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Extraction of Metals from the Electronic Waste by Chemical Degradation Followed by Froth Floatation Cell

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ABSTRACT :

Electronic waste is increasing day by day with a huge amount. And there are no sufficient recyclers to recycle the e-waste. In the e-waste, the Printed circuit boards contains precious metals and toxic chemicals. While disposing them in the environment without any proper knowledge causes the pollution to environment. PCBs are coated with brominated epoxy resin to act as insulator in circuit boards. The metals which are present in PCBs are rare earth metals, while extracting these metals furans and dioxins released by the brominated epoxy resin which is harmful to our health. To remove the BER, Chemical degradation with a solvent NaOH at STP conditions with an optimum time of 8 hours. The whole epoxy layer was peeled off from the e-waste, and to separate the plastic and metals into fraction centrifugation was used with an optimum time of 10-15 minutes at 1000 rpm. After the separation of metals sample was analyzed using the SEM-EDS.

Keywords: PCBs, Centrifugation, BER

INTRODUCTION :

The amount of solid waste has sharply increased along with industrialization, the development of society, and the expansion of the economy. Electronic waste is a huge part of solid waste, accounting for around 5% of all waste generated annually. E-Waste is an inevitable by-product of technological advancement, especially in this day of fast development. In India, there will be an estimated 2 million tons of e-waste generated annually by 2021, and that number is projected to increase by 5-7% annually. China, the United States of America, Japan, and India are the next-largest producers of e-waste. The two most important problems with e-waste are environmental impact and resource depletion. Consumer gadgets including old phones, laptops, TVs, and other electronics are the main source of e-waste. Valuable non-ferrous metals like Au, Ag, Pd, and Cu are present in e-waste trash. The improper disposal of e-waste in India has major health and environmental consequences because it includes toxic chemicals that can leach into the land and water and harm the wellness of both humans and animals. These metals have a huge, large demand and are more expensive in society. As a result, before disposing of e-waste into the environment, the metals must be extracted. The recovery of metals from e-waste has a number of advantages, including a reduction in the environmental impact of electronic waste, a decrease in the need for mining, and the provision of a source of valuable materials that can be recycled in the creation of new products. However, the extraction procedure must be both affordable and environmentally friendly. In order to do this, electronic waste must first undergo chemical degradation in order to remove brominated epoxy resin from printed circuit boards (PCB), and then it must undergo froth flotation to selectively separate metals from other metals.

Fig.01 Disposal of Electronic Waste on the ground
Source: https://images.app.goo.gl/

Fig.02 Heap of e-waste on the ground
Source: https://api.time.com/wp-content/

Metals extracted from electronic waste can be used in a variety of applications, like the production of new electronic devices and components, the Manufacturing of Jewelry items, Production of various parts and components in the automotive industry, Overall, the extracted metals have a wide range of applications, many of which have an impact on the environment, economy, and the quality of life of people.

Statistics of Electronic Waste Generation in India

India produces 3.23 million tonnes of e-waste annually, making it the third-largest producer in the world behind the US and China. Around 9.79% of the total amount of created e-waste in 2017–2018 was managed and recycled. This percentage rises from 9.79% to 21.35% in 2018–2019. This proportion rises to 22.7% of the total amount of created e-waste in 2019–2020.

Fig.03 Forecasting of e-waste generation from 2007-2025
Source: https://www.researchgate.net/profile/

Fig.04 Ports where e-waste received and dispatched
Source: https://www.researchgate.net/profile/

Composition of Metals in WPCBs

Waste Printed Circuit Boards are the main components of electronic devices and contain valuable metals. And one-third of PCBs (Printed Circuit Boards) weight are made up of metals, copper (16%), tin (4%), iron (3%), nickel (2%), and zinc (1%). In addition, there are many rare metals, such as Au (0.039%), Ag (0.156%), and Pad (0.009%).[1]

