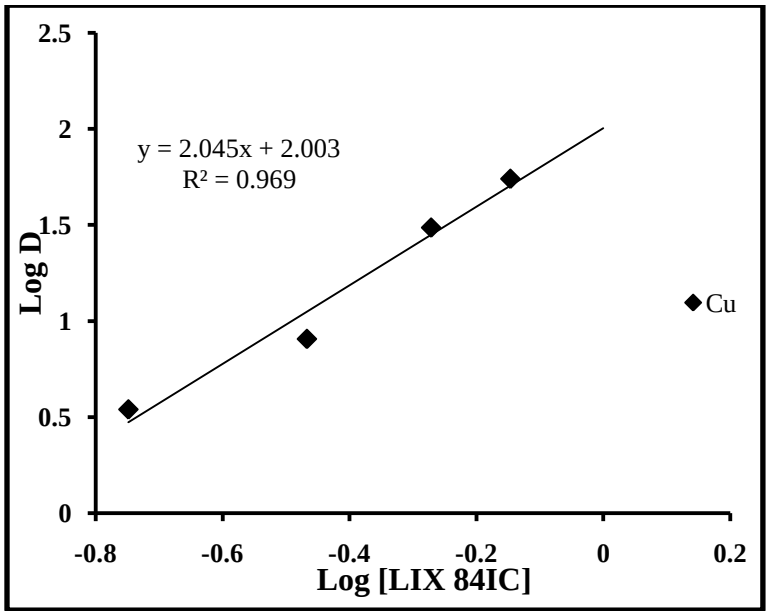


Fig. 9 Log D vs Log [LIX 84IC].

6.2.1.3.4. <u>Effect of phase ratio on copper extraction</u>

The effect of O/A ratio on extraction of Cu and along with co-extraction of Ni were also studied from original leach liquor solution containing 10.76 g/L Cu, 0.38 g/L Ni and 0.07 g/L Pb using 10% LIX 84IC diluted in kerosene at equilibrium pH 2.5 for 5 min. It was noticed that extraction of Cu and Ni increases from 32.6 to 99% and 1.55 to 15.2%,

respectively, with increase in O/A ratio from 1/3 to 3/1 with a contact time of 5 min as shown in Fig. 10. To determine the number of stages required for complete recovery of copper from leach liquor, Mc-Cabe Thiele plot was drawn using phase variation data as shown in Fig. 11, which indicate that two stages are required for maximum extraction of Cu at O/A ratio 1/1 maintaining mixing time 5 min. At pH 2.5, 88.4% Cu was extracted in first stage along with 5.07% Ni. In second stage, 99% Cu extraction was observed with 6.83% Ni co-extraction. Further increase in pH initiated precipitation of metals from leach liquor, and phase separation became complicated.

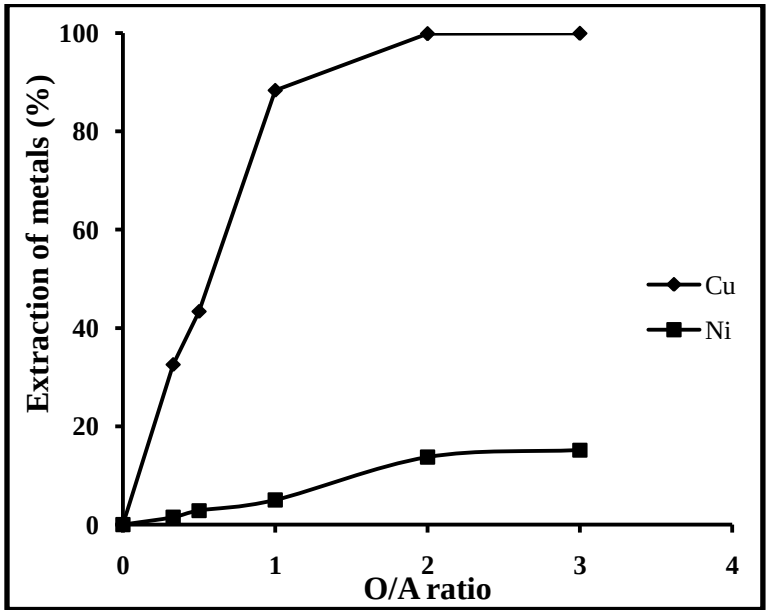


Fig. 10. Effect of O/A ratio on extraction of Cu.
[Experimental Conditions: Aq. Phase = 10.76 g/L Cu, 0.38 g/L Ni & 0.07 g/L Pb, Org. Phase = 10% LIX 84IC, Time = 5 min, pH = 2.5].

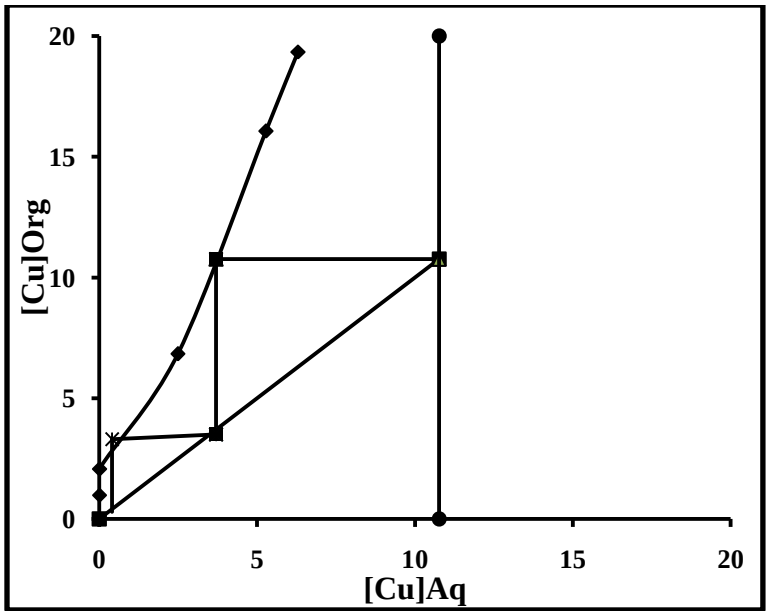


Fig. 11. Mc-Cabe Thiele plot for extraction of Cu.

6.2.1.3.5. Loading Capacity of LIX 84IC

Loading capacity of the 10% LIX 84IC was determined by repeated contact with the leach liquor (after acid extraction and iron removal) of poly-cracked (pyrolysed) PCBs at O/A ratio 1/1 for 5 min. In five contacts, 10% LIX 84IC got completely saturated with Cu and Ni and its loading capacity was found to be 10.38 g/L Cu and 0.0031g/L Ni as shown in Fig. 12.

6.2.1.3.6. Stripping of loaded LIX 84IC

Cu was stripped from the loaded LIX 84IC using 10% (v/v) sulfuric acid. In each set of experiment organic to strip solution ratio was maintained at 1/1. The results presented in Fig. 13 indicates that 99.99% Cu was stripped from loaded organic within 5 contacts at a phase ratio (O/A) of 1/1. Cu was recovered by electrolysis/crystallization from the strip solution.

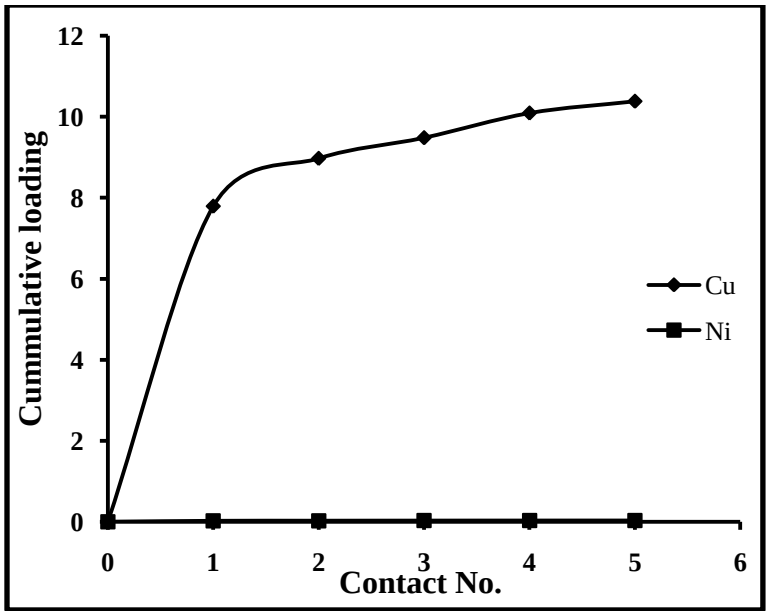


Fig. 12 Loading capacity of 10% LIX 84IC.
[Experimental Conditions: Aq. Phase = 10.76 g/L Cu, 0.38 g/L Ni & 0.07 g/L Pb, Org. Phase = 10% LIX 84IC, O/A= 1/1, Time = 5 min, pH = 2.5].

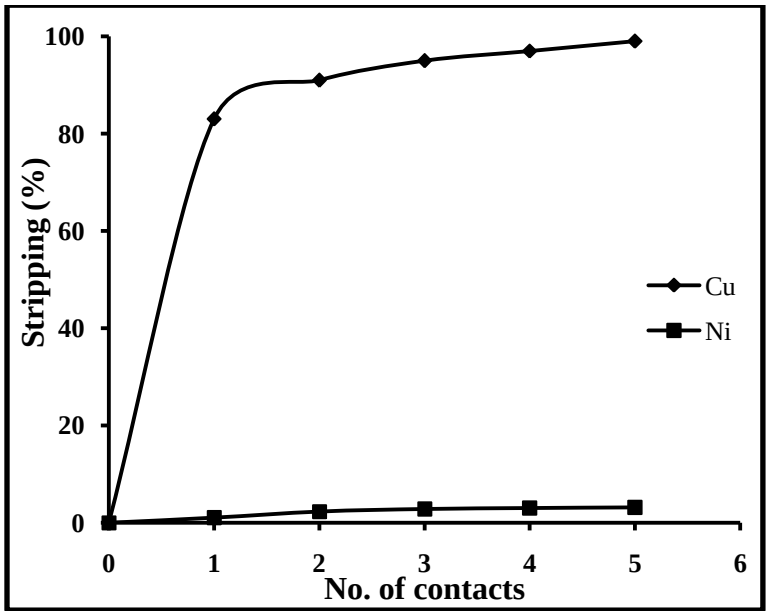


Fig. 13 Stripping of loaded 10% LIX 84IC.
[Experimental Conditions: Aq. Phase = 10% H_2SO_4, O/A= 1/1, Time = 5 min].

6.2.1.4. <u>Solvent extraction of nickel</u>

6.2.1.4.1. <u>Effect of pH on nickel extraction</u>

1% (v/v) LIX 84IC diluted in kerosene was used to extract Ni from the original leach liquor which are free from the acid, Fe and Cu. The effect of pH was studied for the extraction of Ni from the leach liquor containing 0.35 g/L Ni and 0.07 g/L Pb. The

extraction of Ni is mainly affected by the equilibrium pH, adjusted to a desired range. Using 1% LIX 84IC, Ni extraction increases from 5.20–95.30% as the pH increases from 3.67-5.48 as shown in Fig. 14 using O/A ratio 1/1 and maintaining equilibrium time of 15 min. A plot of Log D vs. pH was also made as shown in Fig. 15 which have slop value ~2 indicating that 2 mole of extractants are associated with 1 mole of extracted metal species.

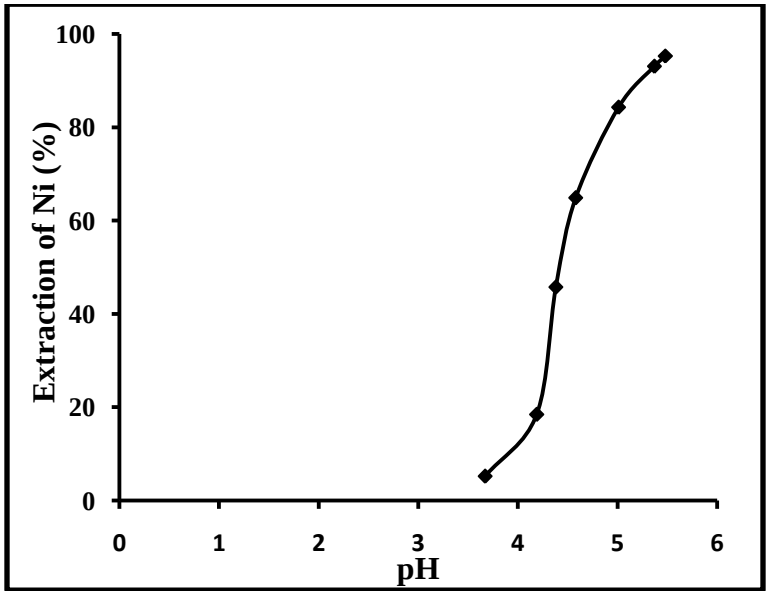


Fig. 14 Effect of pH on extraction of Ni using 1% LIX 84IC.
[Experimental Conditions: Aq. Phase = 0.35 g/L Ni & 0.07 g/L Pb, Org. Phase = 1% LIX 84IC, O/A ratio = 1/1, Time = 15 min].

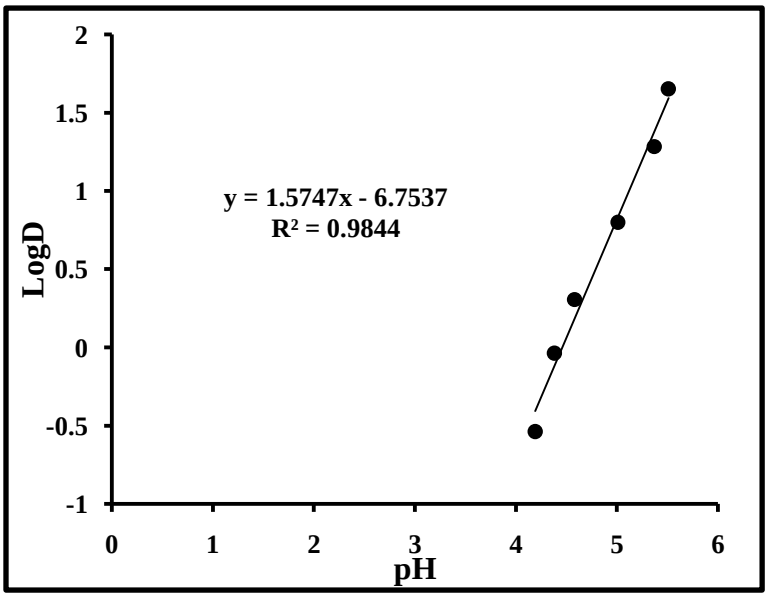


Fig. 15 Log D versus pH.

6.2.1.4.2. Effect of extractant concentration

The extraction of nickel was carried out using different concentration of LIX 84-IC diluted in kerosene in the range of 1-4%. Fig. 16 shows that extraction of Ni increases from 64.88-99.83% as the extractant concentration increases from 1–4% maintaining equilibrium pH 4.6, time 15 min at phase ratio O/A of 1/1.

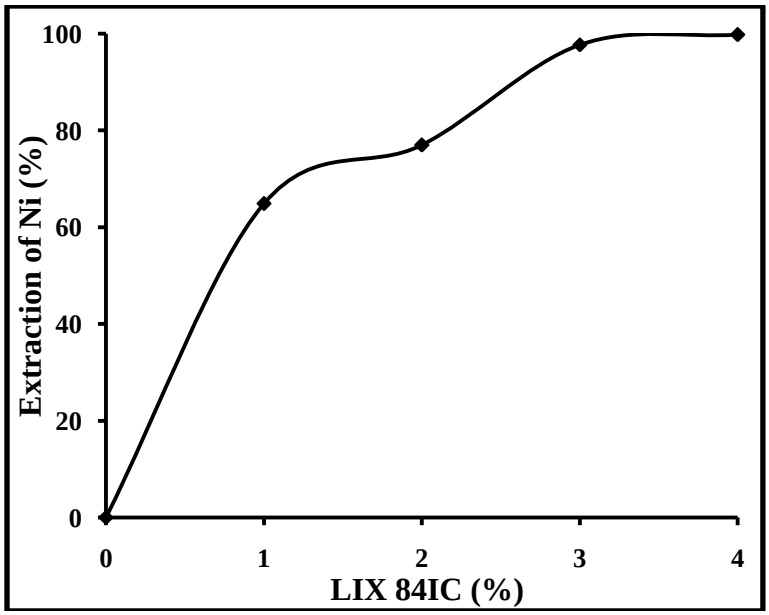


Fig. 16 Effect of extractant concentration on nickel extraction.
[Experimental Conditions: Aq. Phase = 0.35 g/L Ni & 0.07 g/L Pb, O/A ratio = 1/1, Time = 15 min, pH = 4.6].

6.2.1.4.3. Effect of phase ratio on nickel extraction

Phase ratio variation was also carried out with 1% LIX 84IC in the range of 1/3 to 3/1. The extraction of Ni increases from 34.08-96.59% with increases in O/A ratio from 1/3 to 3/1 as shown in Fig. 17. 96.22% nickel was extracted at O/A ratio 2/1, equilibrium pH 4.58 in contact time 15 min. In order to determine number of theoretical counter current stages required for complete extraction of nickel from leach liquor, Mc-Cabe Thiele (Fig. 18) was constructed using ratio variation data. The results presented in figure showed requirement of two stages for complete extraction nickel at O/A ratio is 2/1.

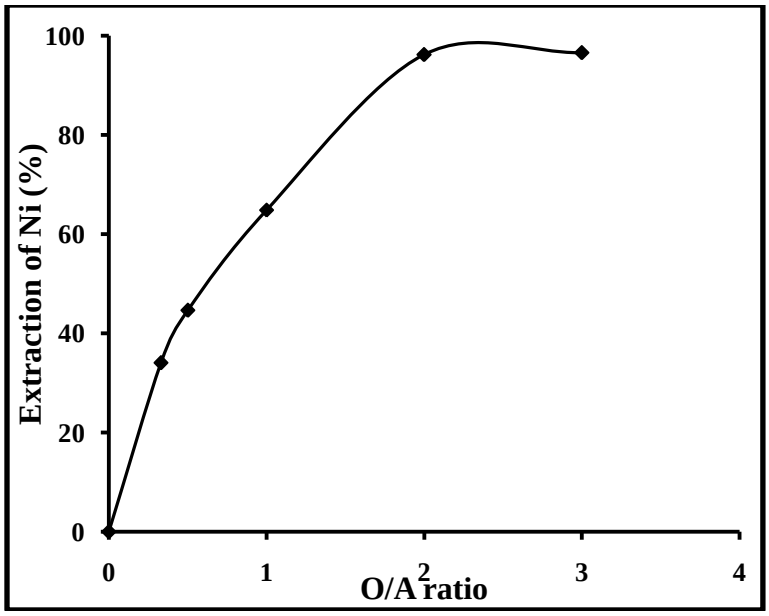


Fig. 17 Effect of O/A ratio on extraction of Ni.
[Experimental Conditions: Aq. Phase = 0.35 g/L Ni & 0.07 g/L Pb, Org. Phase = 1% LIX 84IC, Time = 15 min, pH = 4.58]

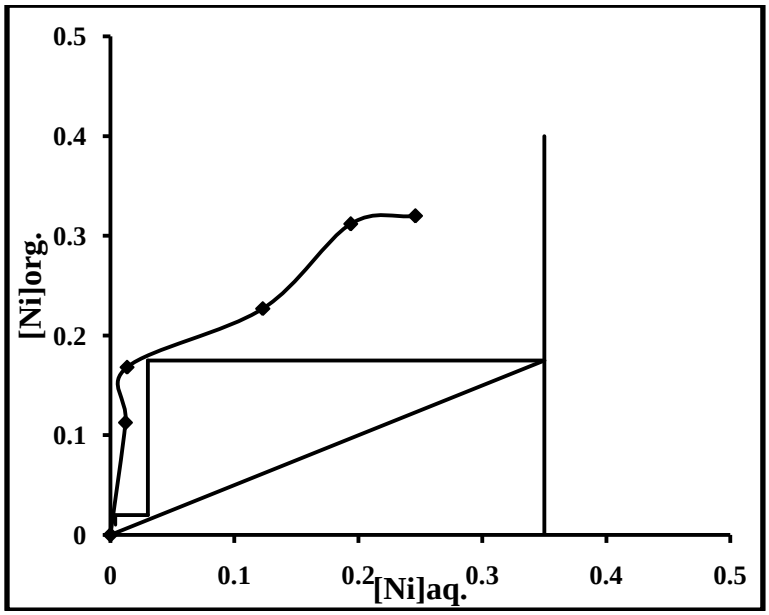


Fig. 18 Mc-Cabe Thiele plot for extraction of Ni.

6.2.1.4.4. Loading capacity of LIX 84IC

Loading capacity of the 1% LIX 84IC was determined by repeated contact of 1% LIX 84IC with fresh leach liquor. In five contacts, 1% LIX 84IC got saturated and loading capacity of the solvent was found to be 1.047 g/L at equilibrium pH 4.58, time 15 min. at O:A ratio 1:1.

6.2.1.4.5. Stripping of loaded LIX 84IC

Ni was stripped from the loaded LIX 84IC using 10% (v/v) sulfuric acid. 99.99% Ni was stripped from loaded organic in a single contact at a phase ratio (O/A) of 1/1 maintaining equilibrium time 5 min. Ni could be recovered by electrolysis/crystallization from the strip solution.

In complex system where more than one metals are present in the solution, the solvent-extraction is recommendable as it is more selective in comparison to Ion-exchange. Therefore, the solvent-extraction studies is feasible technique for the recovery of Ni from the leach liquor. Organic can be regenerated and cost of produced Ni competes the feasibility of Ni.

6.2.2. Conclusions

- Leach liquor obtained containing 2.2M H_2SO_4, 10.76 g/L Cu, 0.38 g/L Ni, 0.07 g/L Pb & 2.55 g/L Fe was subjected to acid extraction using 70% TEHA diluted in kerosene. It was found that three stages are required for complete acid extraction taking O/A ratio 2/1 and mixing time of 5 min.
- Prior to Cu extraction, air sparging is essential to remove Fe content as its presence might reduce the efficiency of Cu metal sheet during the process of electrowinning.
- Further, 10% LIX 84IC diluted in kerosene was used for complete extraction of Cu which requires two stages at pH 2.5 maintaining O/A ratio 1/1 and mixing time of 5 min. Ni was left in the raffinate with its minor co-extraction of 6.83% along with Cu. 99.99% Cu was stripped from loaded organic using 10% (v/v) sulfuric acid within 5 contacts at a phase ratio (O/A) of 1/1.
- Further, 1% LIX 84IC diluted in kerosene was used for complete extraction of Ni which requires two stages at pH 4.58 maintaining O/A ratio 2/1 and mixing time of 15 min. Ni was stripped from the loaded LIX 84IC using 10% (v/v) sulfuric acid. 99.99% Ni was stripped from loaded organic in a single contact at a phase ratio (O/A) of 1/1 maintaining equilibrium time 5 min.

The complete process flow-sheet for the recovery of metals from waste PCBs is presented in Fig. 19.

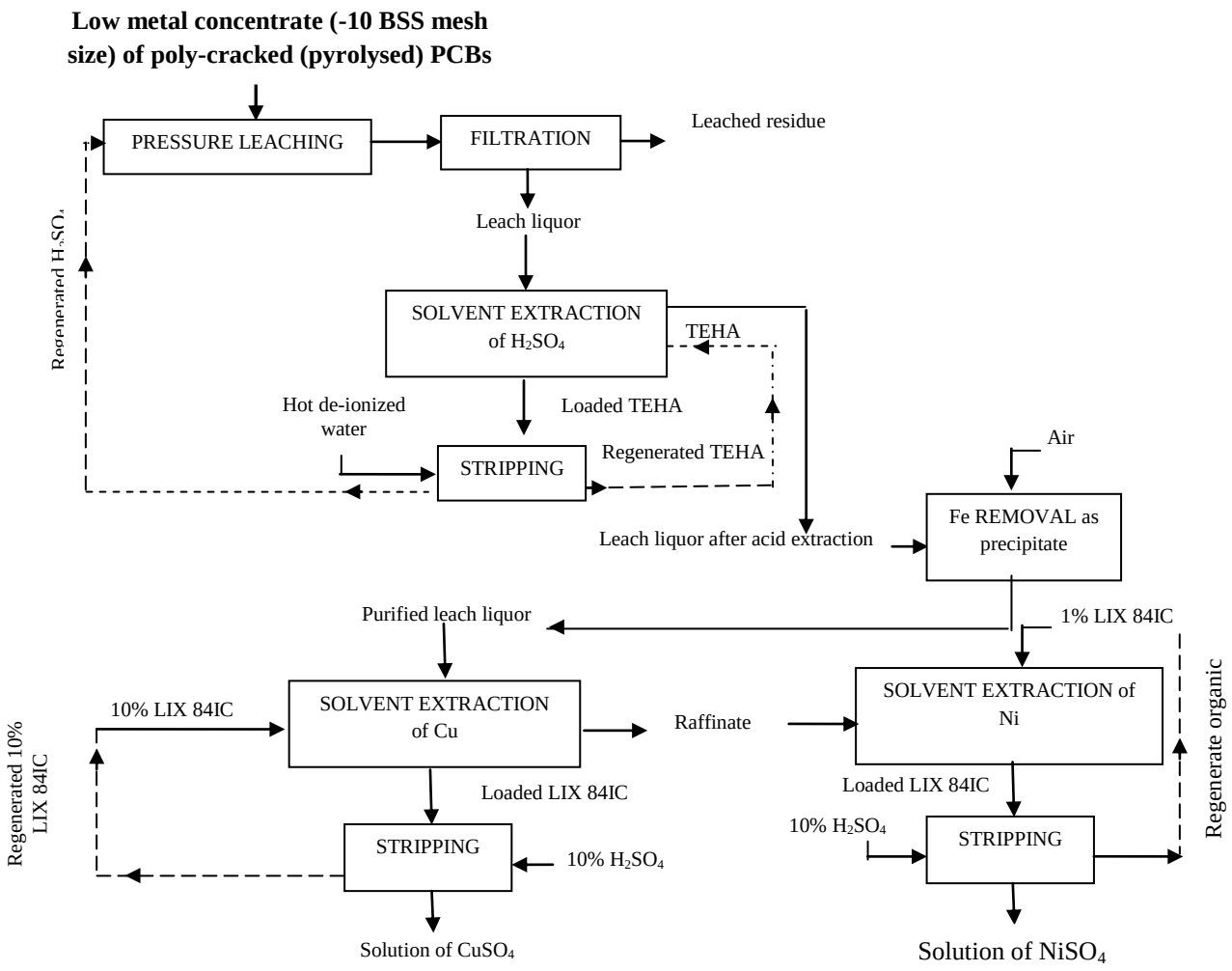


Fig. **19** Process flow sheet for recovery of metals from low metal concentrate (-10 mesh size, i.e. < 2mm size) of poly-cracked (pyrolysed) PCBs.

6.3. Extraction of nitric acid and metals from Leach liquor-II (nitrate leach liquor of high metal concentrate (+10 mesh size) of poly-cracked (pyrolysed) PCBs)

6.3.0. Materials & methods

Leach liquor containing HNO_3-3.6M, Cu-20.72 g/L, Ni-0.0156 g/L, Fe-0.058 g/L and Pb-0.0475 g/L was generated by atmospheric leaching of high metal concentrate (+10 mesh size i.e, >2mm size) of pyrolysed PCBs in nitric acid. This leach liquor was subjected to solvent-extraction for recovery of acid and metals. The effect of various process parameters viz. time, pH, extractant concentration, O/A ratio were studied during solvent-extraction studies. The aqueous raffinate was analysed to know metals present. Organic reagent tri-butyl phosphate (TBP) was (supplied by Luoyang Aoda Chemical Ltd., China) used for acid extraction. 2-hydroxy-5-nonylacetophenone oxime, commercially known as LIX 84IC employed for extraction of copper and nickel was supplied by M/s Cognis Corporation, Ireland (Earlier M/s Henkel Inc., Tucson). Aqueous samples were prepared using distilled water. All other chemicals used were of analytical grade reagents.

6.3.1. Results & discussion

6.3.1.1. Solvent extraction of nitric acid

The acidic content of the leach liquor was found to be 3.6M, removal of which is essential prior to metal extraction from industrial and environmental point of view. The solvent tri-butyl phosphate (TBP) was used for extraction of nitric acid from leach liquor of metal enriched poly-cracked (pyrolysed) PCBs. Various process parameters viz. extractant concentration, O/A ratio were studied to optimized the experimental condition for the extraction of nitric acid.

6.3.1.1.1. Effect of extractant concentration on nitric acid extraction

Extraction of nitric acid from leach liquor was carried out using different concentration of TBP in the range of 15.0 to 60.0% (v/v) diluted in kerosene. The results presented in Fig. 20 show that extraction of HNO_3 increases from 16.7 to 45.8% with increase in extractant concentration 15 to 60% (v/v) at O/A of 1/1 and mixing time of 12 min. During the

extraction of nitric acid by TBP from leach liquor, the co-extraction of other metals was not found.

A plot of Log D vs. Log TBP was also plotted as shown in Fig. 21, which have a slope value of 1.08 indicating the involvement of one mole of TBP for the extraction of one mole of nitric acid from the leach liquor. The extraction equilibrium for nitric acid using TBP can therefore be expressed as:

$$TBP.H_2O_{org} + HNO_{3aq} = TBP.\ HNO_{3org} + H_2O_{aq} \quad (37)$$

A strong $TBP.HNO_3$ complex forms by hydrogen bonding at the P=O site of the TBP replacing the more weakly held water of a $TBP.H_2O$ complex and causing the water content of the organic phase to decrease [192].

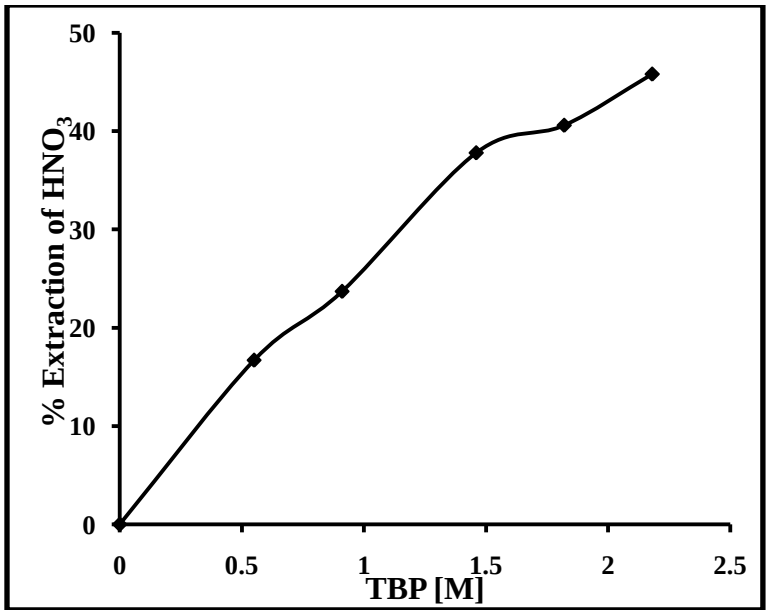


Fig. 20 Effect of extractant concentration on extraction of nitric acid.
[Experimental Conditions: Aq. Phase 20.72 g/L Cu, 0.0156 g/L Ni, 0.058 g/L Fe & 0.0475 g/L Pb O/A ratio 1/1, Time 12 min].

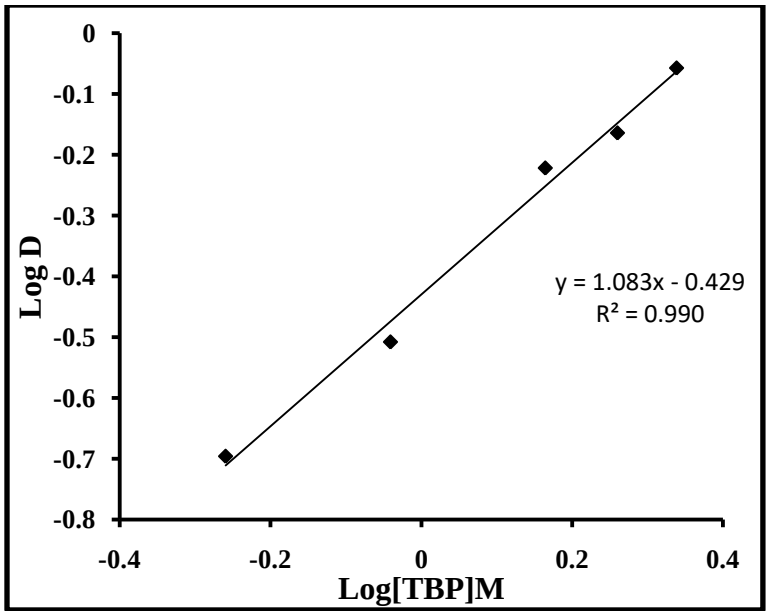


Fig. 21 Log D vs. Log [TBP].

6.3.1.1.2**.** Effect of phase ratio (O/A) on nitric acid extraction

The effect of O/A ratio on HNO_3 extraction was also studied from leached solution containing 3.6M acid concentration. It was observed that extraction of HNO_3 increases with the increase in O/A ratio. The maximum extraction of HNO_3 was found 76.4% using 60.0% TBP at O/A ratio 3/1 in 12 min as shown in Fig. 22. In order to determine the number of stages required for complete nitric acid recovery from leach liquor of high metal concentration of poly-cracked PCBs, Mc-Cabe Thiele plot was drawn using phase variation data (Fig. 23) which indicate that three stages are required for 98% nitric acid extraction at O/A ratio 3/1 with contact time of 12 min. After the solvent extraction of nitric acid from the leach liquor using TBP as extractant around 0.07M (0.001 g/L) acid was found to be left in the solution.

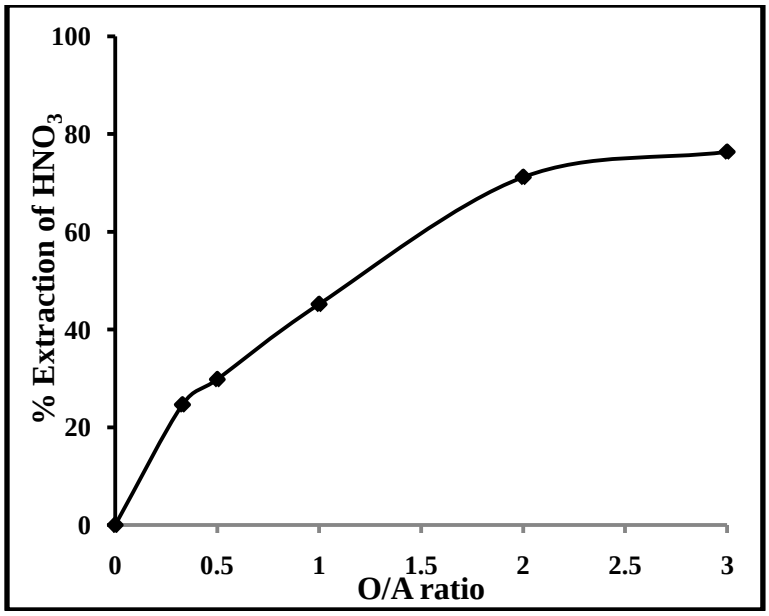


Fig. 22 Effect of O/A ratio on extraction of nitric acid.
[Experimental Conditions: Aq. Phase 3.6M HNO_3, 20.72 g/L Cu, 0.0156 g/L Ni, 0.058 g/L Fe & 0.0475 g/L Pb, Org. Phase 60% TBP, Time 12 min].

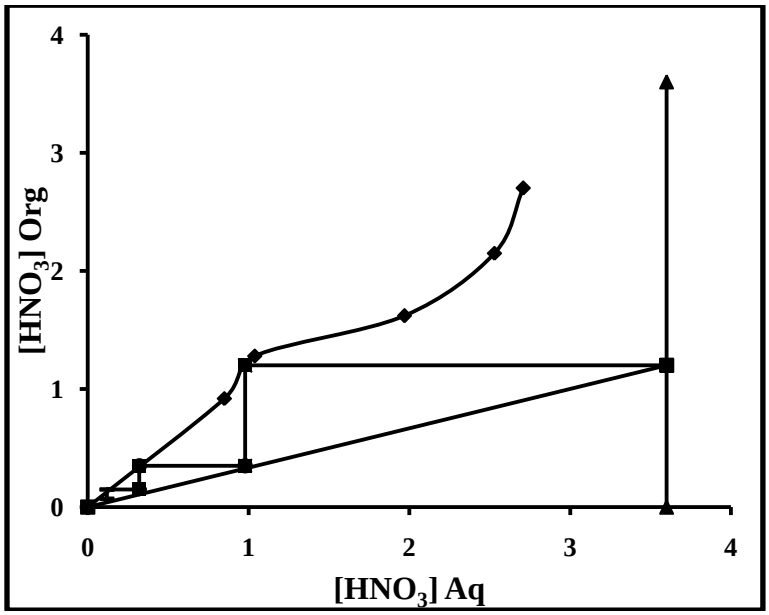


Fig. 23 Mc-Cabe Thiele plot for extraction of nitric acid.
[Experimental Conditions: Aq. Phase 3.6M HNO_3, 20.72 g/L Cu, 0.0156 g/L Ni, 0.058 g/L Fe & 0.0475 g/L Pb, Org. Phase 60% TBP, O/A ratio 3/1, Time 12 min].

6.3.1.1.3. Loading capacity of TBP

Loading capacity of the solvent was studied by repeated contact of 60% TBP with leach liquor of high metal concentrate of poly-cracked (pyrolysed) PCBs at O/A ratio of 1/1 for 12 min. In four contacts, maximum loading capacity of TBP was found to be 2.7M and

after that the reagent got saturated. Stripping of the loaded TBP was carried out using de-ionized water and was observed that complete stripping of nitric acid takes place in 4 stages maintaining O/A ratio of 1/1 and mixing time of 12 min.

Solvent-extraction of HNO_3 using 60% TBP at O/A ratio 3/1 and stripping of HNO_3 at O/A ratio 1/1 seems to be very feasible in comparison to the process reduced pressure distillation as it is energy intensive. However, in solvent-extraction technique extractant can be recycled. The recycling of extractant makes the process feasible and eco-friendly.

6.3.1.2. Removal of iron

After acid extraction, leach liquor of high metal concentrate of poly-cracker ash of PCBs contained 0.001 g/L (0.07 M) HNO_3, 20.72 g/L Cu, 0.0156 g/L Ni, 0.058 g/L Fe & 0.0475 g/L Pb. Air sparging technique was used for the removal of iron as precipitate. The presence of iron may reduce the efficiency of copper metal deposition during electrowinning. For proper precipitation of Iron, NaOH was added in the leach liquor (free from acid) to increase its pH in the range of 3.5 to 4.0 and heated at 80°C. Further, Fe was removed from the acid free leach liquor, Fe get precipitated as ferric hydroxide by air sparging. Acid and iron free leach liquor could be used for the separation of copper from actual leach solution by solvent extraction/electro-winning.

6.3.1.3. Solvent extraction of copper

6.3.1.3.1. Effect of pH on copper extraction

After the removal of acid and iron from the leach liquor of high metal concentrate of poly-cracked PCBs, the leach liquor was further used for the copper extraction process. The effect of pH was studied for the selective extraction of copper from the leach liquor containing 0.001 g/L HNO_3, 21.8 g/L Cu, 0.0018 g/L Fe, 0.016 g/L Ni & 0.048 g/L Pb. Fig. 24 shows that the extraction of copper increases from 30.46 to 99.78% with increase in pH from 0.81 to 3.1 by using 25% LIX 84IC at O/A ratio 1/1 and maintaining equilibrium time of 20 min. It was observed that at pH 2.5, 92.4% Cu along with 7.97% Ni was co-extracted. It was observed that extraction of nickel was very low in comparison to copper extraction. In Fig. 25, Log D vs pH is shown in which the plots are linear with a slope of 1.63, indicating the release of two H^+ ion leading to extraction of

copper. The extraction equilibrium of Cu(II) from the leach liquor with LIX 84IC as an extractant may be represented as:

$$Cu^{2+}_{aq} + 2RA_{org} \longrightarrow CuR_{2(org)} + 2H^{+}_{aq} \quad (38)$$

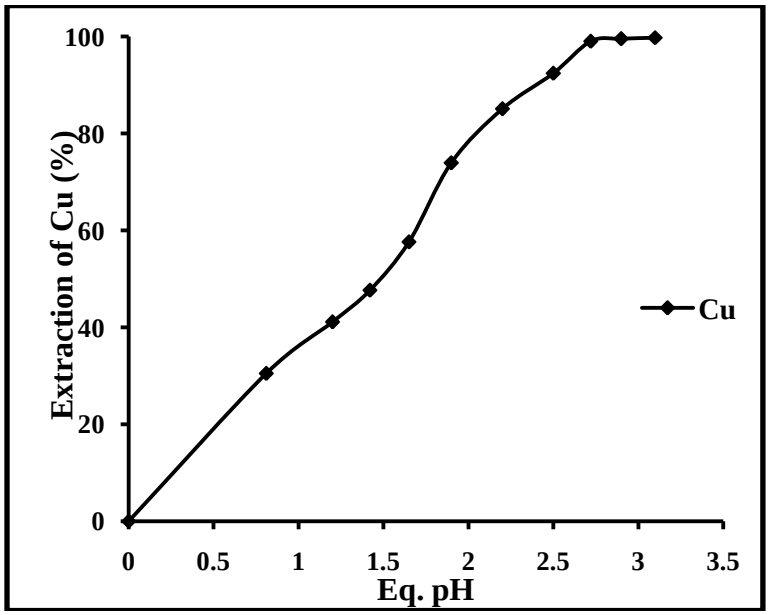


Fig. 24 Effect of pH on extraction of Cu using 25% LIX 84IC.
[Experimental Conditions: Aq. Phase 21.8 g/L Cu, 0.0156 g/L Ni & 0.0475 g/L Pb, Org. Phase 25% LIX 84IC, O/A ratio 1/1, Time 20 min].

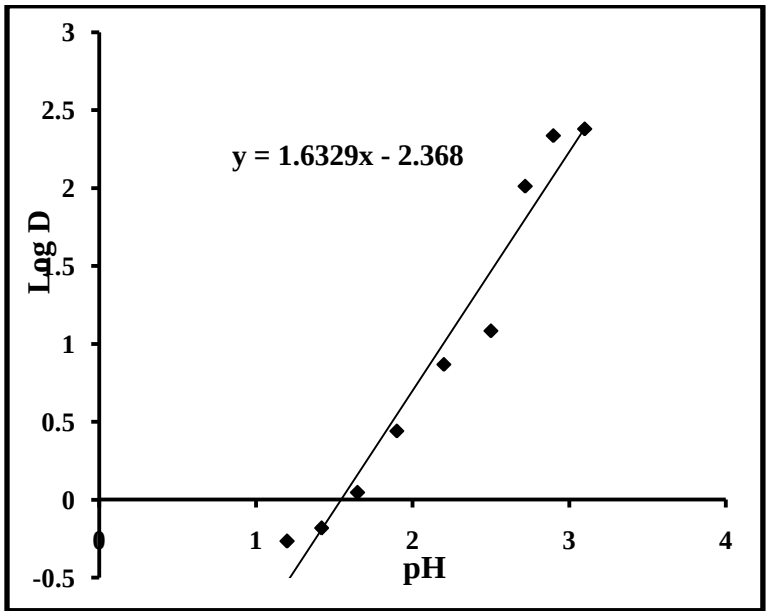


Fig. 25 Log D vs pH.

6.3.1.3.2. Effect of phase ratio on copper extraction

The effect of O/A ratio was studied for the extraction of copper from leach liquor solution containing 0.001 g/L HNO_3, 21.8 g/L Cu, 0.0018 g/L Fe, 0.016 g/L Ni & 0.048 g/L Pb using 25% LIX 84IC diluted in kerosene at equilibrium pH 2.5 and mixing time 20 min. The extraction of Cu increases from 33.5 to 99.8% with increase in O/A ratio from 1/3 to 3/1 with a contact time of 20 min as shown in Fig. 26.

To determine the number of stages required for complete recovery of copper from leach liquor, Mc-Cabe Thiele plot was drawn using phase variation data as shown in Fig. 27, which indicate that two stages are required for complete extraction of Cu at O/A ratio 1/1 maintaining mixing time 20 min. At pH 2.5, 92.4% and 99.9% Cu was extracted in first stage and second stage, respectively. Further, increase in pH initiated precipitation of metals from leach liquor, and phase separation became complicated.