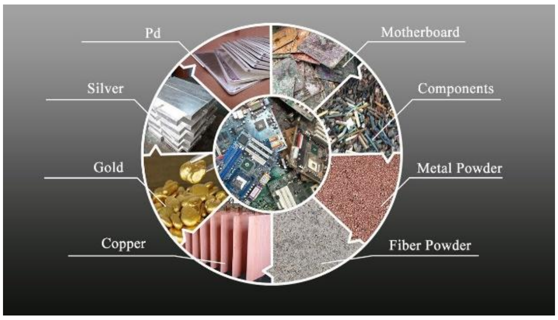

Fig.05 Composition of WPCB
Source: https://www.sunygroup.cn/e-waste

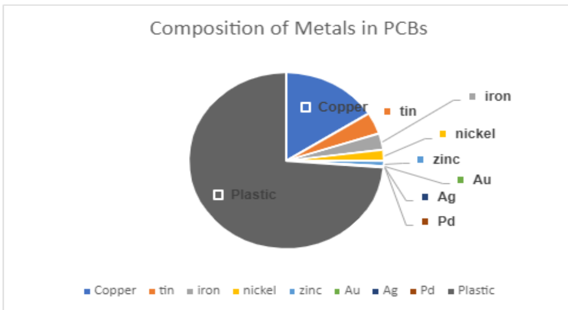

Fig.06 Composition of WPCB in the form of Pie-chart

Effects of WPCBs on the Environment

WPCBs are a significant source of e-waste. When PCBs are not properly disposed of, toxins can leach into the land, water, and air. And, when recycling, they can be exposed to an acid bath, which releases harmful fumes into the air and water. These hazardous substances also accumulate in the food chain, threatening human and animal health. Toxins lead to brain damage, hair loss, renal failure, and other harmful consequences.

Fig.07 Soaring of e-waste
Source: https://www.soaring-e-waste-affects

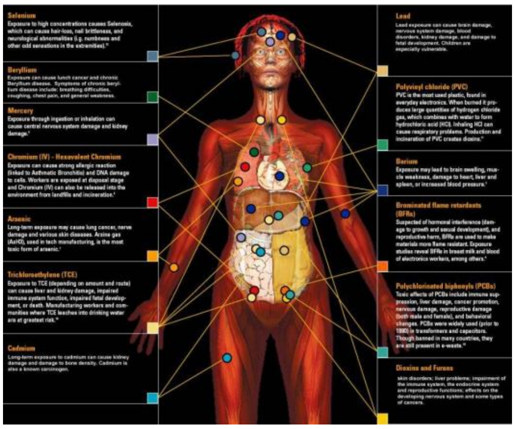

Fig.08 Harmful effects of e-Waste dumping
Source: https://learn-more/harmful-effects/

REVIEW OF LITERATURE :

Pre-Processing of the WPCBs is the first task during extracting the non-ferrous metals from e-waste. For this, there are many methods to adopt from the following papers. Tatarants et al.[2] have done the crushing of the electronic waste to make it into a fine powder. To extract the metals from the following sample. And Mallampati et al.[3] have done the pre-processing by ball-milling the electronic waste. From this electronic waste, small pieces were get converted into a fine powder, then it will be easy to extract the non-ferrous metals by froth floatation.

WPCBs are coated with the BER to prevent electrical shocks and it acts as a flame retardant. Where before extracting the non-ferrous metals from the e-waste, BER must be removed for this there are some procedures like chemical degradation. From the various works, they use solvents like NaOH, DMF, H_2SO_4, etc. There are some studies on the dissolution of the BER of e-waste before the extraction of precious metals. Tatarants et al.[2] had used the Ultra-Sonication process, In which they used the DMF in the solid-to-liquid ratio of 1:6 (weight/Volume). This whole process is done at the conditions of temperature 50°C with an optimum time of 4 hours. The ultrasonic bath was done at the frequency 40kHz, this dissolution of BER was done in the organic solvent to break the internal Vander Waals bonds of BER between the metals and plastic particles. In another research paper Balaji et al.[4], they used the solvent NaOH to remove the BER from the e-waste. And they used the process of autoclave treatment with operating conditions of temperature 121°C and pressure of 1.1 kg/cm^2 to remove the 100% epoxy resin from the PCBs. The optimal time for the whole process is 1 hour with an optimal concentration of 0.25N of NaOH. Panda et al.[5], they have used the DMF for the dissolution of BER at the temperature of 140°C. The separation of the BER from the metallic surfaces reduces the formation of toxic PBDD/Fs during the roasting process. While extracting the metals. The removal of epoxy resin is proven by Tatarants et al.[2], use the EDS analysis and SEM images. After the BER removal, e-waste collaborates with both metals and plastic. To separate these particles, Choubey et al.[6] have done the density separation method. And further, they used the Electromagnetic separator to separate the ferrous and non-ferrous metals. They selected the non-ferrous metal powder for the further process like extraction of precious metals like Cu, Ag, and Au.

Electronic waste contains various metals, in that there are some non-ferrous metals like gold, silver, copper, etc. Birloaga et al.[7], they used Hydrometallurgical methods for the recovery of copper, gold, and silver from the PCBs. For the copper dissolution they use the two-step counter current leaching with a solvent 1.7N H_2SO_4, 17% H_2O_2 with a solid/liquid ratio of 15 gm/lt. The optimal duration of the following experiment is 1 hour with continuous stirring at 200 rpm at room temperature. And they used the thiourea as a reagent, meanwhile, they use the tri-ferric ion as an oxidizing agent for the dissolution of gold and silver. They used the AAS and XRF for the analysis of copper and precious metals. Another process for the extraction of precious metals from the e-waste is the froth floatation process to separate the metals and waste matrix from the slot, it was done by Dinç et al.[8] and they used methyl isobutyl carbinol as the frother to produce stable foams. Oliveira et al.[9] used gravity and electrostatic separation. And subsequently, they used magnetic separation with gravity and electrostatic separation. After the electrostatic separation, the product obtained was 88% for the lower particle size (<0.3 mm) and 62% for particle sizes (>1.18 mm). Hilal et al.[10] have done the adsorption, they used the solvent which was manufactured by in-situ polymerization of the polyacrylic acid and aquaria (1:3 HNO_3:HCl). Accurately they take 5gm of the e-waste, and they showed the results adsorption efficiency of gold is higher than silver ion from adsorbent material. To extract the copper from the e-waste Annamalai et al.[11] have done the bio-leaching process. It is an eco-friendly process to recover metals from e-waste, and it shows the highest dissolution rate at 32.4%, which was achieved after 7 days of leaching by using the Acidithiobacillus ferrooxidans. Zhao et al.[12] have done the bio-leaching process to extract precious metals from the e-waste. They use extreme acidophiles as a solvent to leach the precious metals. Where they concluded this bio-leaching technology is a promising technology for the recovery of metals from electronic waste. Karume et al.[13] have done the extraction of the gold from the electronic waste by using the α-cyclodextrin (α-CD). They had taken the 300 g of e-waste and dissolved it in a 500 mL sodium bromide/nitric acid mixture and these were all characterized by AAS using AA500 to determine the amount of gold present. And they maintained a pH of 4-6 by adding the KOH (1M) then, α-CD added and it becomes a reddish-brown color precipitate. And it was dispersed in 50 ml of distilled water and then reduced by $Na_2S_2O_3$. They concluded that elemental gold was extracted by this process.

Rafael et al.[14], they explained various perspectives of extracting the metals from e-waste by using deep eutectic solvents (DES). They have done the leaching process with the following solvent. Lukomska et al.[15], they have discussed various methods to recover metals from printed circuit boards by

Ionic Liquids, DESs, and, organophosphorus. They have done the acid extraction. Choubey et al.[6],they used electrolysis to extract the precious metals from the e-waste, and mainly they used this technique to extract the copper from the sample. They dissolved the sample in an H_2SO_4 for 4 hours and stirred at a temperature of 80°C after they add 30 ml HCl and 10 ml HNO_3. They used copper as a cathode and iron as an anode.