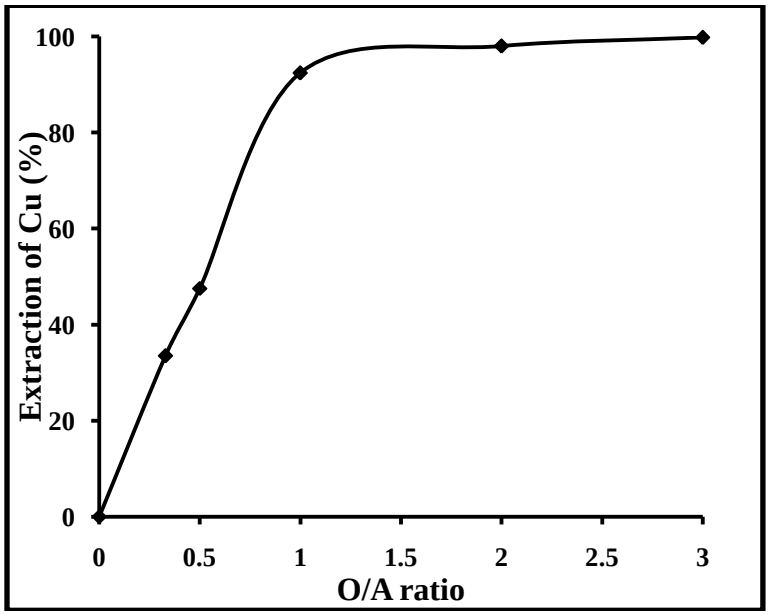


Fig. 26 Effect of O/A ratio on extraction of Cu using 25% LIX 84IC.
[Experimental Conditions: Aq. Phase 21.8 g/L Cu, 0.0156 g/L Ni & 0.0475 g/L Pb, Org. Phase 25% LIX 84IC, pH 2.5, Time 20 min].

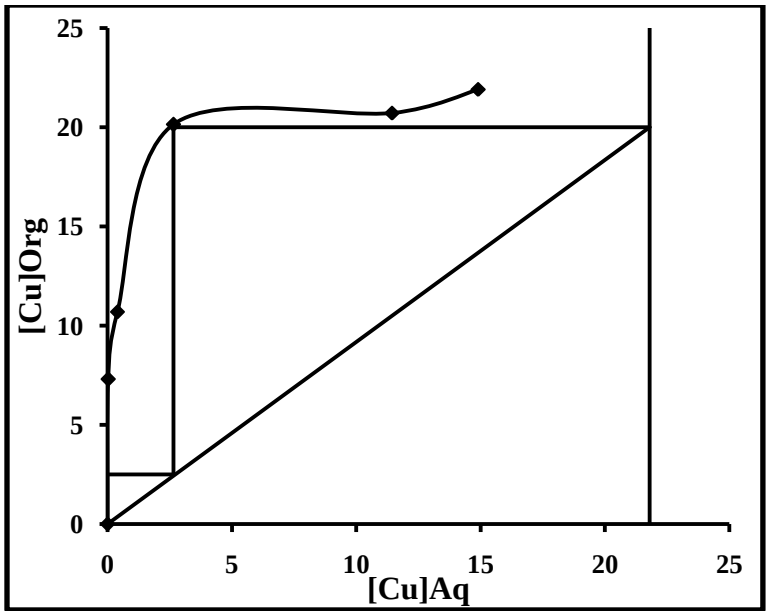


Fig. 27 Mc-Cabe Thiele plot for extraction of Cu.

6.3.1.3.3. Loading capacity of 25% LIX 84IC

Loading capacity of the 25% LIX 84IC was determined by repeated contact with the leach liquor (after acid extraction and iron removal) of poly-cracked (pyrolysed) PCBs at O/A ratio 1/1 for 5 min. In five contacts, 25% LIX 84IC got completely saturated with Cu its loading capacity was found to be 22.7 g/L Cu.

6.3.1.3.4. Stripping studies

Cu solution was stripped from the loaded LIX 84IC using 10% (v/v) sulfuric acid. In each set of experiment organic to strip solution ratio was maintained at O/A ratio of 1/1. 99.9% Cu was stripped from loaded organic within five contacts at a phase ratio (O/A) of 1/1. The obtained strip solution ($CuSO_4$ solution) was further processed for copper electrowinning to obtain copper sheet (discussed in chapter-8). The raffinate obtained after extraction of acid, Fe & Cu having composition 0.0143 g/L Ni & 0.0473 g/L Pb.

6.3.1.4. Solvent extraction of nickel

After the extraction of acid, iron and copper, the solution was evaporated to make concentrate solution containing 0.28 g/L Ni & 0.89 g/L Pb solution. 1% (v/v) LIX 84IC diluted in kerosene was used to extract Ni from the concentrate leach liquor. The effect of

pH was studied for the extraction of Ni. Using 1% LIX 84IC, Ni extraction was found to be increased from 6.2–95.1% with the increase in pH from 3.5-5.2 as shown in Fig. 28 using O/A ratio 1/1 and maintaining equilibrium time of 15 min. Ni was stripped from the loaded LIX 84IC using 10% (v/v) sulfuric acid. 99.99% Ni was stripped from loaded organic in a single contact at a phase ratio (O/A) of 1/1 maintaining equilibrium time 5 min. Ni could be recovered by electrolysis/crystallization from the strip solution. After removal of acid, Fe, Cu & Ni from the leach liquor of high metal concentrate of poly-cracked PCBs, the leach liquor was further used for the lead recovery by cementation process (discussed in chapter-7).

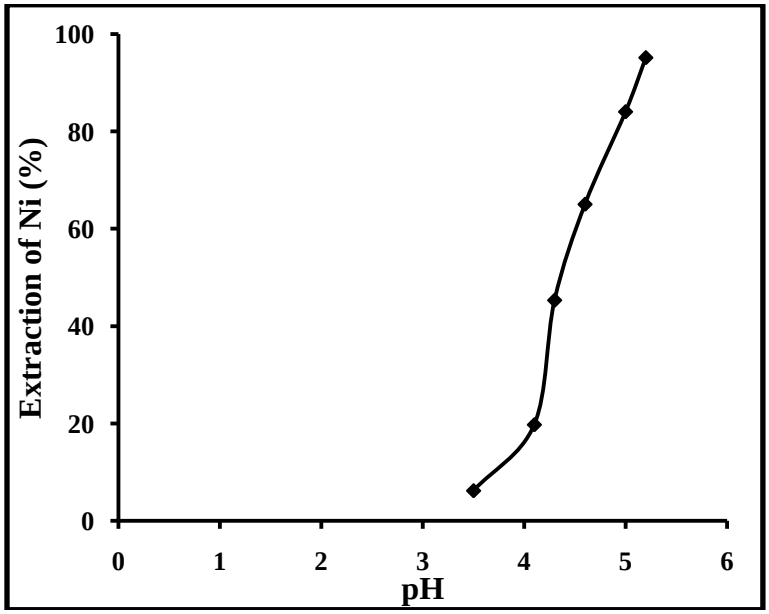


Fig. 28 Effect of pH on extraction of Ni using 1% LIX 84IC.
[Experimental Conditions: Aq. Phase 0.282 g/L Ni & 0.89 g/L Pb, Org. Phase 1% LIX 84IC, O/A ratio 1/1, Time 15 min].

6.3.1.5. <u>Characterization of value added product</u>

The purified copper and nickel sulfate solution (strip solution) obtained after solvent extraction from LIX 84IC from the leach liquor (nitrate and sulfate) of poly-cracked (pyrolysed) PCBs was evaporated to prepare crystals of copper sulfate (99% pure) and nickel sulfate (99% pure). The copper and nickel sulfate salt produced was characterized by XRD (Fig. 29 & 30), which confirms the formation of copper and nickel sulfate. Copper sulfate is used as a mordant in vegetable dyeing, jewelry, medical and public health, manufacture of other salts. It is also used to etch zinc or copper plates

for printmaking. Nickel sulfate is used in the laboratory for manufacture of other salts. It is also useful in biochemistry and molecular biology.

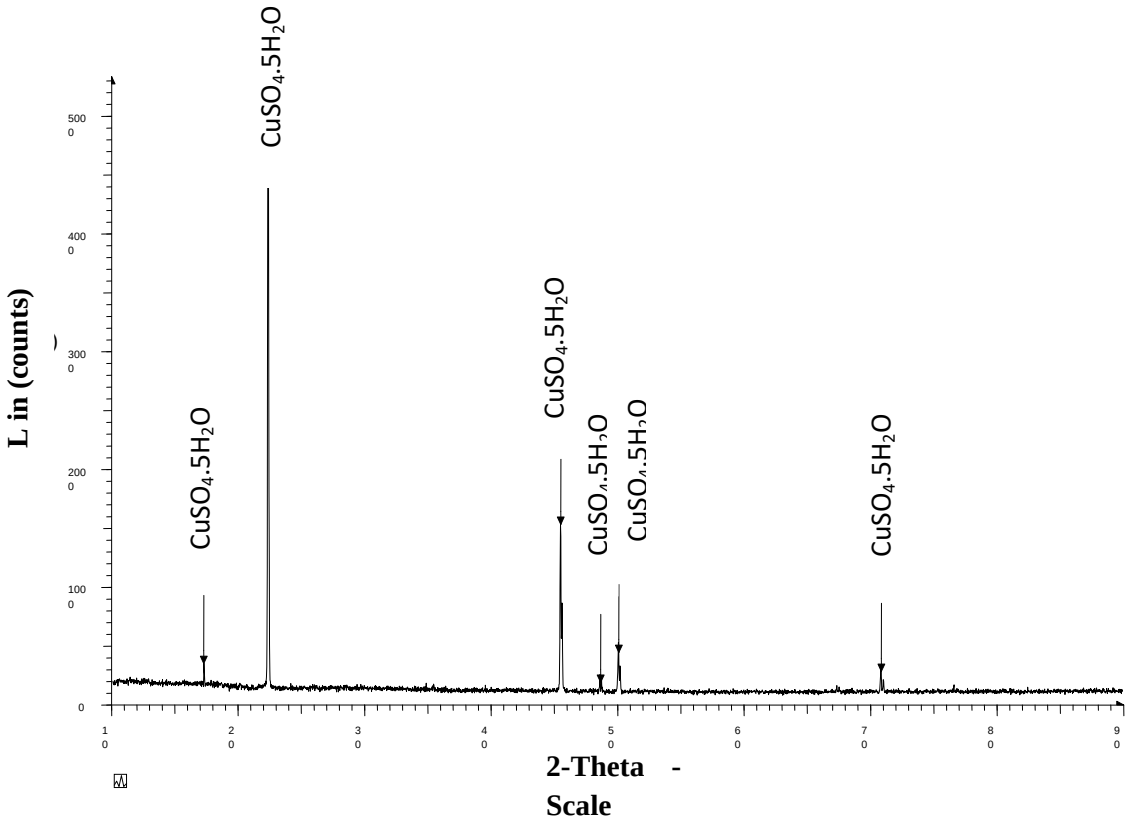


Fig. 29 XRD of copper sulfate salt obtained after evaporation.

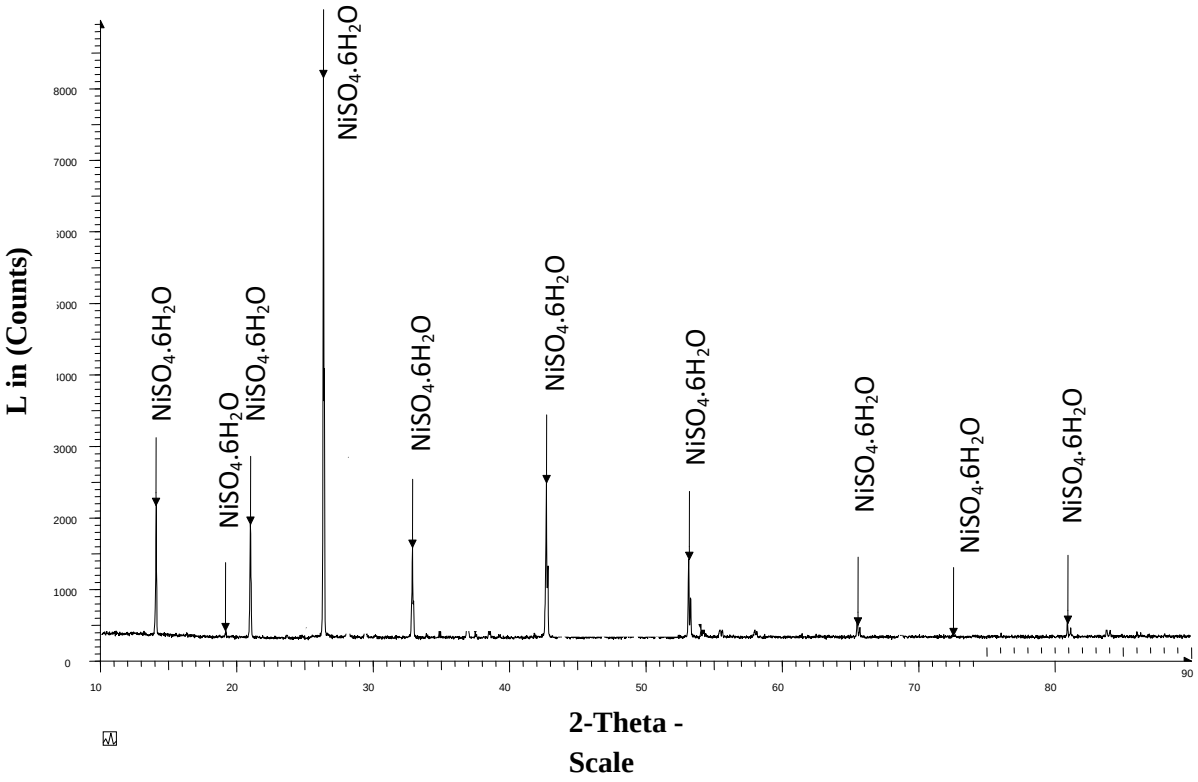


Fig. 30 XRD of nickel sulfate salt obtained after evaporation.

6.3.2. <u>Conclusions</u>

- Leach liquor obtained containing 3.6M HNO_3, 20.72 g/L Cu, 0.0156 g/L Ni, 0.058 g/L Fe & 0.0475 g/L Pb was subjected to acid extraction using 60% TBP diluted in kerosene. It was found that three stages are required for almost complete acid extraction taking O/A ratio 3/1 and mixing time of 12 min.
- Prior to Cu extraction, air sparging was done to remove Fe content, the presence of which reduces the efficiency of Cu metal sheet by the process of electrowinning.
- Further, 25% LIX 84IC diluted in kerosene was used for complete extraction of Cu which required two stages at pH 2.5 maintaining O/A ratio 1/1 and mixing time of 20 min. By 10% H_2SO_4, 99.99% Cu was stripped from loaded organic within five contacts at a phase ratio (O/A) of 1/1.
- Using 1% LIX 84IC diluted in kerosene, 95% Ni was extracted from leached solution (free from acid, Fe & Cu) using O/A ratio 1/1, at pH 5.2 maintaining

mixing time of 15 min. Ni was stripped from the loaded LIX 84IC using 10% (v/v) sulfuric acid. 99.99% Ni was stripped from loaded organic in a single contact at a phase ratio (O/A) of 1/1 maintaining equilibrium time 5 min. Ni could be recovered by electrolysis/crystallization from the strip solution. After removal of acid, Fe, Cu & Ni from the leach liquor of high metal concentrate of poly-cracked PCBs, the leach liquor was further used for the lead recovery by cementation process (discussed in chapter-7). Process flow sheet for extraction of acid and metals from nitrate leach liquor of high metal concentrate of pyrolysed PCBs (Fig. 31).

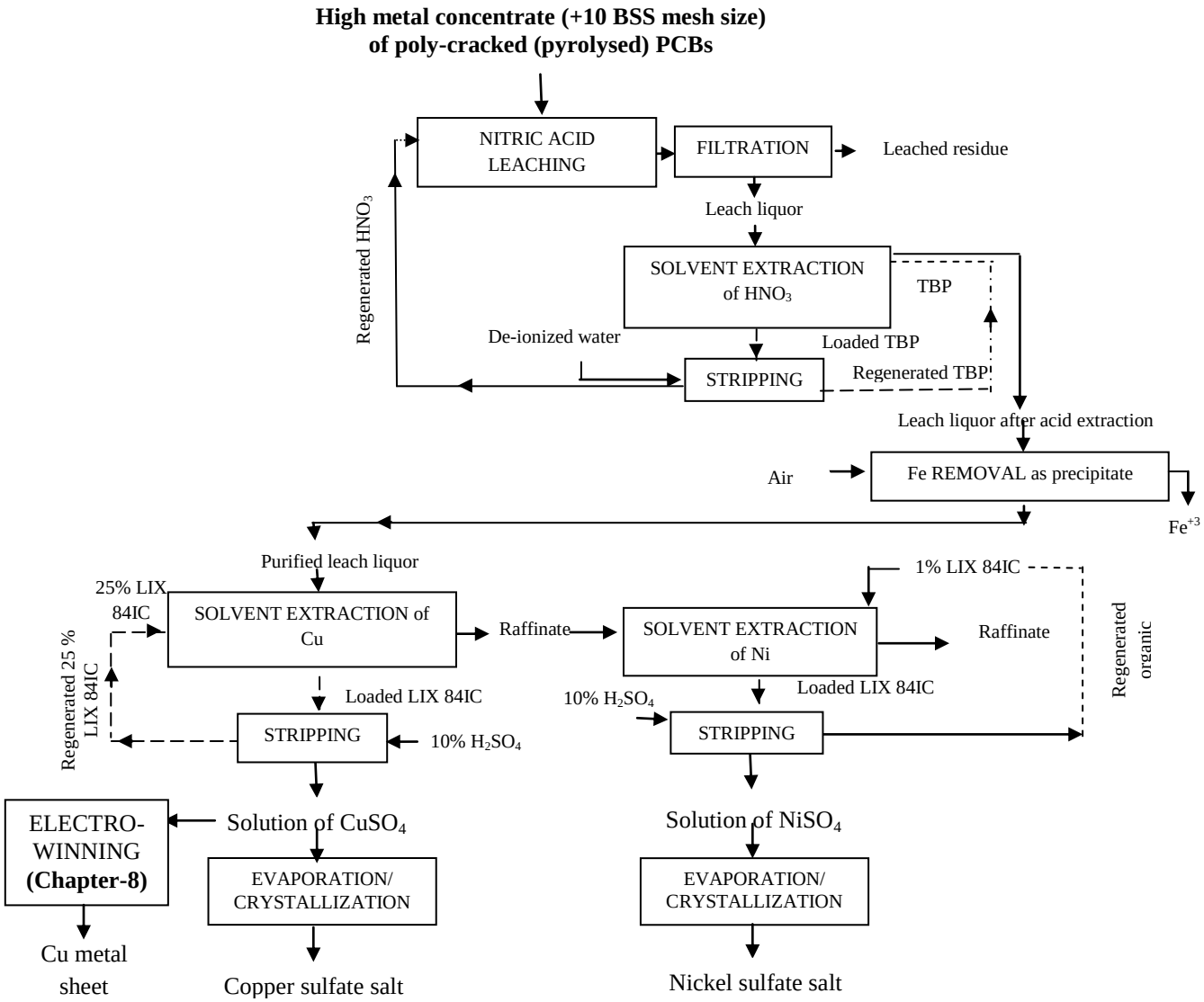


Fig. 31 Process flow sheet for recovery of metals from high metal concentrate (+10 BSS mesh size i.e. > 2mm size) of poly-cracked (pyrolysed) PCBs.

CHAPTER-7

CEMENTATION OF LEAD

CHAPTER-7

CEMENTATION OF LEAD

7.1. Introduction

Lead is an imperative base metal, obligatory for variety of applications in various metallurgical and chemical industries due to its malleability, low melting point and high resistivity to corrosion. It is mainly used as a pure metal, alloyed with other metals, or as chemical compounds [35]. It is used as an industrial raw material for storage battery manufacture, photographic material, matches manufacturing, etc. The chemical and physical characteristics of lead are now often used to line tanks that store corrosive liquids and as a shield against X-rays and gamma-ray radiations. Other uses include the manufacture of paints, lead-acid-batteries, pigments, etc [36].

Cementation is the terminology of those spontaneous electrochemical reactions in which a metal ion in the solution is reduced to the metal with the concurrent oxidation of a less noble metal placed in the same solution. This type of reaction is heterogeneous in nature. This technology is usually applied to hydrometallurgy and the treatment of heavy metal pollution problems. Today, a prime concern of the environmental engineer is the removal of small concentrations of toxic substances from wastewater. Lead is one of these toxic substances Usually, lead is recovered by using chemical precipitation, ion exchange, reverse osmosis and electrodialysis; all of these methods have drawbacks, however. Chemical precipitation requires extremely long settling times. The other methods (ion exchange, reverse osmosis and electrodialysis) require elaborate and expensive equipment and have high operating costs. The research reported herein examines an alternative procedure for removing lead from wastewater by cementation on a rotating iron disc. The cementation treatment process has several advantages. These include simple control requirement, low energy consumption and recovery of valuable or toxic metals. The main disadvantage is excess less noble metal consumption. In simple terms, the reaction can be represented by equation. [157].

$$Pb^{2+} + Fe \longrightarrow Pb + Fe^{2+} \qquad (39)$$

This reaction of cementation occurs simultaneously with the discharge of H^+:

$$2H^+ + 2e^- \longrightarrow H_2 \quad (40)$$

Similarly, The recovery of metallic lead by cementation with aluminum is an electrochemical process involving the oxidation of aluminum and the reduction of lead nitrate. The metal to be reduced from aqueous solutions is more noble, having greater electron affinity, than the precipitating metal. The overall stoichiometry for the reaction is as follows [153].

$$3Pb^{2+} + 2Al = 2Al^{3+} + 3Pb \quad (41)$$

The cementation studies have been carried out for the recovery of metal from leach liquor obtained after extraction of acid, iron, copper and nickel by solvent-extraction techniques. Various process parameters viz. effect of different reagents, Al/Pb ratio, temperature, pH were studied to optimize favorable conditions for recovery of lead metal.

7.2. Material and Methods

The leach liquor obtained after extraction of acid, iron, copper and nickel by solvent-extraction techniques was used further for recovery of lead by cementation process. Recovery of lead by cementation process in Pyrex reactor was carried out from leached solution (free from acid, iron, copper and nickel) containing 0.89 g/L Pb and negligible amount of Ni. Cementation is the terminology of those spontaneous electrochemical reactions in which a metal ion in the solution is reduced to the metal with the concurrent oxidation of a less noble metal placed in the same solution.