The extraction of non-ferrous metals from the WPCBs is not the easiest work. For this, there are some older methods like the autoclave method using solvent NaOH, Ultra-sonication method in the presence of the solvent DMF, Hydrometallurgy process, Pyro metallurgy process, Chelating, Pyrolysis, etc. And these processes are mainly for the removal of BER and are followed by the extraction of non-ferrous metals. By the latest technologies under the STP conditions, the chemical degradation of the BER is possible and the selective separation of the non-ferrous metals will be done by the froth floatation cell. Previously many authors have done a study on the froth floatation dynamics for the extraction of non-ferrous metals through the froth floatation cell with different frothers and depressants.

The main purpose of the removal of BER from the PCBs, while extracting the non-ferrous metals from the PCBs. It may be reacted or it must be heated to get a desired product whereas during these conditions it may affect our health because it releases toxic fumes. And the main cause of selecting this study is to reduce the pollution to the environment by e-waste (Solid waste pollution). The metals which are used in the manufacturing of various PCBs and other boards are precious and rare earth metals and expensive, during disposal time there may be a chance of releasing toxic gases. To sustain these conditions extraction of non-ferrous metals is the best way.

Overall objective of the work

The overall objective of the following term paper is to extract the metals from E-Waste by chemical degradation followed by the froth floatation cell.
Specific Objective 1: Pre-Processing of electronic waste.

- Collecting the E-waste, and removing the transistors from Waste Printed circuit boards.
- Pulverization of the e-waste, And the removal of Brominated Epoxy resin through chemical degradation.

Specific Objective 2: Separation of the metals from the electronic waste.

- By using centrifugation in the presence of the di-methyl formaldehyde.
- Separation of metal particles from the fiber particles through gravity settling.
- Specific Objective 3: Extraction of metals from electronic waste.
- Extraction of metals selectively from the e-waste through froth floatation cell.

MATERIALS AND METHODS :

Materials Required

Waste printed circuit boards, Sodium hydroxide pellets, Mechanical tools, Domestic mixer grinder.

Pre-Processing of Electronic Waste

The Waste Printed Circuit Boards are collected from the television and radio repair shops (figure.07), and the components like transistors, resistors, etc. from the printed circuit boards with the help of some mechanical tools (figure.08). For shredding and size reduction, a domestic mixer grinder can be used to make the PCBs into a fine powder (figure.09).

Fig.09 Printed Circuit Board

Fig.10 Printed Circuit Board Chips

Fig.11 Fine Powder of PCBs

Table.01 Mesh Analysis of Sample

SI no	Mesh no	Weight (grams)	Weight faction	D_{pi} (mm)	X_i/D_{pi}	(X_i/D_{pi}^3)
1	20	52.03	0.386	1.1001	0.350877	1.331363
2	48	45.92	0.34	0.356	0.955056	0.045118

3	65	18.05	0.134	0.252	0.531746	0.016003
4	100	12.16	0.09	0.147	0.612245	0.003177
5	150	4.96	0.0368	0.104	0.353846	0.001125
6	200	1.57	0.0116	0.089	0.130337	0.000705
7	pan	0	0	0	0	0
		134.69			2.934108	1.39749

Note: The volume surface mass diameter of a sample is **0.3488mm**
The volume mean diameter of a sample is **0.8943mm**

After the size reduction of electronic waste. The Brominated Epoxy resin in the electronic waste can be removed. And for this chemical degradation is the best technique with the solvent Sodium Hydroxide with a concentration of 5N taken along with an electronic waste sample in the ratio of 1:6 (weight/volume) (figure.10). At the standard temperature and pressure (273°K, 1atm) with an optimum time of 8 hours. The solvent sodium hydroxide breaks the internal Vander Waals bonds of the brominated epoxy resin. From the figure.12 shows the separation of two layers after the BER removal from the e-waste sample with a duration of 8 hours. While chemical degradation BER floats on the solvent NaOH (figure.13).