7.3. Results & discussion

7.3.1. Selection of cementing reagent

Recovery of lead by cementation process in Pyrex reactor was carried out from leached solution (free from acid, iron, copper and nickel) containing 0.89 g/L Pb and negligible amount of Ni. The choice of a reagent for cementation process is an essential factor for metal recovery. It should led to maximum cementation of metal without itself being reacted and must be economical. During cementation procedure, two reagents of iron powder (1.78 g/L) and aluminum foils (1.78 g/L) were used. Fig. 1 shows that aluminum foil was more effective for cementation of metallic Pb as it recovers 99% metal as

compared to iron which cemented only 37.4% of Pb present in the liquor. This might be due to the presence of nitrate ions in the leach liquor. It has been reported that the removal of Pb by iron cementation was found to be reduced in presence of nitrate ions because interference of nitrate on rate of Pb cementation on iron surface was attributed to the reduction of nitrate to nitrite by ferrous ion described as follow:

$$2Fe^{2+} + NO^{3-} + 2H^{+} = 2Fe^{3+} + NO + H_2O \quad (42)$$

The formation of highly reactive ferric ion, Fe^{3+}, can further induce the dissolution of metallic iron and lead as described below

$$2Fe^{3+} + Fe = 3Fe^{2+} \quad (43)$$

$$2Fe^{3+} + Pb = 2Fe^{2+} + Pb^{2+} \quad (44)$$

The formation of ferrous ion, Fe^{2+}, consumes excessive metallic iron and causes more obvious inhibition on the Pb cementation

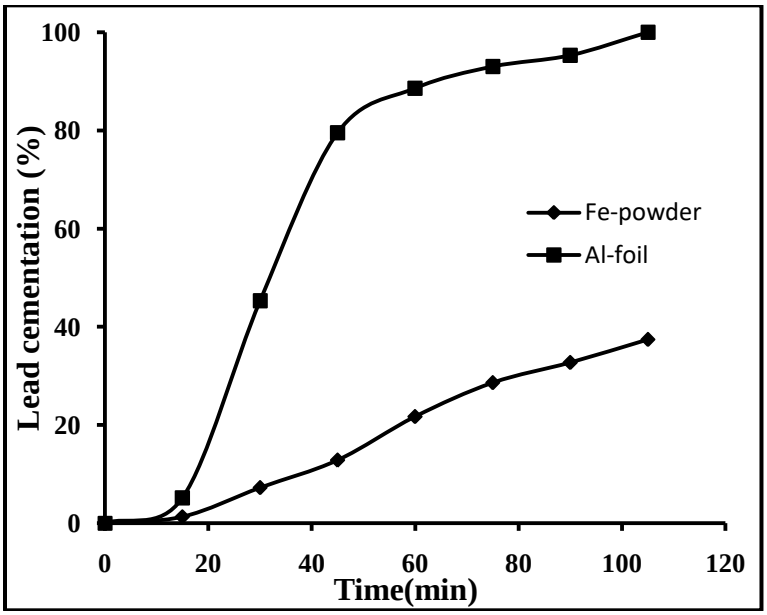


Fig. 1 Effect of different reagents on lead cementation
[Experimental Conditions: Aq solution- 0.89 g/L Pb, Fe & Al = 1.78 g/L, pH = 1.7, Temp- 90°C, Stirring speed = 370 rpm].

7.3.2. Effect of aluminum foils particles quantity

The effect of Al/Pb ratio (wt/vol) on cementation of lead was also studied from leached solution (free from acid, iron, copper and nickel) containing 0.89 g/L Pb and negligible amount of Ni. In order to optimize the quantity of aluminum foil needed, experiments were carried out at the temperature of 90°C, stirring speed of 370 rpm at pH 1.7. Fig. 2

shows that the cementation of lead at a certain time increases with increasing amount of aluminum added to the solution. This might be due to greater surface area of aluminum foils particles per lead ion as quantity of aluminum foil particles increases. It was observed that cementation of lead using Al/Pb ratio 1/1 and Al/Pb ratio 2/1 increases from 3.8 to 84.7% and 5.1 to 99.99% respectively with increased in time from 15 to 105 min.

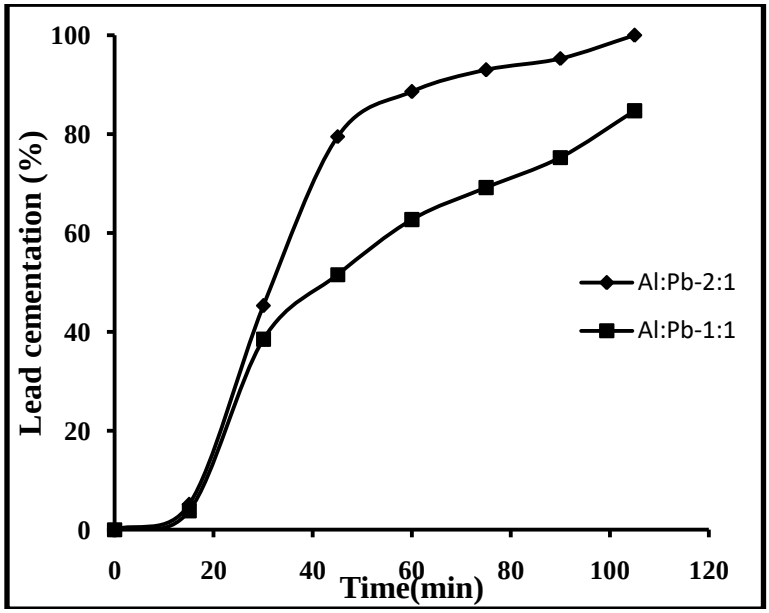


Fig. 2 Effect of aluminum foils quantity on the cementation of lead.
[Experimental Conditions: Aq solution- 0.89 g/L Pb, pH = 1.7, Temp- 90°C, Stirring speed = 370 rpm].

7.3.3. Effect of temperature

The effect of temperature on Pb cementation was studied in the range of 60–90°C using Al:Pb ratio 2:1 at pH 1.7 maintaining stirring speed 370 rpm. Fig. 3 shows that the cementation of lead increases with the increase in reaction temperature, in which the oxide film has been destroyed and higher cementation efficiency has been obtained [153]. A maximum efficiency of 99% was obtained after 105 min at 90°C. Thus, the optimum temperature for cementation of Pb from leach liquor was found to be 90°C. Further, increase in temperature shows negligible effect on Pb recovery.

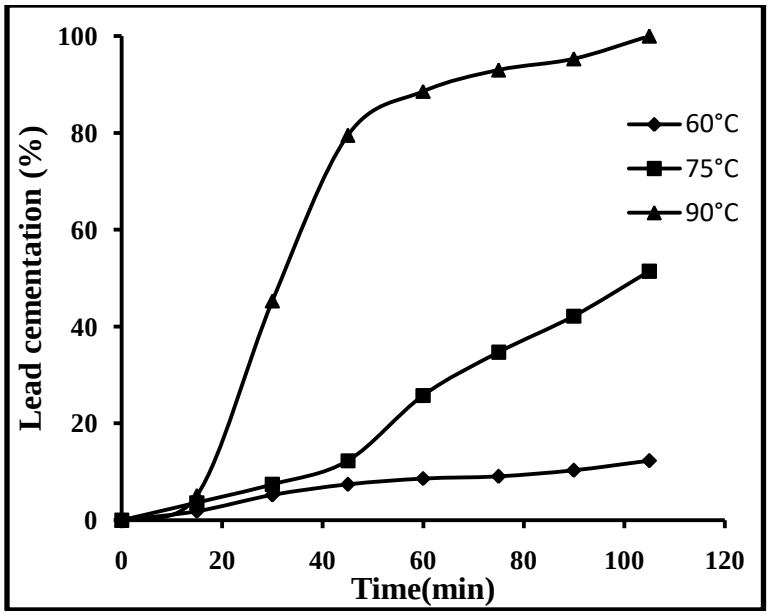


Fig. 3 Effect of temperature on the cementation of lead.
[Experimental Conditions: Aq solution- 0.89 g/L Pb, Al:Pb = 2, pH = 1.7, Stirring speed = 370 rpm]

7.3.4. Effect of pH

The effect of pH was studied for the cementation of lead from the leach liquor containing 0.89 g/L Pb and negligible amount of Ni. The pH of solution determines the surface charge of the cementation and degree of ionization. pH effect on Pb cementation was investigated in the range of 1.7–2.7 as shown in Fig. 4 using Al/Pb ratio 2/1 at temperature 90°C maintaining stirring speed 370 rpm. It was found that the cementation of lead decreases from 99 to 39.8% with increased in pH from 1.7 to 2.7. This is due to the displacement of Pb ions with Al ions decreases with the reduction of hydrogen ion (i.e. at increased pH). Fig. 5 shows the XRD graph of the lead cemented residue which was obtained after cementation at obtained conditions in which only peaks of lead obtained which was also validated with the results.

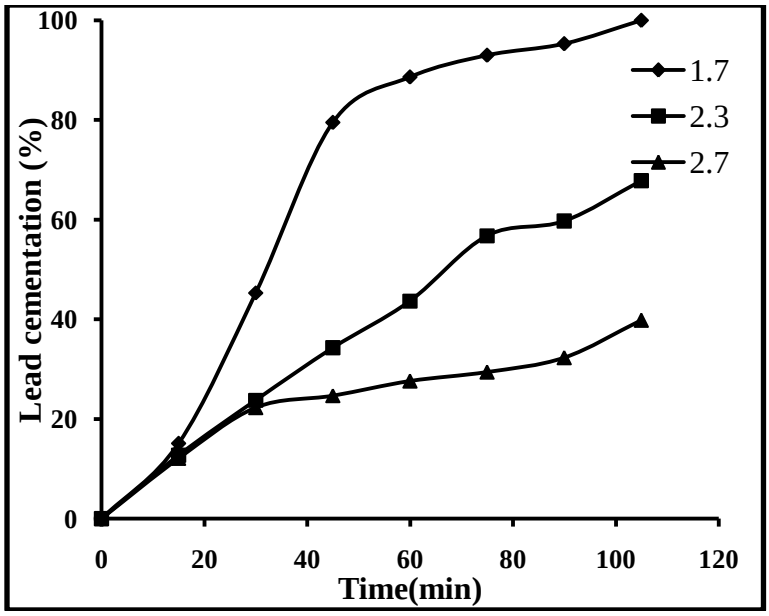


Fig. 4 Effect of pH on the cementation of lead.
[Experimental Conditions: Aq solution- 0.89 g/L Pb, Al:Pb = 2, Temp- 90°C, Stirring speed = 370 rpm].

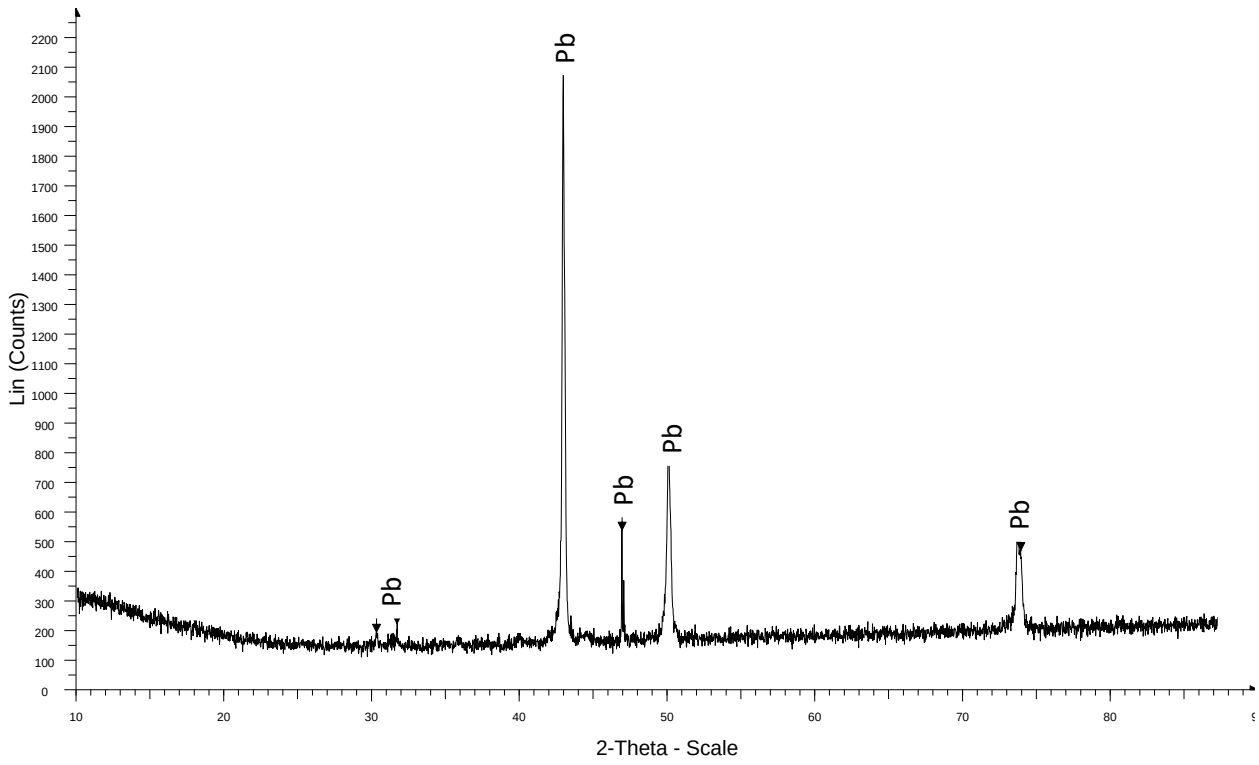


Fig. 5 XRD of lead cemented residue.

7.4. Conclusion

99% lead metal was recovered from leached solution (free from acid, Fe, Cu & Ni) by cementation process at pH 1.7, 90°C, Al:Pb ratio 2 and stirring speed of 370 rpm for 105 min. It was also validated by XRD graph of cemented residue which shows the peaks of lead metal. The chemical composition of the precipitated lead at optimum conditions is as follows: Pb-99.49%and Al-0.51%.

CHAPTER-8

ELECTROWINNING OF COPPER

CHAPTER-8

ELECTROWINNING OF COPPER

8.1. Introduction

Copper is a soft and pliable in its pure form, it is a good conductor of heat and electricity. It is a slow corrosive metal which doesn't react with water but reacts to atmospheric oxygen and forms a layer on the surface. It is an important and valuable metallic element from both industrial and environmental point of view and is widely used in its pure state as well as in alloys with other metals [25]. It is used in defense, space programme, railways, power cables, mint, telecommunication cables, etc. In addition, copper is essential element for all living organisms in traces as a dietary mineral. Copper compounds are also used in fungicides and wood preservatives.

Electrowinning is the electrodeposition of metals from the solution by the process of electrolysis. In this process, current is passed from an inert anode through a liquid leach solution containing the metal so that the metal is extracted as it is deposited in an electroplating process onto the cathode. Most metals occur in nature in their oxidized form (ores) or salts and thus must be reduced to their metallic forms. The ore is dissolved following some preprocessing in an aqueous electrolyte and the resulting solution is electrolyzed. The metal is deposited on the cathode (either in solid or in liquid form), while the anodic reaction is usually oxygen evolution.

Conventional technology for the recovery of copper metal by aqueous way deals with leach liquor (contains minimum 20 to 25 g/L Cu) generated by H_2SO_4 leaching of copper salts. The leach solution can alternatively be purified and upgraded by solvent-extraction prior to electrolysis so that high quality copper can result.

When acidic copper sulfate solution is subjected to electrolysis between a copper cathode and insoluble anode (say a Pb alloy), the following reaction take place at the electrode:

Cathode: $Cu^{+2} + 2e \longrightarrow Cu \quad E^o = +0.337\ V$ (45)

The only other cation, H^+ present in the solution is more electropositive (reduction potential) than Cu^{+2}. Hence it does not get discharged:

Anode: $H_2O \longrightarrow 1/2\ O_2 + 2H^+ + 2e \quad E^o = -1.229\ V$ (46)

The net cell reaction is therfore:

$$Cu^{+2} + H_2O \longrightarrow Cu + 1/2\ O_2 + 2H^+ \quad (47)$$

If a copper electrowinning cell operates ideally, all the current passing through it would be effective in deposing the copper metal. The theoretically amount of deposition is given by the well known Faraday's law, according to which a gram equivalent of copper (31.77 g) should deposit by passing 96,500 C (26.8 Ah) of electricity. In actual practice, however, the amount of electricity required to deposit a 1-g equivalent of copper is greater than the theoretical amount and this being due to current loss. Current losses can occur because of poor connection, leakage in various parts of the circuit, insufficient circulation of the electrolyte, or short circuit of the electrode due to dendrite growth of the depositing copper. Thus, the current efficiency, which is defined as the ratio of the theoretical amount of electricity needed to deposit a given quantity of copper to actual amount used, is always less than 100%. The cell performance is also sometimes evaluated by energy efficiency term which is defined as follows:

$$\text{Energy efficiency in \%} \quad \frac{\text{Reversible decomposition voltage * Current efficiency in \%}}{\text{Applied voltage}}$$

The electrowinning studies was carried out for the copper metal sheet from strip solution (pure copper sulfate solution) obtained after solvent-extraction process. Process parameters viz. concentration of the solution and cathode current density were optimized initially using model synthetic solution. Further, the stripped solution of $CuSO_4$, obtained was validated with the conditions obtained. The investigation is discussed below.

8.2. Material and Methods

From the obtained pure solution of $CuSO_4$, pure copper metal sheet was obtained by the process of electrowinning. Laboratory scale study was performed by maintaining required parameters in a glass tank employing unalloyed cathode of Titanium and anode of Lead-Antimony alloy (antimonial lead) containing antimony in range of 2-6 wt%. Process parameters viz. concentrations of the solution and cathode current density were optimized initially using model synthetic solution. Further, the stripped solution of $CuSO_4$ obtained (after solvent-extraction) was validated with the conditions obtained.

8.3. Results & discussion

8.3.1. Effect of copper concentration

Electrowining was performed using a model synthetic solution containing 180 g/L H_2SO_4 and copper concentration varying from 5.0-61.63 g/L at temperature of 30°C, time 4 hr and current density 200 A/m^2. The result presented in Fig. 1, shows that the current efficiency increased from 43.0-99.9% with the increase in copper concentration from 5.0-22.45 g/L. From this figure it was noticed that after increasing the concentration from 22.45-61.63 g/L, current efficiency was same in all the cases. At the time of electrowinning process, when the copper concentration was low then brittle, stressed and powdery metal was deposited at the cathode which got separated easily from cathode and in case of higher concentration, copper metal sheets was obtained. Thus, 61.63 g/L copper concentration was optimized and used for further set of experiments.

The energy required and applied voltage was decreased with increased in copper concentration as shown in Fig. 2 & 3. This is an obvious consequence of the lower voltage requirement (due to higher conductivity) at the higher Cu concentration and the increased current efficiency.

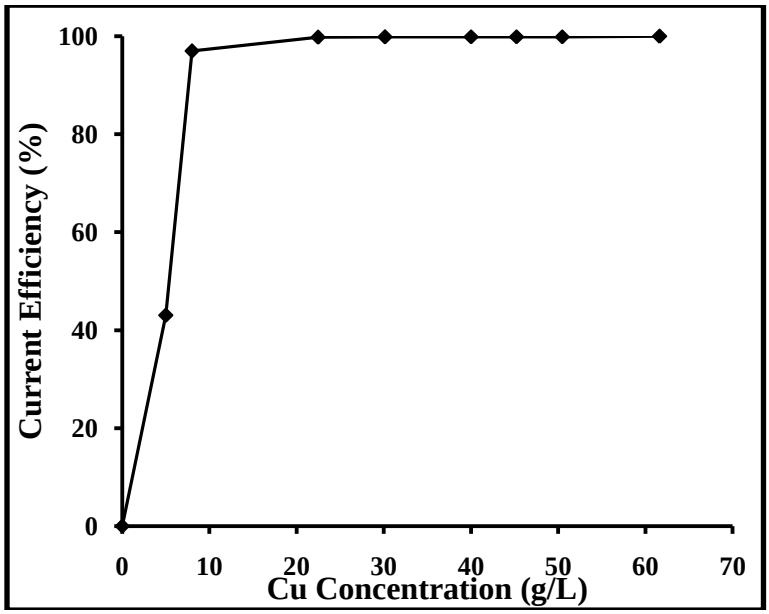


Fig. 1 Effect of Cu concentration on current efficiency.
[Experimental Conditions: H_2SO_4 concentration 180 g/L, Cathode Current Density 200 A/m^2, Temperature 30°C, Time 4 h]

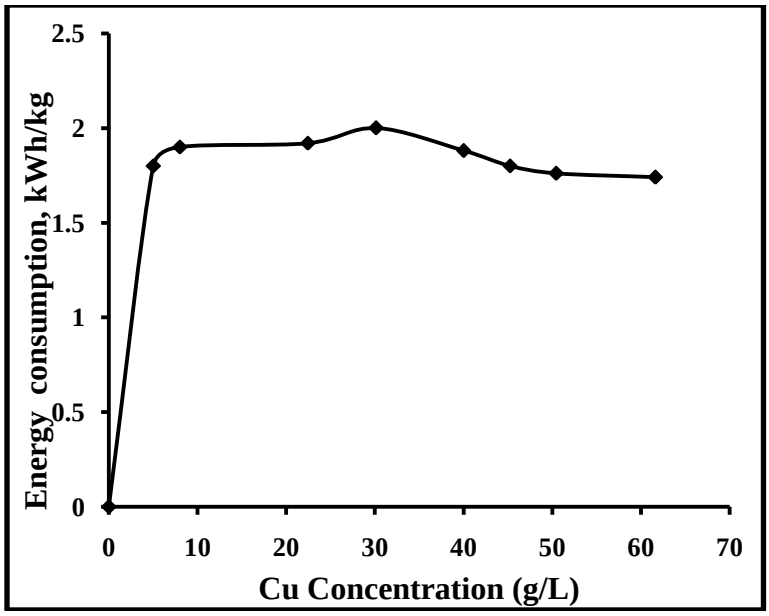


Fig. 2 Effect of Cu concentration on energy consumption.
[Experimental Conditions: H_2SO_4 concentration 180 g/L, Cathode Current Density 200 A/m^2, Temperature 30°C, Time 4 h].

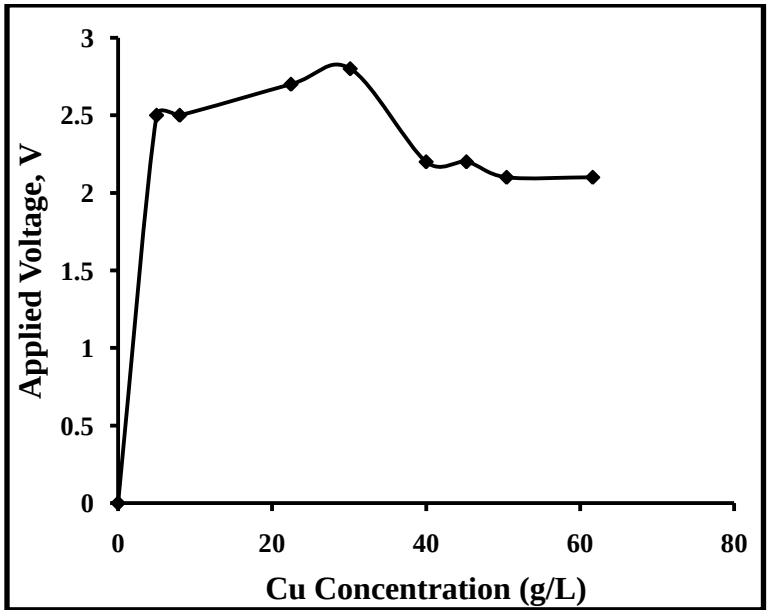


Fig. 3 Effect of Cu concentration on the applied voltage.
[Experimental Conditions: H_2SO_4 concentration 180 g/L, Cathode Current Density 200 A/m^2, Temperature 30°C, Time 4 h].

8.3.2. Effect of cathode current density

Further experiments were carried out to see the effect of cathode current density during the electrowinning of copper from the solution containing 180 g/L H_2SO_4 and 61.63 g/L Cu concentration at temperature of 30°C for time 4 hr. In Fig. 4, it was noticed that with

the increase in cathode current density from 100-400 A/m^2, current efficiency was almost same in all the cases. When 200 and 300 A/m^2 cathode current density were used for electrowinning experiment then metal sheets of copper formed in both cases but when the cathode current density was increased to 400 A/m^2 then copper powder was formed after electrowinning. 200 A/m^2 cathode current density was optimized and used for further set of experiments.

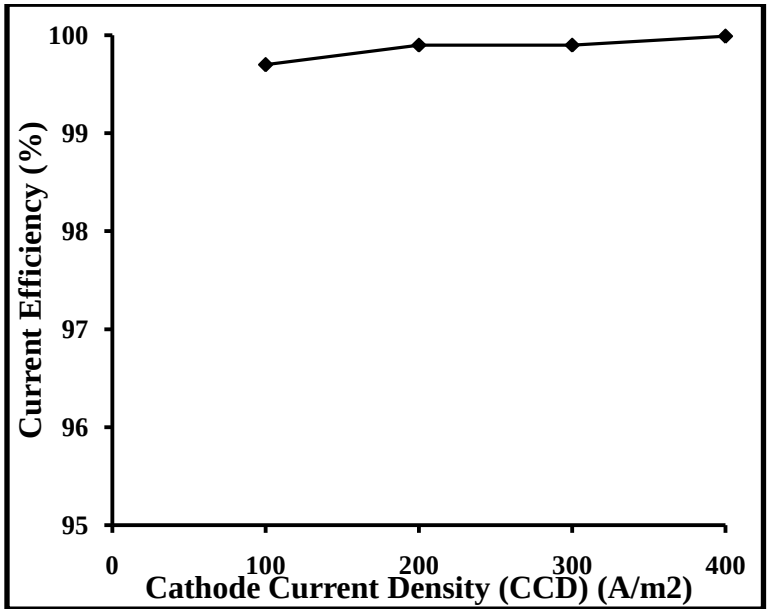


Fig. 4 Effect of cathode current density on current efficiency.
[Experimental Conditions: Cu concentration 61.63 g/L Cu & H_2SO_4 concentration 180 g/L, Temperature 30°C, Time 4 h].

8.3.3. Effect of nickel concentration on electrowinning of copper

Experiments were carried out to see the effect of nickel concentration (1.07-2.8 g/L) on the electrowinning of copper from the solution containing 180 g/L H_2SO_4 and 61.63 g/L Cu concentration at temperature of 30°C for time 4 hr using cathode current density 200 A/m^2. In Table. 1, it was noticed that with the increase in nickel concentration from 1.07-2.8 g/L, current efficiency was same in all the cases and 7.2 g Cu-metal sheet deposited in all the cases. After the electrowinning copper, it observed that the concentration of nickel before and after was almost same in all cases. Fig. 5 shows the XRD graph of the copper metals sheet which was obtained after electrowinning in which only peaks of copper was obtained and it noticed that nickel was not present in the sheet. So, copper electrowinning from the solution was not affected by the presence of nickel.

Table. 1 Effect of nickel concentration on electrowinning of copper.

Cu conc (g/L)-BEW	Ni conc (g/L)-BEW	Ni conc (g/L)(AEW)	Metal deposited (g)	Morphology	C.E(%)
61.63	1.07	1.07	7.21	Cu-Sheet form	99.99
61.63	1.75	1.75	7.43	Cu-Sheet form	99.99
61.63	2.803	2.81	7.24	Cu-Sheet form	99.99

B.E.W-Before electrowinning, A.E.W- After electrowinning

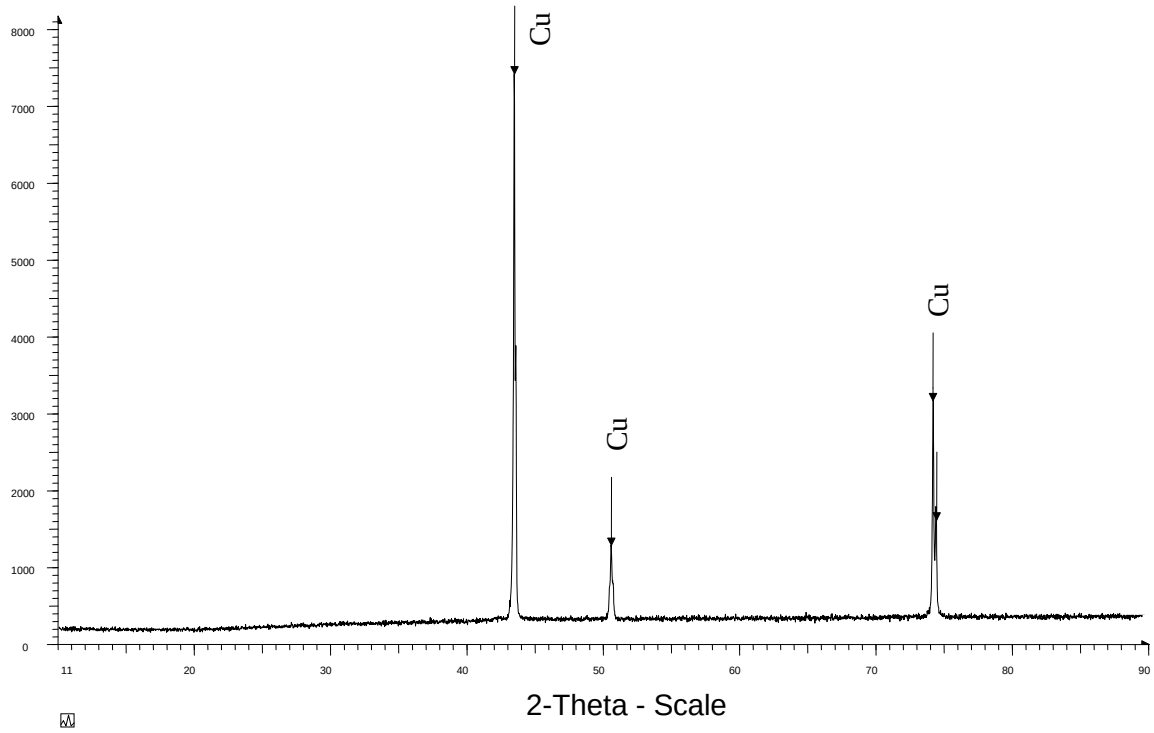


Fig. **5** XRD of copper metal sheet.
[Experimental condition: CCD-200 A/m^2,Cocentration- 61.63 g/L Cu & 2.8 g/L Ni, 4 h]

8.3.4. Electrowinning of copper from strip solution

After getting the optimum conditions from experiments carried out using model synthetic solution, the further experiments for electrowinning of copper from actual stripped solution were carried out. Strip solution was obtained from the loaded LIX 84IC using 10% (v/v) sulfuric acid by maintaining O/A ratio 3/1 containing 61.23 g/L Cu and 0.0037 g/L Ni (similar to the model leach liquor). The electrowinning was very selective for copper leaving Ni in the bath solution. 7.26 g of Cu metal sheet was formed on single cathode in 4 hours with the current efficiency of 99% at temperature of 30°C and cathode current density 200 A/m^2. The chemical composition of the copper metal sheet at optimum conditions is as follows: Cu-99.98% & Ni-0.02%.

8.4. Conclusion

7.26 g of Cu metal sheet was formed from the strip solution by electrowinning process on single cathode in 4 hours with the current efficiency of 99% at temperature of 30°C and cathode current density 200 A/m^2. Copper electrowinning from the solution was not affected more by the presence of nickel and it was also validated by XRD peaks. The chemical composition of the copper metal sheet at optimum conditions is as follows: Cu-99.98% & Ni-0.02%.

CHAPTER-9

COPPER RECOVERY FROM SMALL ELECTRONIC DEVICES POPULATED ON WASTE PRINTED CIRCUIT BOARDS

CHAPTER-9
COPPER RECOVERY FROM SMALL ELECTRONIC DEVICES POPULATED ON WASTE PRINTED CIRCUIT BOARDS

9.1. Introduction

During the manufacturing of PCBs, the unused tiny parts are also collected and both of these are mixed together and separated according to different sizes. From this, one section of particles is chosen containing the semiconductor devices, especially MOSFETs are in abundant. MOSFET (metal oxide semiconductor field effect transistor) is one of the components employed in printed circuit boards (PCBs) of electrical and electronic equipments. More than 99% of ICs are MOSFET, these ICs are mainly used for random access memory, flash memory, processors, ASICs (application-specific integrated circuits) etc. [193]. It is also used in various portable equipments/instruments such as mobile phones, differential scanning calorimetric (DSC) to measure heat change, power management, load switches, battery chargers, DC/DC converter, notebooks etc due to their small size. Their small size enable higher integration for smaller design, energy saving etc [194]. The huge amount of discarded/waste MOSFETs is generated during its production or after the end of life of the PCBs. MOSFET is a semiconductor device and has huge business globally. It was worth about US$300 billion in 2011, with a compounded annual growth rate of 7 to 12% [195]. In Austria, 3.5 billionth high-voltages MOSFET are produced, making it the world's most successful supplier of these 500 to 900 V transistors [196]. In the year 2000, 10^6 MOSFETs per person per year were manufactured [193]. In PCBs, MOSFETs is present which contain valuable metals, copper is in major amount along with other associated metals such as Fe, W, Pb, Si, C, Sn, Mo, Ni etc. and plastic materials

Present study is focused on the recovery of copper from the depopulated small electronic devices using physical communition followed by acid leaching and solvent extraction. From this, one section of particles is chosen containing the semiconductor devices, especially MOSFETs are in abundant. Various process parameters were studied to enrich the metallic concentrate and was further hydrometallurgically treated using suitable leaching agent. The metals from the leached solutions was recovered by solvent

extraction to get pure metal in the liquid form which was further processed to get metal or salt as value added product using electro-winning.

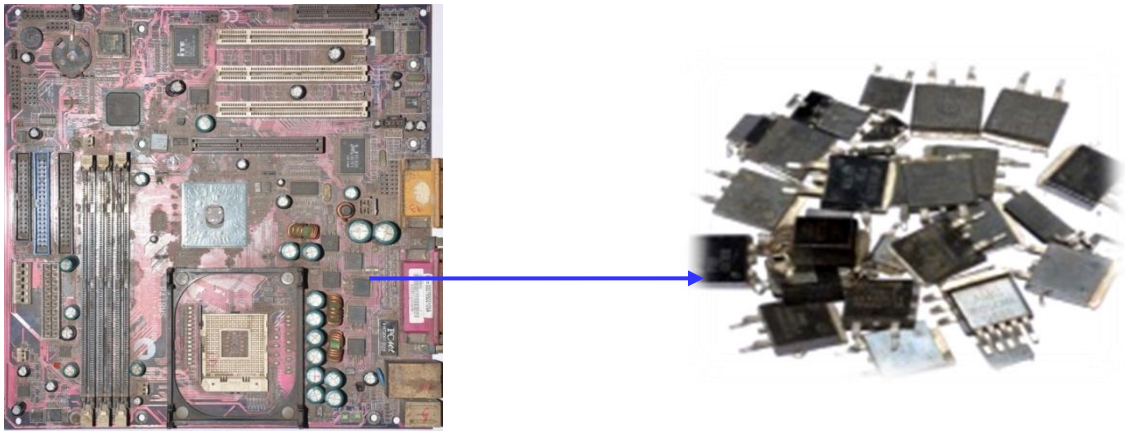
9.2. Material & methods

Waste PCBs for carrying out the research work are procured from different sources and the unwanted attachments of cords, wires, small devices, etc. were removed manually and collected. Moreover, the unused devices during PCB's manufacturing were also gathered. All these small electronic devices were then separated size wise and the one bearing size up to 1cm i.e. the semiconductor devices, especially MOSFETs was alienated apart. Each PCBs contain about 12 MOSFETs with ~0.95 g Cu per MOSFET and other minor metals such as Fe, Ni, W, Sn, etc. These semiconductors weighing 1.43 g each with dimension 9mm×8mm×0.65mm (Fig. 1) were physically beneficiated using Vibrating Cup Mill Pulverisette (Made in Germany) running at 1500 rpm for 2 min. The powder obtained after crushing was screened using vibrating sieve shaker for particle size distribution. Particles of various mesh size was obtained and analysed, among which +14 mesh (BSS) (Fig. 2) was opted for the experimental purpose due to the presence of large amount of metals in it. This concentrate was processed without any size reduction. Elemental analysis of the concentrates is presented in Table 1. XRD analysis using Bruker AXS D8 instrument running at 0.2 sec/step showed various diffraction peaks of Cu and other metals (Fig. 3).

The metallic components (+14 BSS mesh size) were initially leached using acidic medium in a temperature controlled closed three necked Pyrex glass reactor fitted with condenser where the sample pieces were put in the leachant after obtaining temperature in a particular S/L ratio using hot plate. Continuous mechanical agitation was provided during the experiment using a stirrer to ignore the mass transfer effect on dissolution. The samples were drawn at a desired time interval and analyzed. Apart from this, the electrode potential and the pH of the leached solution was also observed to validate the dissolution of Cu in different acids. Satisfactory mass balance was obtained with a maximum deviation of +2%. Leach liquor generated was then pumped to solvent extraction process as a feed solution for acid extraction and then from the solution left (containing dissolved metals), Fe was precipitated by air-sparging and then electro

winning was used to separate Cu as pure metal sheets. The spent electrolyte containing other metals is stored for further processing or sent to effluent treatment plant.

The metal content of the concentrate obtained was analyzed using ICP-OES (VISTA-MPX, CCD Simultaneous ICP-OES make in VARIAN, Australia). Samples taken at different interval were determined using atomic absorption spectrometer (AAS) (Perkin Elmer model, Analyst 200; USA).



Waste PCBs (With populated parts) **MOSFETs**

Fig. 1 Waste PCBs showing the presence of MOSFETs.

Fig. 2 +14 mesh size (BSS) of MOSFETs.

Table 1 Analysis of the metallic content in different fraction of crushed MOSFETs.

Mesh size of particles (BSS)	Metal (wt %)									
	Cu	Ni	Fe	Si	W	Mo	Pb	Sn	Ca	C
+ 14	66.99	0.18	0.016	2.27	0.001	0.082	3.07	0.14	0.28	NF
-32 + 48	0.97	0.22	0.12	40.15	0.033	0.12	1.01	0.43	1.36	16.39
-65 + 100	0.45	0.05	0.18	47.47	0.035	0.13	1.04	0.48	1.79	16.57
-150 +200	1.27	0.22	0.31	70.94	NF	NF	1.75	1.78	2.17	NF

Where NF = Not found

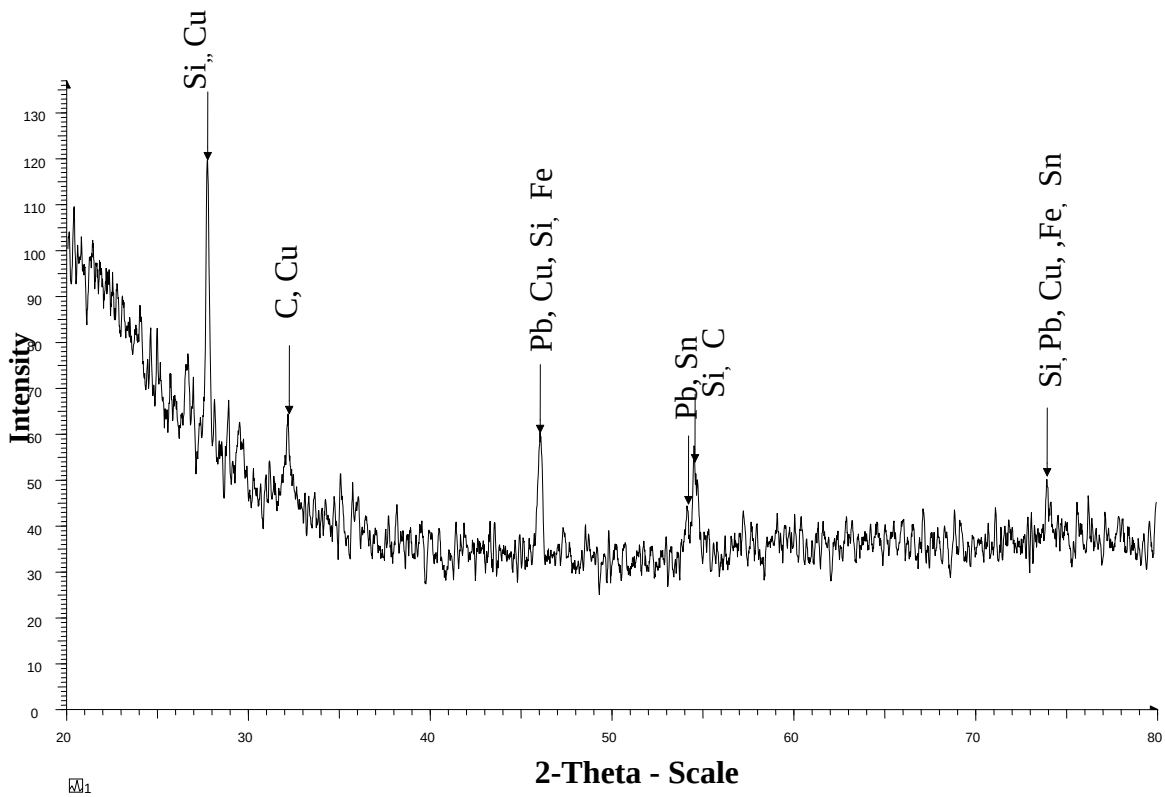


Fig. 3 XRD of +14 mesh size (BSS) of MOSFET samples.

9.3. Results and discussion

9.3.1. Leaching studies

9.3.1.1. Effect of nitric acid concentration

For efficient leaching of metals, appropriate maintenance of leachant concentration is essential. Temperature, pulp density, time, etc. are the important factors having pronounced effect on dissolution of metals and are studied to optimize the condition for complete metal recovery. Leaching of Cu metal from crushed MOSFETs samples was examined by altering HNO_3 concentration over a range of 1 to 5M at 90°C keeping pulp density 10 g/L and stirring at a speed of 100 rpm for 75 min. It was found that Cu dissolution increases with time using different acid concentration as increase in acid concentration increases the flux of H^+ ion across the particle boundaries, thus enhancing the rate of reaction. Fig. 4 shows that percentage leaching of Cu increases from 8.7 to 78.90% in 75 min as the acid concentration increases from 1 to 2M. However, 3M HNO_3 requires only 30 min for complete Cu dissolution. 90°C temperature was taken to be optimum during the whole experiment as increased temperature intensifies the reactive activity of HNO_3, thus increasing the rate of Cu leaching.

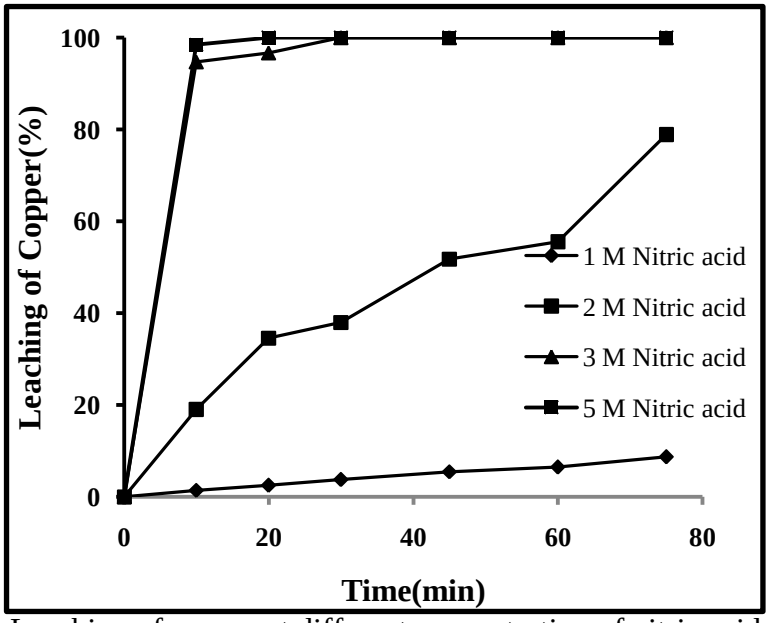


Fig. 4. Leaching of copper at different concentration of nitric acid.
[Experimental Conditions: Particle size= +14 mesh size (BSS), Temperature = 90°C, Time = 75 min, Pulp density= 10 g/L, Stirring speed = 100 rpm].

9.3.1.2. Effect of pulp density

Pulp density is also an important process parameter for the leaching of metals. Its influence was studied in the range of 10 g/L to 70 g/L pulp density under the conditions: 90ºC, 3M HNO_3, stirring speed 100 rpm. The leach recovery of copper was found to increase with time from 10 min to 75 min under the different pulp density as shown in Fig. 5. At the lower pulp density of 10 g/L, the leaching efficiency was high and 99% equilibrium dissolution was achieved in 30 min whereas at higher pulp density of 30, 50 and 70 g/L, the leaching recovery was obtained to be 96.98, 95.88 and 72.75% respectively under the similar experimental condition of 90ºC and 3M HNO_3 concentration. This may be due to lower acid concentration per unit mass of the copper during the leaching. However, total dissolution of copper was achieved in 45 min at a pulp density of 30 g/L and 50 g/L. At a pulp density of 70 g/L, the recovery of copper obtained was 87.19% even in 75 min. Thus, the dissolution of metal decreases with increase in pulp density. Further experiments were performed at 10 g/L pulp density.