Fig.12 e-waste and NaOH are Combined in the ratio 1:6

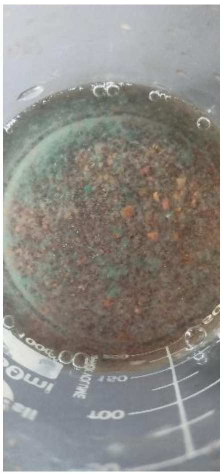

Fig.13 During the chemical degradation of BER taking place

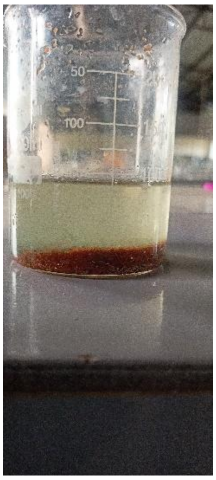

Fig.14 After the Chemical degradation of sample with an optimum time of 8 hours

The chemical degradation is followed by the separation of the BER from the sample which is done with the help of filter paper. And the BER there in green color, and it can be observed in the below figure.15.

Fig.15 Image of the Brominated Epoxy Resin

Separation of Plastic (fiber particles) from Electronic Waste

When the Brominated Epoxy Resin is removed the electronic waste sample contains both metal particles and fiber particles. And fiber particles are getting separated by the Centrifugation Process with an optimum time of 15 to 20 minutes. The metal particles are getting separated by the gravity separation technique based on the density difference between the fiber particles and [illegible] Centrifugation technique, the overlap zone between the metal particles and the fiber particles is in the below figure.16.

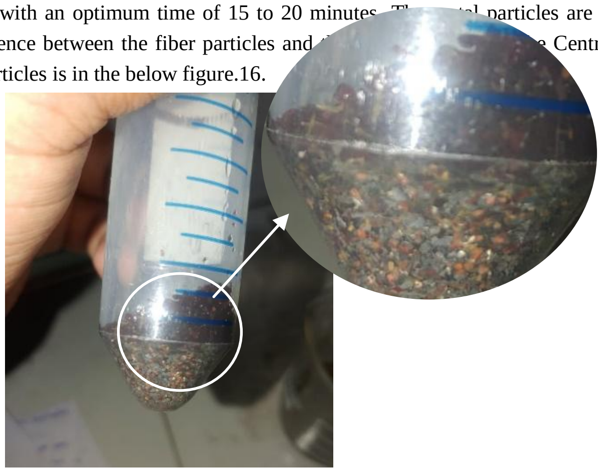

Fig.16 Overlap Zone between the metal particles and plastic particles after the centrifugation

The metals and fiber particles are getting separated by the Sink and Float method which is the principle of the density difference between the particles. The particles which have a low density than the solvent float on the solution. The following figure.17 shows the separation of particles through the sink and float method.

Fig.17 Sink and Float method for separation of metals and plastic particles

Fig.18 Centrifugation Equipment

RESULTS & DISCUSSION :

Removal of Brominated Epoxy Resin from the Waste Printed Circuit Boards

The removal of Brominated epoxy resin takes place through chemical degradation, the following chemical reaction takes in the removal of BER (Figure.19). In this following reaction Sodium hydroxide reacts with the BER and forms the sodium salts, by the formation of this salt the concentration of the NaOH decreases from 5N to 2N.