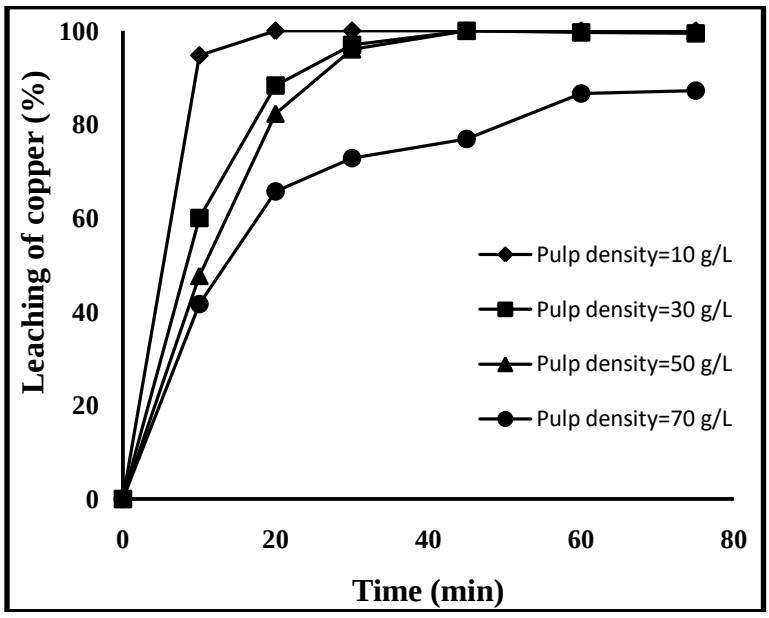


Fig. 5. Effect of pulp density on leaching of copper from crushed MOSFETs. Experimental Conditions: Particle size =+14 mesh size (BSS), HNO_3= 3 M, Temp = 90°C, Time =75 min, Stirring speed = 100 rpm.

9.3.1.3. Effect of temperature

The leaching experiments were carried out at different temperatures such as 30°C, 50°C, 75°C and 90°C keeping pulp density 10g/L with time variation of 10 to 75 min. The

leaching reaction at different temperatures shows the recovery of copper from crushed MOSFET (Fig. 6). The results shows that the percentage leaching of copper increases from 9.2 to 99.9% with increase in temperature from 30-90ºC using 3M HNO_3 in 75 min due to increase in reaction rate and diffusivity with temperature. The rate of dissolution of copper was found to be high at 90°C in comparison to other lower temperature and reaches almost 94.74% in 10 min, whereas even in 75 min only 90.61% copper dissolution was observed at 75°C under the same experimental condition. At higher temperature, the solubility of metal in aqueous solution increases, thus improving the leaching rate. The studies revealed that the maximum dissolution of Cu takes place at a temperature of 90ºC with 3M HNO_3 and 10 g/L pulp density

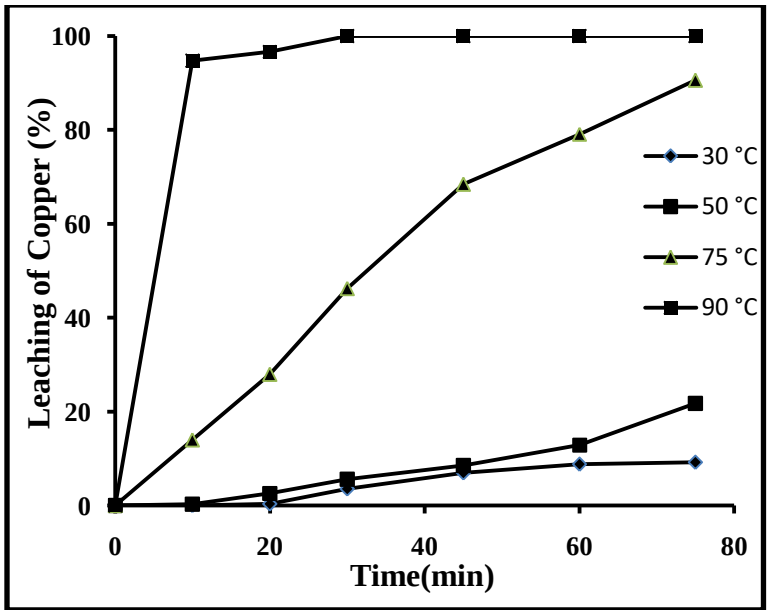


Fig. 6. Effect of temperature on leaching of copper in different time.
Experimental Condition: Particle size = +14 mesh size (BSS), HNO_3= 3 M, Pulp density = 10 g/L, Stirring speed = 100 rpm.

9.3.1.4. Characterization studies

The characterisation of the residue samples after leaching was carried out by using different methods. X-ray diffraction performed using Bruker AXS D8 instrument running at 0.2 s/step shows various diffraction peaks. XRD peaks of the dry residue obtained after leaching in 3M HNO_3 is shown in Fig.7, which showed that there was no peak for the copper as total metal was dissolved in higher concentration of acid. This is also evident from the experimental studies carried out with 3M HNO_3. 83.6% of MOSFETs sample

were dissolved in 3M nitric acid at 90°C in 75 min using 10 g/L pulp density that means 0.82 g leached residues were obtained after leaching of metals.

The leaching studies showed that nitric acid is the effective reagent to leach out copper from the crushed MOSFET (+14 BSS mesh size) of PCBs. The recovery of copper increases with increase in temperature and acid concentration. 99.9% of copper was recovered using 3M nitric acid at the experimental conditions 90°C, 10 g/L and 100 rpm in 30 min. Leach liquor generated was further put to solvent extraction process for the extraction of HNO_3 which can be further used for pure metal extraction.

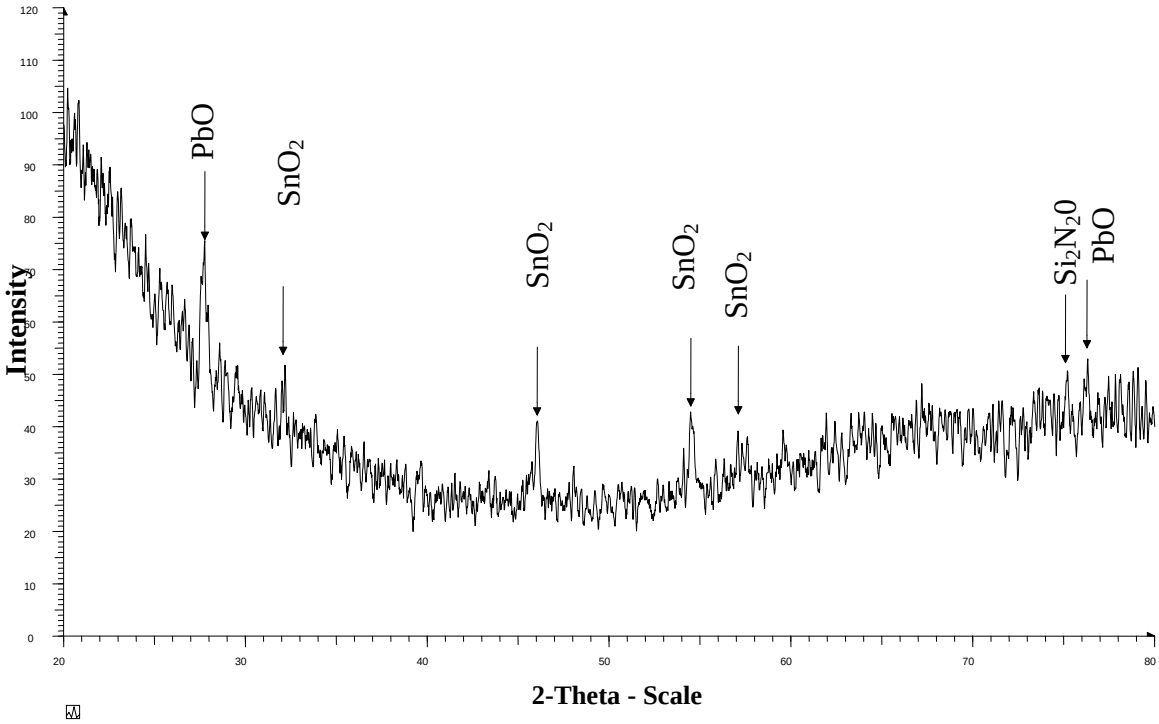


Fig. 7 XRD of dry residue which is left after leaching in 3M HNO_3.

9.3.2. <u>Solvent Extraction of nitric acid</u>

Leach liquor generated was analyzed and found to contain 6.535 g/L Cu (with other metals) and 3M acid content. It was pumped to solvent extraction for selective acid extraction, the removal of which is essential prior to Cu extraction from industrial point of view. As mentioned in many literatures, the solvent, Tri-n-butyl Phosphate (TBP), was used for extraction of HNO_3 from leach liquor to obtain acid free solution which can be later used for metal extraction and disposal without harming the environment. Different

process parameters were studied for the extraction of HNO_3 and were found that TBP (supplied by Luoyang Aoda Chemical Ltd., China) extracts HNO_3 in 15 min taking O/A ratio 3:1 and the MaCabe-Thiele plot suggests that three counter current stages are required for complete extraction of HNO_3. Stripping of the loaded TBP was carried out using de-ionized water and was observed that complete stripping of HNO_3 takes place in 4 stages maintaining O/A ratio 1:1 and mixing time 15 min.

After complete extraction of acid, the solution containing Cu along with other metals was needed to be converted to sulfate medium for effective electro winning of the Cu metal sheet. The sulfate concentration in the solution was maintained to be 2M. But prior to copper extraction, removal of iron is must as it greatly effects the operation as cyclic oxidation and reduction of dissolved iron significantly reduces the efficiency. Thus, air sparging was used for iron removal.

The leached solution, (now free from acid) contains 0.016 g/L Fe in which NaOH was added to increase the pH of solution from 3.5-4.0 and was mixed at 80°C. Fe was removed from the aqueous solution as it get precipitated as ferric hydroxide by sparging air and then only minor amount of Fe (0.003 g/L) left in the leach solution. Now the acid and Fe free solution could be used for the separation of Cu from actual leach solution by electro-winning.

9.3.3. Electrowinning of copper

Electro-winning was performed using the purified leached solution containing H_2SO_4 (2M) and Cu (concentration varying from 5 to 28 g/L) at 30°C for 4 hrs maintaining current density 200 A/m^2. The result presented in Fig. 8 shows that the current efficiency increases with increase in Cu concentration. If lower concentration of Cu solution was used for electro wining, brittle stressed and powdery metal was deposited at the cathode which gets easily separated. Thus, 20-30 g/L Cu concentration, formation of thin metal sheet of Cu and powder layer upon the sheet was observed.

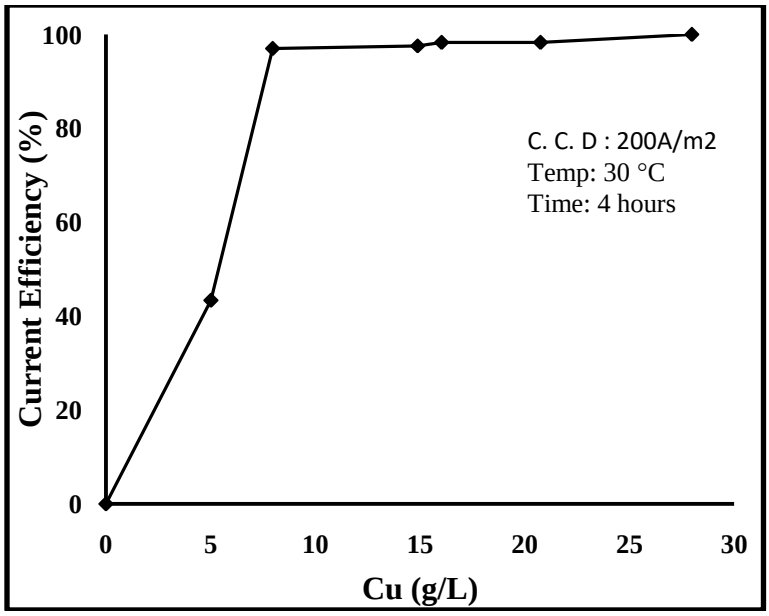


Fig. 8 Effect of Cu Concentration on current efficiency.

9.4. Conclusion

From the above study, it was concluded that a good amount of metals can be recovered from small electronic devices (MOSFETs) of WPCBs generally separated apart during its recycling. It was concluded that a semiconductor MOSFET, when leached in 3M HNO_3 at 90°C for 30 min at 10 g/L pulp density, almost 99% Cu dissolved. Further, TBP was used for complete extraction of HNO_3 in three stages at O/A ratio 1:1 maintaining mixing time 15 min. Air-sparging was then carried out to precipitate all the Fe content in the solution as its presence will affect electro winning of Cu. Finally, pure Cu metal sheet and small amount of powder upon the sheet was obtained by carrying out the experiment at 30°C for 4 h and current density 200 A/m^2. The complete process flow-sheet for recovery of Cu from small electronic devices of waste PCBs is presented in Fig. 9. The spent electrolyte containing other metals is stored for further processing or will be sent to effluent treatment plant.

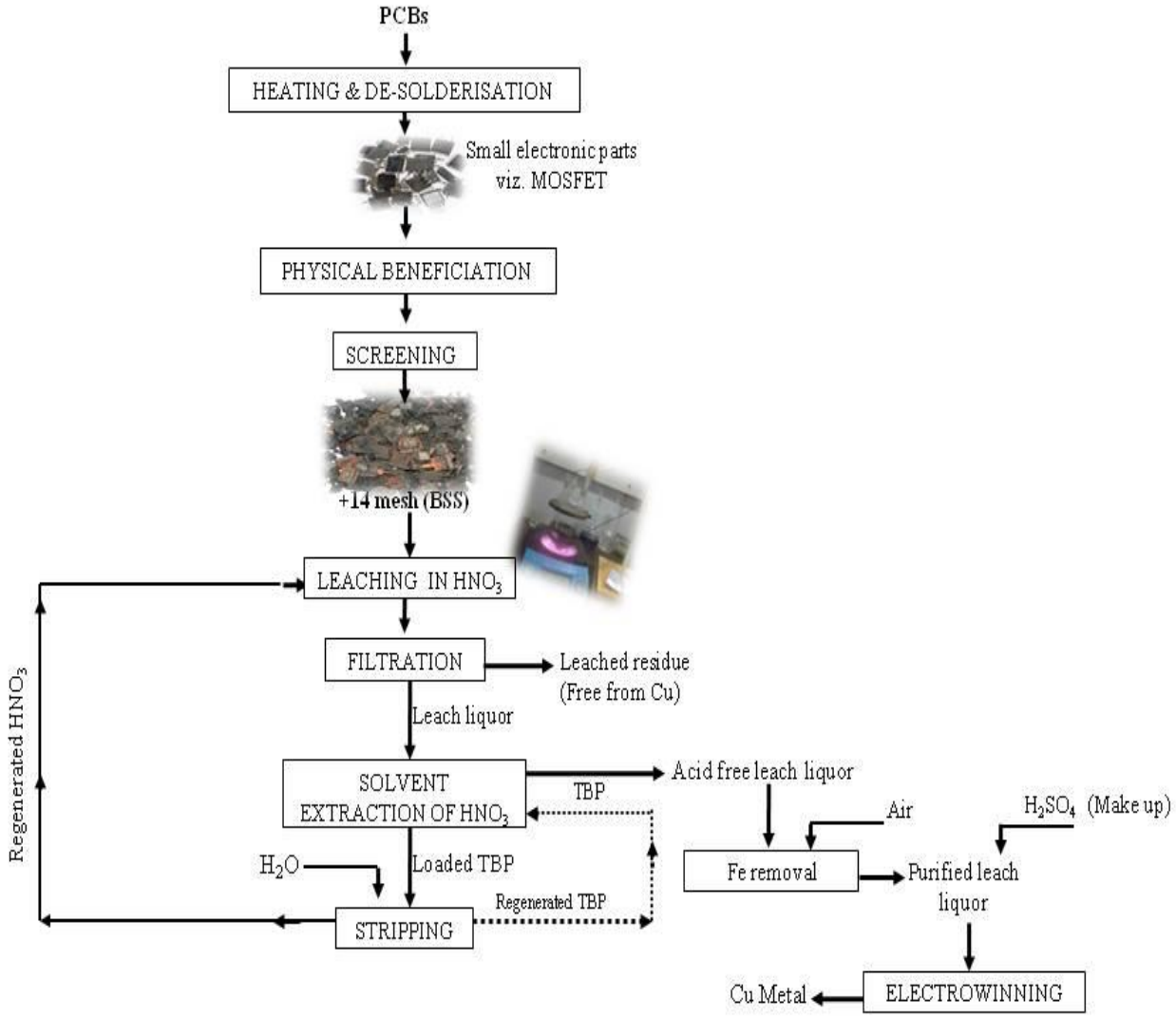


Fig. 9 A complete process flow sheet for the recovery of copper from small electronic devices (MOSFETs) of WPCBs.

CHAPTER-10

MAJOR CONCLUSIONS

CHAPTER-10

MAJOR CONCLUSIONS

- A novel process for the pyrolysis of PCBs was carried out. The process consists of heating PCBs in a flowing stream of inert gas such as argon at a low temperature of about 275°C for a period of 4 minutes. Complete pyrolysis of the waste is achieved during this period at the temperature used. Under similar conditions, a temperature of 360°C is required for the pyrolysis of the PCBs in air. If the waste is heated in air for 4 minutes only 2-6% of mass loss is observed in the waste. In other side it was also noticed that, mass loss (%) during pyrolysis of WPCBs in vacuum atmosphere is less as compare to argon atmosphere. Material obtained after pyrolysis of WPCBs under argon and vacuum atmosphere is same but the energy consumption is less in case of argon atmosphere. So, it reduces the temperature of pyrolysis leading to a saving energy and also reduce the time required for pyrolysis thereby enhancing the productivity and process efficiency. The fumes was also generated during the pyrolysis get condensed to generate marketable LD-oil (low density oil). About 10% of the mass of the WPCB could be recovered as oil during experiments which were conducted in argon and vacuum atmosphere. The oil was characterized using FT-IR and found to contain radicals of O-H, C-C, C-H and C-O.
- The poly-cracked (pyrolysed) PCBs was subjected to physical beneficiation for the separation of metallic from non-metallic fractions using scutter crusher and grinding mills. Further, the ground poly-cracked PCBs was scrubbed/washed with water without using any additives to enrich the metallic concentrate up to 97.8%. The scrubbed sample was further screened to separate low metal concentrate (-10 mesh i.e. <2 mm size) and high metal concentrate (+10 mesh i.e. >2 mm size).
- 99.99% copper recovered from low metal concentrate (-10 mesh size i.e. <2 mm size) of poly-cracked (pyrolysed) PCBs by pressure leaching in an autoclave using 2.4M applying 20 bar oxygen pressure at at 150°C for 90 min keeping pulp density 100 g/L.
- In 4M HNO_3 at 90°C for 60 min, pulp density of 30 g/L and maintaining stirring speed 250 rpm, 99% Cu, Fe, Pb, Zn and 57% Ni were recovered from high metal

concentrate (+10 mesh size i.e. >2 mm size) of poly-cracked PCBs by atmospheric leaching process.

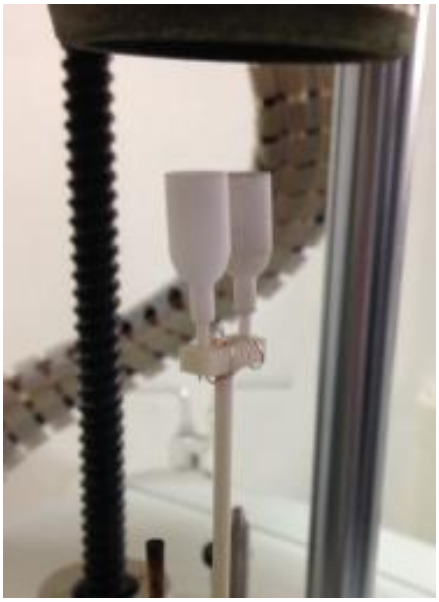
- Leach liquor-I obtained after pressure leaching in sulfuric acid containing 2.2M H_2SO_4, 10.76 g/L Cu, 0.38 g/L Ni, 0.07 g/L Pb & 2.55 g/L Fe was subjected to sulfuric acid extraction using 70% TEHA diluted in kerosene. It was found that three stages are required for complete sulfuric acid extraction taking O/A ratio 2/1 and mixing time of 5 min. Prior to Cu extraction, air sparging is essential to remove Fe content as its presence might reduce the efficiency of Cu metal sheet during the process of electrowinning. Further, 10% LIX 84IC diluted in kerosene was used for complete extraction of Cu which requires two stages at pH 2.5 maintaining O/A ratio 1/1 and mixing time of 5 min. 99.99% Cu was stripped from loaded organic using 10% (v/v) sulfuric acid within 5 contacts at a phase ratio (O/A) of 1/1. Ni was left in the raffinate with its minor co-extraction of 6.83% along with Cu. Further, 1% LIX 84IC diluted in kerosene was used for complete extraction of Ni which requires two stages at pH 4.58 maintaining O/A ratio 2/1 and mixing time of 15 min. Ni was stripped from the loaded LIX 84IC using 10% (v/v) sulfuric acid. 99.99% Ni was stripped from loaded organic in a single contact at a phase ratio (O/A) of 1/1 maintaining equilibrium time 5 min.
- Leach liquor-II obtained after atmospheric leaching in nitric acid containing 3.6M HNO_3, 20.72 g/L Cu, 0.0156 g/L Ni, 0.058 g/L Fe and 0.0475 g/L Pb was subjected to acid extraction using 60% TBP diluted in kerosene. It was found that three stages are required for almost complete nitric acid extraction taking O/A ratio 3/1 and mixing time of 12 min.. Further, 25% LIX 84IC diluted in kerosene was used for complete extraction of Cu which required two stages at pH 2.5 maintaining O/A ratio 1/1 and mixing time of 20 min. By 10% H_2SO_4, 99.99% Cu was stripped from loaded organic within five contacts at a phase ratio (O/A) of 1/1.Using 1% LIX 84IC diluted in kerosene, 95% Ni was extracted from leached solution (free from acid, Fe & Cu) using O/A ratio 1/1, at pH 5.2 maintaining mixing time of 15 min. Ni was stripped from the loaded LIX 84IC using 10% (v/v) sulfuric acid. 99.99% Ni was stripped from loaded organic in a single

contact at a phase ratio (O/A) of 1/1 maintaining equilibrium time 5 min. Ni could be recovered by electrolysis/crystallization from the strip solution.

- 99% lead was recovered from leached solution (free from acid, Fe, Cu & Ni) by cementation process at pH 1.7, 90°C, Al:Pb ratio 2 and stirring speed of 370 rpm for 105 min.
- 7.26 g of Cu metal sheet was formed from the strip solution by electrowinning process on single cathode in 4 hours with the current efficiency of 99% at temperature of 30°C and cathode current density 200 A/m^2. Copper electrowinning from the solution was not affected by the presence of nickel and it was also validated by XRD peaks.
- Semiconductor MOSFET was leached in 3M HNO_3 at 90°C for 30 min at 10 g/L pulp density, almost 99% Cu dissolved. Further, TBP was used for complete extraction of HNO_3 in three stages at O/A ratio 1:1 maintaining mixing time 15 min was required. Air-sparging was then carried out to precipitate all the Fe content in the solution as its presence will affect electro winning of Cu. Finally, pure Cu metal sheet and small amount of powder upon the sheet was obtained by electrowinning process.

Equipments used during the experiments

Thermal gravimetric analysis (TGA)

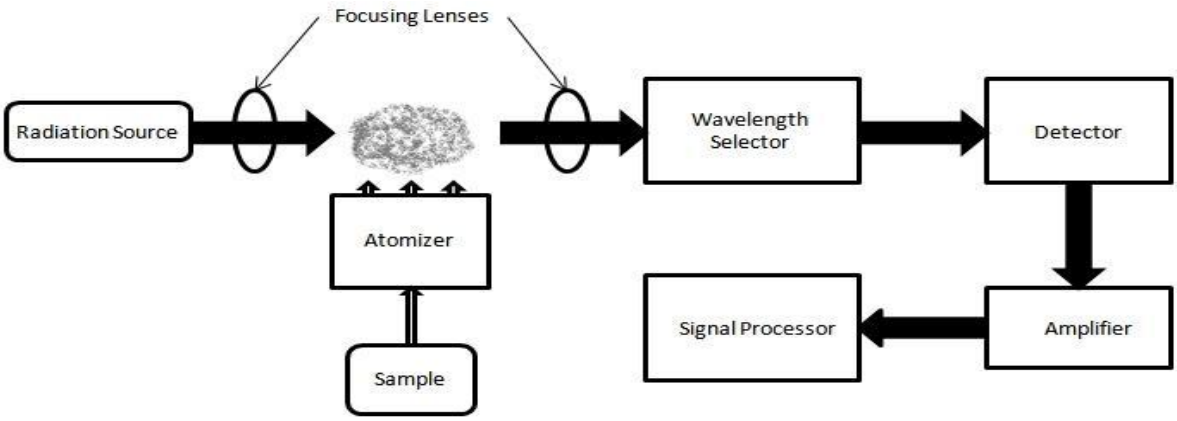


Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss) . TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions. TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture).

Atomic Absorption Spectroscopy (AAS)

Model: AAS 200 Make:Perkin Elmer

It is a spectro analytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electrothermal (graphite tube) atomizers. The atoms should then be irradiated by optical radiation, and the radiation source could be an element-specific line radiation source or a continuum radiation source. The radiation then passes through a monochromator in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector. The atom then emits energy in the form of light as the



electron falls back into the lower energy. Energy is absorbed or emitted, when an electron moves from one state to another. The emission spectrum consists of groups of discrete lines corresponding to electronic transitions.

Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES)

Model: VISTA-MPX; Make: Varian Inc., USA

ICP/OES is the most powerful chemical analytical tool for determination of trace elements in a myriad of sample types. Inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for measuring the concentration of trace metals present in solution. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. Unlike atomic absorption spectroscopy, which can only measure a single element at a time ICP-OES has the capability to scan for all elements simultaneously. This allows rapid sample processing.

The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in a RF discharge. In this project, ICP/OES was used to estimate the contents of elements such as Pb, Cr, W, Ag, Cu, Zn and so on. The picture of ICP/OES is shown in Fig.

SEM-EDS

Model: Nova Nano SEM 430; Make: FEI, USA

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) is the best known and most widely-used of the surface analytical techniques. High resolution images of surface topography, with excellent depth of field, are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5-30 kV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam.

In addition to low energy secondary electrons, backscattered electrons and X-rays are generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays (EDX or EDS analysis) emitted from the sample gives more quantitative elemental information.SEM, accompanied by X-ray analysis, is considered a relatively rapid, inexpensive, and basically non-destructive approach to surface analysis. It is often used to

survey surface analytical problems before proceeding to techniques that are more surface-sensitive and specialized.

Micro pH meter

Model: LT pH 102; Make: LABARD, India

A pH meter is an electronic device used for measuring the pH (acidity or alkalinity) of a liquid or sometimes a semi liquid. A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures pH and reading is displayed on screen At the bottom of the probe there is a bulb that contains the sensor which is a sensitive to pH and temperature. The probe is fitted in an arm known as the probe arm. To measure the pH of a solution, the probe is dipped into the solution. For normal use calibration should be performed at the beginning of each day. The reason for this is that the glass electrode does not give a reproducible e.m.f. over longer periods of time. Calibration should be performed with at least two standard buffer solutions that span the range of pH values to be measured. For general purposes buffers at pH 4.01 and pH 9.00 are acceptable. The pH meter has one control (calibrate) to set the meter reading equal to the value of the first standard buffer and a second control (slope) which is used to adjust the meter reading to the value of the second buffer. A third control allows the temperature to be set. The calibration process correlates the voltage produced by the probe (approximately 0.06 volts per pH unit) with the pH scale. After each single

measurement, the probe is rinsed with distilled water or de-ionized water to remove any traces of the solution being measured, blotted with a scientific wipe to absorb any remaining water which could dilute the sample and thus alter the reading, and then quickly immersed in another solution. When not in use, the glass probe tip must be kept wet at all times to avoid the pH sensing membrane dehydration and the subsequent dysfunction of the electrode.

<u>Hot Plate</u>

Model: RCT basic; Make: IKA, USA

Hot Plate is very useful equipment used in laboratory. It is used for heating liquid kept in flat bottom glassware (beakers, Flasks etc.) at required temperature. Basically it is an electric stove. Maximum temperature of 300 ^{0}C can be achieved. Temperature can be adjusted according to requirement using knob provided. The difference between other heating apparatus and hot plate is that it comes with temperature sensor. The apparatus auto cuts the power supply when the sensor senses a particular temperature is reached. The Hot Plate comes in built with magnetic stirrer (to be used in combination with a magnetic bar), used for mixing and stirring liquid uniformly.

Future scope of research activity

Based on the above studies, scale-up work will be required for the recovery of valuable and hazardous metals in large scale. The data obtained will be used for the pilot/commercial application to produce valuable products from purified solution.

REFERENCES

References

1. Jha, M.K., Choubey, P.K., Jha, A.K., Kumari, A., Lee, J.-C., Kumar, V., Jeong, J., 2012. Leaching studies for tin recovery from e-scrap. Waste Manage. 32 (10), 1919-1925.

2. Lee, J.-C., Yoo, J.M., Jeong, J., Jha, M.K., 2007. Novel pre-treatment process for liberation of metals from waste printed circuit boards using organic solution, International patent application number WO/2009/064063, dated: 28th July 2009.

3. Long, L., Sun, S., Zhong, S., Dai, W., Liu, J., Song, W., 2010. Using vacuum pyrolysis and mechanical processing for recycling waste printed circuit boards. J. Hazard. Mater. 177, 626-632.

4. Zhou, Y., Wu, W., Qiu, K., 2010. Recovery of materials from waste printed circuit boards by vacuum pyrolysis and vacuum centrifugal separation. Waste Manage. 30, 2299–2304.

5. Jha, M.K., Choubey, P.K., Kumari, A., Kumar, R., Kumar, V., Lee, J.-c., 2011. Leaching of lead from solder materials used in electrical and electronic equipments. Proceeding of second symposium, TMS 2011, San Diego, California, pp. 25–31.

6. Kumar, V., Garg, R., Rahman, Z., Kazmi, A.A., 2011. Sustainability and E-waste Management Scenario in India. The First International Conference on I nterdisciplinary Research and Development, 31 May - 1 June 2011, Thailand.

7. Borthakur, A., Sinha, K., 2013. Generation of electronic waste in India: Current scenario, dilemmas and stakeholders. Afr. J. Environ. Sci. Technol. 7(9) 899-910.

8. Cobbing, M., 2008. Toxic tech not in our backyard, uncovering the hidden flows of e-waste. Amsterdam: Greenpeace International.

9. Wath, S.B., Dutt, P.S., Chakrabarti, T., 2011. 'E-waste Scenario in India, its management and applications'; Environment Monitoring and Assessment, Springer, Jan, 172 (1-4).

10. Skinner, A., Dinter, Y., Lloyd, A., Strothmann, P., (2010). The challenges of e-wastes management in India: Cn India draw lessons from the EU and and the USA? ASIEN 117, 7-26.

11. Streicher-Porte, M., Widmer, R., Jain, A., Bader, H.P., Scheidegger, R., Kytzia, S., 2005. Key driver of the e-waste recycling system assessing and modelling e-waste processing in the informal sector in Delhi, Environ, Impact Assess. Rev. 25, 472-491.

12. UNEP, 2007. E-waste-volume1 inventory assessment manual, United Nations Environmental Programme.

13. MAIT (Manufacturers Association for Information Technology) (2010), 'Annual Report 2010';Available at: www.mait.com/Mait-Annual-Report-20-9-10.pdf.

14. TRAI (Telecom Regulatory Authority of India) (2009), 'Annual Report 2008-09', Available at www.trai.gov.in/annualreport/TRAIAR2008_09E_Add.pdf.

15. Singh, R.P., 2013. India: A Matter of Electronic Waste; the Government Initiatives. J. Business Manag. Soci. Sci. Res. 4 (2).

16. Jayapradha, A., 2015. Scenario of E-waste in India and application of new recycling approaches for E-waste management. J. Chem. Pharma. Res. 7(3), 232-238.

17. Compare Risk Reduction Monograph No 1 Lead - Background and national experience with reducing risk, OECD Paris, (1993).

18. Environmental alert bulletin, (2005).www.unep.org.

19. A featured article on, E-Waste – Boom and Banehttp://www.janmanch.org/environment/environment.asp?oth_id = 13

20. http://www.toxiclinks.org.

21. Puckett, J., Smith, T., 2002. The Basel Action Network. Seattle7 Silicon ValleyToxics Coalition.

22. Ramachandra, T.V., Saira, V.K., 2004. Environmentally sound options for e-wastes management. Envis Journal of Human Settlements.

23. Rani, B., Singh, U., Maheshwari, R., Chauhan, A.K., 2012. Perils of electronic waste: issues and management strategies. J. Adv. Sci. Res. 3(1), 17-21.

24. Saini, A.K., Taneja, A., 2012. Managing E-Waste in India- A Review. Inter. J. Appl. Eng. Res. 11 (7).

25. Youcef, M.H., Benabdallah, T., Ilikti, H., 2006. A study on copper (II) extraction from sulfate medium via cloudpoint extraction with N-salicylideneaniline ligand in presence of non-ionic surfactant. Canadian Journal of Analytical Sciences and Spectroscopy 51(5).

26. http://metalpedia.asianmetal.com/metal/copper/resources&production.shtml.

27. http://www.commoditiescontrol.com/eagritrader/staticpages/index.php?id=77.

28. Jha, M.K., Nguyen, N.V., Lee, J.C., Jeong, J., Yoo, J.M., 2009 a. Adsorption of copper from the sulfate solution of low copper contents using the cationic resin Amberlite IR 120. Journal of Hazardous Materials 164, 948–953.

29. Campbell, D.E., Nguyen, T., Jams, D.K., 2001. Process for treating waste water containing copper. US patent 6, 203,705.

30. Kumar, V., Sahu, S.K., Pandey, B.D., 2010. Prospects for solvent extraction processes in the Indian context for the recovery of base metals: A review. Hydrometallurgy 103, 45–53.

31. Swaddle, T.W., 1997. Inorganic Chemistry: An Industrial and Environmental Perspective. Academic Press, San Diego.

32. Banza, A.N., Gock, E., Kongolo, K., 2002. Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction. Hydrometallurgy 67, 63–69.

33. Forgan, R.S., 2008. Modification of phenolic oximes for copper extraction. Ph.D. Thesis, University of Edinburgh, 3–30.

34. Ritcey, G.M., Ashbrook, A.W., 1979. Solvent Extraction, Principles and Applications to Process Metallurgy. Elsevier Scientific Publishing Co., Amsterdam, 201–220.

35. http://www.gravitaexim.com/usesoflead.html

36. http://www.lme.com/metals/non-ferrous/lead/production-and-consumption.

37. http://mysite.du.edu/~jcalvert/phys/lead.htm.

38. http://www.ees.ufl.edu/homepp/townsend/publications/EWasteDisposal.htm.

39. http://www2.bren.ucsb.edu/~dturney/port/papers/Electroless/09.pdf.

40. http://metalpedia.asianmetal.com/metal/nickel/resources&production.shtml.

41. Kumari, A., Jha, M.K., Kumar, V., Jeong, J., Lee, J.c., 2010. Recovery of lead from the solder of waste printed circuit boards. Proceeding of X1 International Seminar, MPT 2010, Jamshedpur, India, 891–897.

42. Jha, M.K., Kumar,V., Singh, R.J., 2001. Review of hydrometallurgical recovery of zinc from industrial wastes. Resour. Conserv. Recy. 33, 1-22.

43. Cui, J., Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: A review, J. Hazard. Mater.158, 228-256.

44. Lee, J-C., Koyanaka, S., Lee, M., Ohya, H., Endoh, S., 1997. Recovery of copper, tin and lead from printed circuit boards (PCBs) by the shape separation method, Shigen-to- Sozai, 113 (5), 357-362

45. Veit, H.M., Diehl, T.R., Salami, A.P., Rodrigues, J.S., Bernards, A.M., Tenorio, J.A.S., 2005. Utilization of magnetic and electrostatic separation in the recycling of printed circuit boards scrap. Waste Manag. 25, 67-74.

46. Eswaraiah, C., Kavitha, T., Vidyasagar, S., Narayanan, S.S., 2008. Classification of metals and plastics from printed circuit boards (PCB) using air classifier. Chem. Eng. Process. 47(4), 565-576.

47. Gungor, A., Gupta, S.M., 1998. Disassembly sequence planning for products with defective parts in product recovery, 35, 161–164.

48. Owada, S., Kiuchi, Y., Yamagata, S., Harada, T., in: H. Hoberg, and H. von Blottnitz (Eds.), (1997). Physical separation of the devices in televisions and personal computers for elemental concentration, in: Proceedings of the XX International Mineral Processing Congress, vol.5, Aachen, Germany, GDMB, Clausthal-Zellerfeld, Germany, 261-272.

49. Wills, B.A., 1988. Mineral Processing Technology, 4th ed., Pergamon Press, Oxford, England, 377–381.

50. Masavetas, I., Moutsatsou, A., Nikolaou, E., Spanou, S., Zoikis-Karathanasis A., Pavlatou, E.A., Sptrellis, N., 2009. Production of copper powder from printed circuit boards by electro-deposition, Global Nest J. 11, 241-247.

51. Oliveira, P.C., Taborda, F.C., Margarido, F., Nogueira, C.A., 2009a. Physical and chemical processing of printed circuit boards waste. In: Proceedings of 4th International Conference and Exhibition. World Recycling Forum, China, 1-2.

52. Kumar, V., Lee, J.C., Jeong, J., Jha, M.K., Kim, B.S., Singh, R., 2013. Novel physical separation process for eco-friendly recycling of rare and valuable metals from end-of-life DVD-PCBs. Sep. Purif. Technol. 111, 145-154.

53. Ogunniyi, I.O., Vermaak, M.K.G., 2009. Froth Flotation for Beneficiation of Printed Circuit Boards Comminution Fines: An Overview. Miner. Process. Extrac. Metall. Review 30 (2), 101-121.

54. Mankhand, T.R., Singh, K.K., Gupta, S.K., Das, S., 2012. Pyrolysis of printed circuit boards, Int. J. Met. Eng. 1(6), 102-107.

55. Havlik, T., Orac, D., Petranikova, M., Miskufova, A., Kukurugya, F., Takacova, Z., 2010. Leaching of copper and tin from used printed circuit boards after thermal treatment, J. Hazard. Mater. 183, 866–873.

56. Zhou, Y., Qiu, K., 2010. A new technology for recycling materials from waste printed circuit boards. J. Hazard. Mater. 175, 823-828.

57. Molto, J., Font, R., Galvez, A., Conesa, J.A., 2008. Pyrolysis and combustion of electronic wastes. J Anal Appl Pyrolysis doi: 10.1016/j.jaap.2008.10.023.

58. Li, J., Duan, H., Yu, K., Liu, L., Wang, S., 2010. Characteristic of low-temperature pyrolysis of printed circuit boards subjected to various atmosphere. Resour. Conserv. Recy. 54, 810-815.

59. Guo, Q., Yue, X., Wang, M., Liu, Y., 2010. Pyrolysis of scrap printed circuit boards plastic particles in a fluidized bed. Powder Technol. 198, 422-428.

60. Zhan Z-H, Qiu K-Q (2011) Vacuum pyrolysis characteristics of waste epoxy printed circuit boards. J Chongqing Univ 10(3):113-122.

61. Zhan, Z.-H., Qiu, K.-Q., 2011. Pyrolysis kinetics and TG-FTIR analysis of waste epoxy printed circuit boards. J. Cent. South. Univ. Technol. 18, 331-336.

62. Kumar, M., Lee, J.C., Kim, M.S., Jeong, J., Yoo, K., 2012. Leaching of metals from waste printed circuit boards (WPCBs) using sulfuric acid and nitric acid. Environ. Eng. Manag. J. October 2014, 13 (10), 2601-2607.

63. Yoo, K., Lee, J.C., Lee, K.S., Kim, B.S., Kim, M.S., Kim, S.K., Pandey, B. D., 2012. Recovery of Sn, Ag and Cu from waste Pb-free solder using nitric acid leaching. Mater. Transac. 53(12), 2175-2180.

64. Jha, M.K., Shivendra, Kumar, V., Pandey, B. D., Kumar, R., Lee, J.C., 2010. Leaching studies for the recovery of metals from the waste printed circuit boards (PCBs). TMS (The Mineral, Metals & Materials Society), 945-952.

65. Vijayaram, R., Nesakumar, D., Chandramohan, K., 2014. Copper extraction from the discarded printed circuit board by leaching. Inter. J. Chemi. Petrochemi. Technol. (IJCPT), 4(4), 11-16.

66. Vijayaram, R., Nesakumar, D., Chandramohan, K., 2013. Copper extraction from the discarded printed circuit board by leaching. Res. J. Eng. Sci. 2(1), 11-14.

67. Oliveira, P.C., Marta Cabral, Charters Taborda, F. Margarido, F., Nogueira. C.A., 2009. Leaching studies for metals recovery from printed circuit boards scrap. EBR'09 - Electronics & Battery Recycling '09 (Proc. of 2nd Intern. Conf.) June 24 –26, 2009, Toronto, Canada ICM AG, Switzerland.

68. Chaurasia, A., Singh, K.K., Mankhand, T.R., 2013. Extraction of tin and copper by acid leaching of PCBs International J. Metall. Eng. 2(2), 243-248.

69. Le, H.L., Jeong, J., Lee. J.C., Pandey, B.D., Yoo, J.M., Huyunh, T.H., 2011. Hydrometallurgical process for copper recovery from waste printed circuit boards (PCBs). Miner. Process. Extrac. Metall. Rev. 32, 90-104.

70. Demir, H., Ozmetin, C., Kocakerim, M.M., Yapici, S., Copur, M., 2004. Determination of a semi-empirical kinetic model for dissolution of metallic copper particles in HNO_3 solutions. Chemi. Eng. Process. 43, 1095–1100.

71. Xiu, F.R., Zhang, F.S., 2009. Electro kinetic recovery of Cd, Cr, As, Ni, Zn and Mn from waste printed circuit boards: Effect of assisting agents. J. Hazard. Mater. 170(1), 191-196.

72. http://pubs.acs.org/cen/news/89/i22/8922scene1.html.

73. http://www.desolutions.com/lead_free_solder_joint_d.html.

74. Xiu, F., Zhang, F., 2009. Recovery of copper and lead from waste printed circuit boards by supercritical water oxidation combined with electrokinetic process. J. Hazard. Mater. 165, 1002–1007.

75. Oliveira, P.C., Taborda, F.C., Cabral, M., Margarido, F., Nogueira, C.A., 2009b. Leaching studies for metals recovery from printed circuit boards scrap, electronics and battery recycling. Proceeding of 2nd International Conference, Toronto, Canada, 1–2.

76. Mecucci, A., Scott, K., 2002. Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards. J. Chem. Technol. Biotechnol. 77, 449–457.

77. Peres, A.E.S., Pereira, C.A., Martins, A.H., 2012. Tin recovery by recycling of printed circuit boards from obsolete computers in Brazil, Revista De La Facultad De Ingenieria, 27, 45-50.

78. Yazici, E.Y., Deveci, H., 2013. Extraction of metals from waste printed circuit boards (WPCBs) in H_2SO_4-$CuSO_4$-NaCl solutions. Hydrometallurgy, 139, 30-38.

79. Oh, C.J., Lee, S.O., Yang, H.S., Ha, T.J., Kim, M.J., 2003. Selective leaching of valuable metals from waste printed circuit boards. J. Air Waste Manag. Assoc. 53(7), 897-902.

80. Jha, M.K., Lee, J.C., Kumari, A., Choubey, P.K., Kumar, V., Jeong, J., 2011. Pressure leaching of metals from waste printed circuit boards using sulfuric acid. JOM, 63(8).

81. Yang, H., Liu, J., Yang, J., 2011. Leaching copper from shredded particles of waste printed circuit boards. J. Hazard. Mater. 187, 393-400.

82. Gharabaghi, M., Irannajad, M., Azadmehr, A.R., 2013. Leaching kinetics of nickel extraction from hazardous waste by sulphuric acid and optimization dissolution conditions. Chem. Eng. Res. Design, 91(2), 325-331.

83. Kim, E.Y., Kim, M.S., Lee, J.C., Jha, M.K., Yoo, K., Jeong, J., 2008. Effect of cuprous ions on Cu leaching in the recycling of waste PCBs, using electro-generated chlorine in hydrochloric acid solution. Minerals Engineering 21, 121-128.

84. Kim, E.Y., Kim, M.S., Lee, J.C., Yoo, K., Jeong, J., Pandey, B.D., 2011. Leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution. Hydrometallurgy 107, 124–132.

85. Havlik,T., Orac, D., Berwanger, M., Maul, A., 2014. The effect of mechanical–physical pretreatment on hydrometallurgical extraction of copper and tin in residue from printed circuit boards from used consumer equipment. Miner. Eng. 65, 163–171.

86. Wang, M., Cao, H.B., Zhang, Y., 2011. Selective recovery of copper, zinc and nickel from printed circuit boards by ammonia leaching under pressure. 32(2), 596-602 (PMID:21528589).

87. Yang, J.G., Wu, Y.T., Li, J., 2012. Recovery of ultrafine copper particles from metal components of waste printed circuit boards. Hydrometallurgy, 1-6, 121–124.

88. Yazici, E.Y., Deveci, H., 2015. Cupric chloride leaching (HCl–CuCl2–NaCl) of metals fromwaste printed circuit boards (WPCBs). Inter. J. Miner. Process. 134, 89–96.