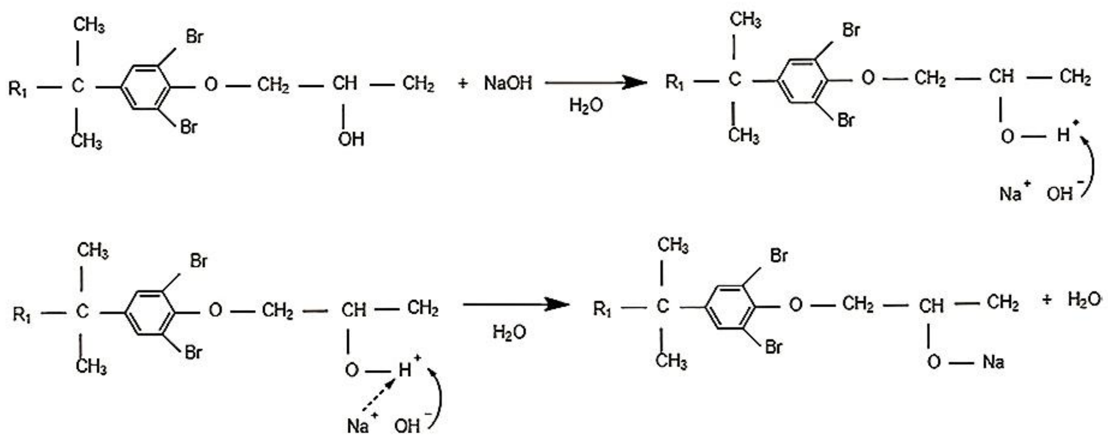

Fig.19 Chemical Reaction between Brominated epoxy resin and NaOH
Source: https://doi.org/10.1016/j.clema.2021.100015

SEM images of the sample before and after the BER removal and plastic separation are given below (Figure.20, Figure.21)