89. Turana., M.D., Altundogan, H.S., Tqmen, F., 2004. Recovery of zinc and lead from zinc plant residue, Hydrometallurgy 75, 169-176.

90. Jha, M.K., Nguyen, N.V., Lee, J.c., Jeong, J., Yoo, J.M., 2009 b. Copper recovery from low concentration waste solution using Dowex G-26 resin. Hydrometallurgy 97, 237-242.

91. Agrawal, A., Kumari, S., Ray, B.C., Sahu, K.K., 2007. Extraction of acid and iron values from sulphate waste pickle liquor of a steel industry by solvent extraction route. Hydrometallurgy 88, 58–66.

92. Agrawal, A., Kumari, S., Sahu, K.K., 2008. Liquid–liquid extraction of sulphuric acid from zinc bleed stream. Hydrometallurgy 92, 42-47.

93. Agrawal, A., Sahu, K.K., 2009. An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries. J. Hazard. Mater. 171, 61-75.

94. Krirsch, T., Maurer, G., 1996. Distribution of oxalic acid between water and organic solutions of tri-noctylamine. Ind. Eng. Chem. Res., 35, 1722-1735.

95. Mikami, Y., Iyatomi, N., 1996. Process for recovering sulphuric acid from metallic sulphate-containing exhaust sulphuric acid. U.S. patent 5, 489-423.

96. Sinha, M.K., Sahu, S.K., Meshram, P., Pandey, B.D., Kumar, V., 2010. Effective separation and recovery of hydrochloric acid and iron values from spent pickle liquor. Proceedings of the XI International Seminar on Mineral Processing Technology (MPT), NML, Jamshedpur, 824-831.

97. Eyal, A.M., Hazan, B., Bolch, R., 1991. Recovery and concentration of strong mineral acids from dilute solutions through LLX. II. Reversible extraction with branched chain amines. Solvent Extr. Ion Exch. 9, 211-222.

98. Shin, C.H., Kim, J.Y., Kim, J.Y., Kim, H.S., Lee, H.S., Mohapatra, D., Ahn, J.W., Ahn, J.G., Bae, W., 2009. Recovery of nitric acid from waste etching solution using solvent extraction. J. Hazard. Mater. 163, 729-734.

99. Spencer, B.B., Counce, R.M., Egan, B.Z., 1997. Extraction of nitric acid from aqueous media with Oϕ D(iB)CMPO–n-dodecane. Environ. Energ. Eng. 43(2), 555-564.

100. Bell, K., Geistb, A., McLachlana, F., Modoloe, G., Taylora, R., Wildene, A., 2012. Nitric acid extraction into TODGA. Procedia Chem. 7, 152-159.

101. Jaiswal, S.K., Mandal, D., Visweswara, R.V.R.L., 2015. Recovery and reuse of nitric acid from effluents containing free nitric acid in absence and presence of metal nitrates. Chem. Eng. J. 266, 271-278.

102. Eyal, A.M., Appelbaum, C., Baniel, A., 1986. Sulfuric acid recovery through solvent aided decomposition of ammonium sulfate. Solvent Extr. Ion Exch. 4, 803-821.

103. Eyal, A.M., Baniel, A.M., 1989. In: M.H.I. Baird (Ed.), Proc. 2nd Int. Conf. in Separation Science and Technology, Can. Soc. Chem. Eng., Ottawa, 667-674.

104. Eyal, A.M., Baniel, A.M., Hadju, K., Mizrahi, J., 1990. New process for recovery of zinc sulfate and sulfuric acid from zinc electro winning bleed solutions. Solvent Extr. Ion Exch. 8, 209-222.

105. Kesieme, U.K., Aral, H., Duke, M., Milne, N., Cheng, C.Y., 2013. Recovery of sulphuric acid from waste and process solutions using solvent extraction. Hydrometallurgy 138, 14-20.

106. Ntengwe, F.W., 2010. Removal of sulphuric acid from electrowin solutions by reactive extraction using alamine 336 in isodecanol-shell sol 2325 solvent mixture. Int. J. ChemTech. Res. 2(4), 2131-2139

107. Haghshenas, D.F., Darvishi, D., Rafieipour, H., Alamdari, E.K., Salardini, A.A., 2009. A comparison between TEHA and Cyanex 923 on the separation and the recovery of sulfuric acid from aqueous solutions. Hydrometallurgy 97, 173-179.

108. Tait B., 1993. The extraction of sulfuric acid by some binary extractants. Hydrometallurgy, 33, 245-251.

109. Scibona, G., Orlandini, F., Danesi, P.R., 1966. Extraction mechanism of HCl, HBR and HI by primary, secondary and tertiary long chain aliphatic amines. J. Ionrg. Nucl. Chem., 28, 1701-1706.

110. Banda, R., Nguyen, T.H., Lee, M.S., 2013. Recovery of hcl from chloride leach solution of spent HDS catalyst by solvent extraction, Chemi. Proce. Eng. 34(1), 153-163.

111. Sun, P.P., Lee, M.S., 2015. Mixer-settler operation for the recovery of platinum, iron and hydrochloric acid from the leaching solution of spent petroleum reforming catalysts. J. Ind. Eng. Chem. 21.

112. Zhang, X., Xingang, Li., Cao, H., Zhang. Y., 2010. Separation of copper, iron (III), zinc and nickel from nitrate solution by solvent extraction using LK-C2. Sep. Purif. Technol. 70(3), 306-31.

113. Lazarova, Z., Lazarova, M, 2005. Solvent extraction of copper from nitrate media with chelating LIX-reagents: Comparative equilibrium study. Solvent Extr. Ion Exch. 23(5), 695-711.

114. Bart, H.J., Marr, R., Bauer, A., Schein, R., Marageter, E., 1990. Copper extraction in nitrate media. Hydrometallurgy, 23, 281–295.

115. Lazarova, Z., Lazarova, M, 2007. Kinetic aspects of copper-LIX® extraction from nitrate/nitric acid aqueous solutions. Solvent Extr. Ion Exch. 25(5), 619-638.

116. Ferreira, A.E., Agarwal, S., Machado, R.M., Gameiro, M.L.F., Santos, S.M.C., Reis, M.T.A., Ismael, M.R.C., Correia, M.J.N., Carvalho, J.M.R., 2010. Extraction of copper from acidic leach solution with Acorga M5640 using a pulsed sieve plate column. Hydrometallurgy 104, 66-75.

117. Kumar, V., Kumar, M., Jha, M.K., Lee, J.C 2009. Extraction and separation of metals using LIX 84 and D2EHPA diluted in kerosene from sulfate solution. EPD Congress, TMS (The Minerals, Metals and Materials Society), 1089-1094.

118. Kumar, V., Jha, M.K., Kumar, M., Jeong, J., Lee, J.C., 2010. Extraction of copper from sulfate leach solution containing minor metallic constituents in mixer settler unit. EPD Congress, TMS (The Minerals, Metals and Materials Society), 413-420.

119. Agrawal, A., Perween, M., Pramanik, S., Sahu, K.K., 2010. Recovery of copper from PCBs leach solution by solvent extraction. Proceedings of the XI International Seminar onMineral Processing Technology (MPT-2010) 1189-1194.

120. Rao, K.S., Devi, N.B., Reddy, B.R., 2000. Technical Note: Solvent extraction of copper from sulphate medium using MOC 45 as extractant, Hydrometallurgy 57, 269-275.

121. Panda, S., Parhi, P.K., Pradhan, N, Mohapatra, U.B., Sukla, L.B., Park, K.H., 2012. Technical Note: Extraction of copper from bacterial leach liquor of a low grade chalcopyrite test heap using LIX 984N-C. Hydrometallurgy 121-124, 116–119.

122. Kongolo, K., Mwema, M.D., Banza, A.N., Gock, E., 2003. Cobalt and zinc recovery from copper sulphate solution by solvent extraction. Miner. Eng. 16, 1371-1374.

123. Kumar, V., Kumar, M., Bagchit, D., Jha, M.K., Jeong, J., Lee, J.C., 2007. Solvent extraction studies for removal of hazardous metals from the sulfate leach solution of electronic wastes. Proceedings of International Symposium of Resource Recycling November 27-28, 2007, Haevichi, Jeju, Korea.

124. Agarwal, S., Ferreira, A.E., Santos, S.M.C., Reis, M.T.A., Ismael, M.R.C., Correia, M.J.N., Carvalho, J.M.R., 2010. Separation and recovery of copper from zinc leach liquor by solvent extraction using Acorga M5640. Inter. J. Miner. Process. 97, 85-91.

125. Sahu, S.K., Agrawal, A., Pandey, B.D., Kumar, V., 2004. Technical Note: Recovery of copper, nickel and cobalt from the leach liquor of a sulphide concentrate by solvent extraction. Miner. Eng. 17, 949-951.

126. Kumar, R., Shah, D.J., Tiwari, K.K., 2013. Separation of copper and nickel by solvent extraction using LIX 664N. J. Environ. Prot. 4, 315-318.

127. Reddy, B.R., Park, K.H., Mohapatra, D., 2007. Process development for the separation and recovery of copper from sulphate leach liquors of synthetic Cu–Ni–Co–Fe matte using LIX 84 and LIX 973N. Hydrometallurgy 87, 51-57.

128. Nam, C.W., Park, K.H., Kim, H.I., 2004. Sulfuric acid pressure leaching of Cu–Ni–Co–Fe matte. Korean Soc. Geosyst. Eng. 41, 413-417.

129. Reddy, B.R., Priya, D.N., 2005. Process development for the separation of copper(II), nickel(II), and zinc(II) from sulphate solutions by solvent extraction. Sep. Purif. Technol. 45, 163-167.

130. Jana, R.K., Pandey, B.D., Kumar, V., Saha, A.K., Akerkar, D.D., 1987. Treatment of ammoniacal leach liquor from reduction roast-leach route of sea nodules by solvent extraction. Trans. Indian Inst. Metals, 40, 479-488.

131. Kumar, V., Pandey, B.D., Bagchi, D., Akerkar, D.D., 1989. Scope of using LIX 84 for separation of copper and zinc from complex sulphide solution. Proceeding of International Conference on Base Metal Technology, Jamshedpur, India, Feb. 8-9, 495-500.

132. Pandey. B.D., Kumar, V., Bodas, M.G., Akerkar, D.D., 1986. Separation and recovery of copper and zinc by solvent extraction and electrowinning from sulphate leach liquor of complex sulphide ore. Proceeding of National Symposium on Separation Techniques, Waltair, India, 136-139.

133. Miguel, E.R.S., Aguilar, J.C., Bernal, J.P., Ballinas, M.L., Rodriguez, M.T.J., Gyves, J., Schimmel, K., 1997. Extraction of Cu(II), Fe(III), Ga(III), Ni(II), In(III), Co(II), Zn(II) and Pb(II) with LIX 984N dissolved in n-heptane. Hydrometallurgy, 47, 19.

134. Amores, M., Coedo, A.G., Alguacil, F.J., 1997. Extraction of copper from sulphate solutions by MOC 45: Application to Cu separation from leachates of a copper flue dust. Hydrometallurgy. 47, 99.

135. Calligaro, L., Mantovani, A., Belluco, U., Acampora, M., 1983. Solvent extraction of copper(II), nickel(II), cobalt(II), zinc(II) and iron(II) by high molecular weight hydroxyoximes. Polyhedron, 2(11), 1189.

136. Lu, J., Dreisinger, D., 2014. Two-stage countercurrent solvent extraction of copper from cuprous chloride solution: Cu(II) loading coupled with Cu(I) oxidation by oxygen and iron scrubbing. Hydrometallurgy 150, 41-46.

137. Lu, J., Dreisinger, D., 2013. Solvent extraction of copper from chloride solution II: Cuprous oxidation by oxygen coupled with simultaneous cupric solvent extraction. Hydrometallurgy 138, 48–53.

138. Devi, A.P., Swain, N., Devi, N.B., 2014. Extraction and separation of Cu(II) in presence of Fe(II) and Fe(III) from acidic solution using LIX 973NS-LV. J. Chemi. Pharm. Res. 6(4), 1047-1052.

139. Sarangi, K., Reddy, B.R., Das, R.P., 1999, Extraction studies of cobalt(II) and nickel(II) from chloride solutions using Na-Cyanex 272. Separation of Co(II)/Ni(II) by the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures. Hydrometallurgy, 52, 253-265.

140. Hubicki, Z., Hubicka, H., 1996. Studies on the extraction process of nickel(II) sulphate purification using Cyanex, 272. Hydrometallurgy, 40(1-2), 65-76.

141. Sarangi, K., Parhi, P.K, Padhan, E., Palai, A.K., Nathsarma, K.C., Park, K.H., 2007. Separation of iron(III), copper(II) and zinc(II) from a mixed sulphate/chloride solution using TBP, LIX 84I and Cyanex 923. Sep. Purif. Technol. 55, 44-49.

142. Belkhouch, N.E., Didi, M.A., 2005. Separation of nickel and copper by solvent extraction using Di-2 Ethylhexylphosphoric acid-based synergistic mixture. Solvent Extr. Ion Exch. 23, 1-17.

143. Zhu, Z., Zhang, W., Pranolo, Y., Cheng, C.Y., 2012. Separation and recovery of copper, nickel, cobalt and zinc in chloride solutions by synergistic solvent extraction. Hydrometallurgy, 127-128, 1-7.

144. Pradhan, S., Devi, N., Mishra, S., 2014. Separation of copper and iron from chloride media using Cyanex 921 in kerosene. J. Cent. South Univ. 21, 1752-1755.

145. Liang, G., Tang, J., Liu, W., Zhou, Q., 2013. Optimizing mixed culture of two acidophiles to improve copper recovery from printed circuit boards (PCBs). J. Hazard. Mater. 250-251, 238- 245.

146. Giannopoulou, I., Panias, D., 2007. Copper and nickel recovery from acidic polymetallic aqueous solutions. Miner. Eng. 20, 753-760.

147. Gameiro, M.L.F., Machado, R.M., Ismael, M.R.C., Reis, M.T.A., Carvalho, J.M.R., 2010. Copper extraction from ammoniacal medium in a pulsed sieve-plate column with LIX 84-I. J. Hazard. Mater. 183, 165-175.

148. Chellammal, S., Raghu, S., Kalaiselvi, P., Subramanian, G., 2010. Electrolytic recovery of dilute copper from a mixed industrial effluent of high strength COD. J. Hazard. Mater. 180, 91-97.

149. Alguacil, F.J., Patricio, N., 2002. Non-dispersive solvent extraction of Cu(II) by LIX 973N from ammoniacal/ammonium carbonate aqueous solutions. Hydrometallurgy 65(1), 77-82.

150. Xie, F., Dreisinger, D.B., 2009. Solvent extraction of copper and cyanide from waste cyanide solution. J. Hazard. Mater. April.

151. Parija, C., Sarma, P.V.R. B., 2000. Separation of nickel and copper from ammoniacal solutions through co-extraction and selective stripping using LIX84 as the extractant. Hydrometallurgy 54, 195-204.

152. Schwartz, L.D., Etsell, T.H., 1998. The cementation of lead from ammoniacal ammonium sulfate solution. Hydrometallurgy 47, 273-279.

153. Farahmand, F., Moradkhani, D., Safarzadeh, M.S., Rashchi, F., 2009. Brine leaching of lead bearing zinc plant residues: process optimization using orthogonal array design methodology. Hydrometallurgy 95, 316-324.

154. Abdollahi, P., Yoozbashizadeh, H., Moradkhani, D., Behnian, D., 2015. A Study on cementation process of lead from brine leaching solution by aluminum powder Open Access Library Journal,2, e990. doi:http://dx.doi.org/10.4236/oalib.1100990.

155. Volpe, M., Oliveri, D., Ferrara, G., Salvaggio, M., Piazza, S., Italiano, S., Sunseri, C., 2009. Metallic lead recovery from lead-acid battery paste by urea acetate dissolution and cementation on iron. Hydrometallurgy 96, 123-131.

156. Raghavan, R., Mohanan, P.K., Swarnkar, S.R., 2000. Hydrometallurgical processing of lead-bearing materials for the recovery of lead and silver as lead concentrate and lead metal. Hydrometallurgy 58, 103-116.

157. Makhloufi, L., Saidani, B., Hammache, H., 2000. Removal of lead ions from acidic aqueous solutions by cementation on iron. Water Res. 34, 2517-2524.

158. Shin, J.H., Kim, K.W., Ahn, H.J., 2000. Preparation of leady oxide for lead–acid battery by cementation reaction. J. Power Sources 89, 46-51.

159. Abdollahi, P., Moradkhani, D., Behnian, D., Yozbashizadeh, H., 2006. Lead recovery from Iranian zinc plant residue using brine leaching method. Proceedings of XXII International Mineral Processing Congress, Istanbul Turkey, 1515-1520.

160. Panda, B., Das, S.C., 2001. Electrowinning of copper from sulfate electrolyte in presence of sulfurous acid. Hydrometallurgy, 59, 55-67.

161. Viswanath, S.G., Sajiml, G., 2011. Electrowinning of copper powder from copper sulphate solution in presence of glycerol and sulphuric acid. Indian J. Chem. Technol. 18, 37-44.

162. Pedro H, B.C., Ruotolo, Luís A.M., 2014. Optimization of copper electrowinning from synthetic copper sulfate solution using a pulsed bed electrode. Hydrometallurgy 150, 52-60.

163. Veglio, F., Quaresima, R., Fornari, P., Ubaldini, S., 2003. Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning. Waste Manage. 23, 245-252.

164. Shakarji, R. A., Yinghe, H., Simon, G, 2011. The sizing of oxygen bubbles in copper electrowinning. Hydrometallurgy 109, 168–174.

165. Pace, G.F., Stauter, J.C., 1974. Direct electrowinning of copper from synthetic pregnant leach solutions utilizing SO_2 and graphite anodes-pilot plant results. Can. Min. Metall. Bull. 67, 85.

166. Bharucha, N.R., Claessens, P.L., Ho, P.P.K., Loutfy, R.O., 1982. Electrowinning of metals, Canadian Patent No.1, 120, March, 23. 423, 13.

167. Gorgievski, M., Bozic, D., Stankovic, V., Bogdanovic, G., 2009. Copper electrowinning from acid mine drainage: A case study from the closedmine "Cerovo". J. Hazard. Mater. 170, 716-721.

168. Xiao, H., Chi, Y., Buekens, A., 2013. Combustion characteristics of waste printed circuit boards in thermogravimetric analyzers. Environ. Prog. Sustain. Energy. doi:10.1002/ep.

169. http://cameochemicals.noaa.gov/chris/PHN.pdf.

170. Zhou, Y., Wu, W., Qiu, K., 2011. Recycling of organic materials and solder from waste printed circuit boards by vacuum pyrolysis-centrifugation coupling technology. Waste Manage. 31, 2569-2576.

171. Feng, Z., Marks, C.R., Barkatt, A., 2003. Oxidation-rate excursions during the oxidation of copper in gaseous environment at moderate temperatures. Oxid. Met. 60, 393-408.

172. http://www.chem.mtu.edu/~fmorriso/cm3215/HeiserChartArticleTransASME1947.pdf.

173. http://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html.

174. http://www.technicalglass.com/technical_properties.html.

175. Williams, P.T., 2010. Valorization of Printed Circuit Boards from Waste Electrical and Electronic Equipment by Pyrolysis. Waste Biomass Valor 1, 107-120.

176. Wang, J., Li,Y., Jin, Y., Wang, Z., 2014. Kinetics and mechanism of thermal decomposition of polyepoxyphenylsilsesquioxane/epoxy resin systems from isothermal measurement. J Macromol Sci, Part A: Pure and Applied Chemistry 51, 249-253.

177. Malathi, M., Kumar, A., Ajmani, S.K., Godiwalla, K.M., Ranganathan, S., 2014. Generation of magnesium for in situ desulphurisation investigation on influence of inert gas flow rate. Tran Ins Miner Met (Accepted).

178. http://www.gsi-net.com/en/publications/gsi-chemical-database/single/441.html.

179. https://books.google.co.in/books?isbn=0891168699.

180. Bird, R.B., Stewart, W.E., Lightfoot, E.N., 1960. Transport Phenomena. 1st ed. Tokyo: Wiley International.

181. Levenspiel, O., 1962, Chem. Reaction Engineering, Wiley, New York, pp.357-377.

182. Smith, J.M., 1981, Chem. Eng. Kinetics, McGraw Hill, New York, pp 642-645.

183. Habashi, F., 1969. In: Extractive metallurgy general principles, Chapter-8, Vol. 1, Gordon and Breach, New York, pp. 154-155.

184. Georgious, D., Papangelakis, V.G., 1998, Sulphuric acid pressure leaching of a limonitic laterite: Chemistry and Kinetics. Hydrometallurgy, Vol. 49, pp. 23-46.

185. Colussi, I., Meriani, S., Monte, U., 1983, Kinetics models for the leaching with s ulphuric acid of zinc-containing slags, Hydrometallurgy, 10, 61-67.

186. Bajpai, A.C., Calus, I.M and Fairley, J.A., 1978. In book; Statistical methods for engineers and scientists, John Wiley & Sons, pp. 368-427.

187. Zerroual, L., Tedjar, F., Guitton, J., Mousser, A., 1993. Mechanism of PbO_2 formation in lead/acid battery positive plate, J. Power Sources 41 (3), 231-238.

188. Abd El Haleem, S.M., Abd El Aal, E.E., 2004. Electrochemical behavior of nickel in HNO_3 and the effect of chloride ions, JMEPEG 13, 784-792.

189. Abd El Aal, E.E., Abd El Wanees, S., Abd El Aal, A., 1992. Autocatalytic dissolution of Pb in HNO_3, J. Mater. Sci. 27, 365-373.

190. Stupnisek-Lisac, E., Karsulin, M., 1984. Electrochemical behaviour of nickel in nitric acid, Electrochim. Acta 29 (10), 1339-1343.

191. Jha, M.K., Kumari, A., Jha, A.K., Kumar, V., Hait, J., Pandey, B.D., 2013. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone, Waste Manag. 33, 1890-1897.

192. Kinney, P.J., 1963. An infrared study of the tributyl phosphate-nitric acid-water solvent extraction system. Retrospective Theses and Dissertations. Paper 2965.

193. http://www.ecse.rpi.edu/~schubert/Course-ECSE-6290%20SDM-2/1%20MOSFET 1%20Basics.pdf.

194. http://www.nxp.com/documents/leaflet/75016946.pdf.

195. http://www.silterra.com/news_20120228.html.

196. http://www.infineon.com/dgdl/Press+Release+-+english.pdf?folderId=db3a304412b407950112b408e8c90004&fileId=db3a30432e07b2f1012e0b0f38cc00e9.

PUBLICATIONS