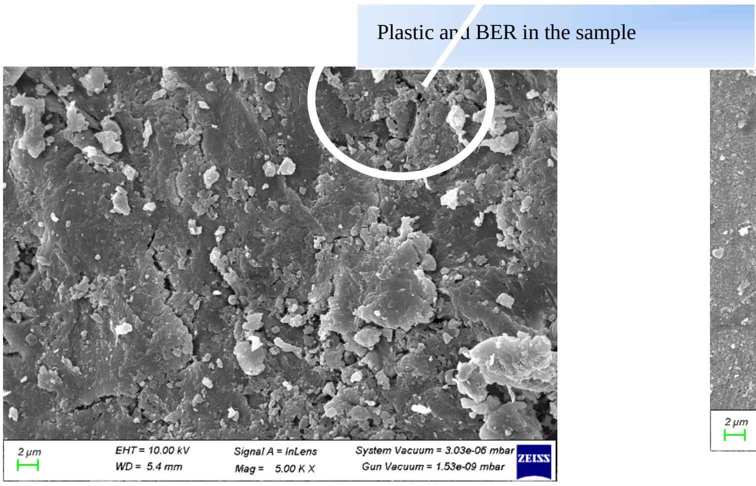

Fig.20 SEM Image of the sample before the BER removal and plastic separation

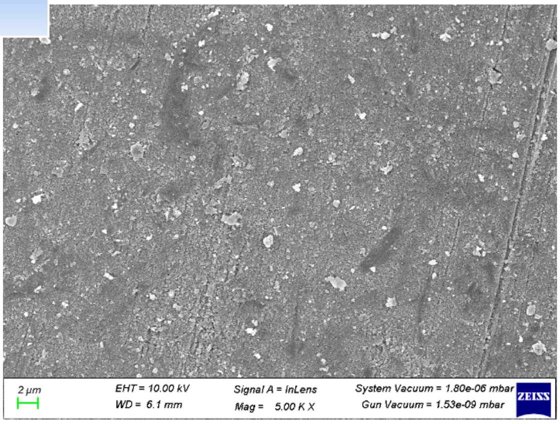

Fig.21 SEM image of the sample after the BER Removal and plastic separation

SEM-EDS Ana

lysis of a sample before and after epoxy removal and plastic removal

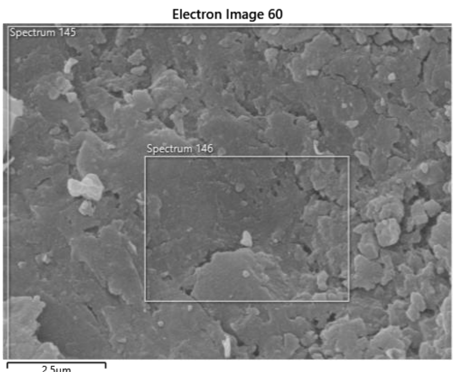

Fig.22 Electron image of a sample before epoxy and plastic removal

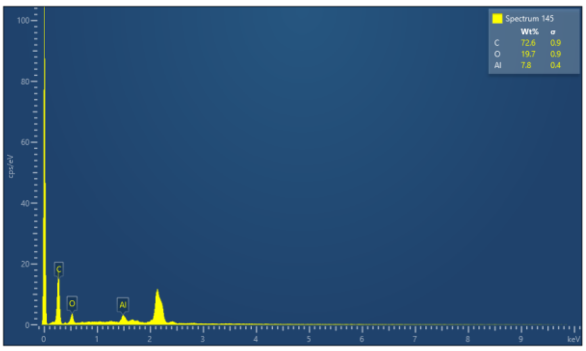

Fig.23 SEM-EDS analysis of a sample before epoxy and plastic removal

Figure.22 shows the electron image (SEM image) of a sample before epoxy and plastic removal. And figure.21 shows the SEM-EDS analysis of a sample, where it represents the presence of three elements - Carbon (C), Oxygen (O), and Aluminum (Al) with the weight percentage of C being the highest at 72.55%, followed by O at 19.68% and Al at 7.76%. In terms of atomic percentage, C is also the most abundant element at 79.92%, followed by O at 16.28%, and Al at 3.81%. In this sample more amount of plastic there than metal. So, the atomic percentage of carbon is more than aluminum. (See Appendix A)

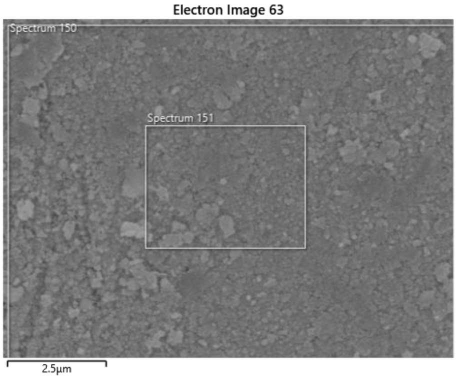

Fig.24 Electron image of a sample after epoxy and plastic removal

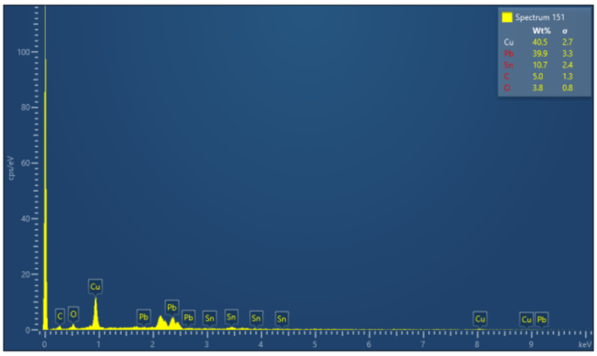

Fig.25 SEM-EDS analysis of a sample after epoxy and plastic removal

Figure. 24 shows the electron image (SEM image) of a sample after epoxy and plastic removal. And figure.25 shows the SEM-EDS analysis of a sample, copper is the most abundant element by weight, with a weight percentage of 40.51%, followed by lead at 39.91%. Carbon and oxygen make up a smaller percentage of weight, at 5.05% and 3.80%, respectively. In terms of atomic percentage, copper is also the most abundant element, with a higher percentage of 40.40%. Lead is again the second most abundant element at 12.20%, with carbon and oxygen following closely behind at 26.62% and 15.05% respectively. After the removal of epoxy and plastic, the metal components are only present there. Therefore, from the graph, we can conclude that the non-ferrous metal copper is present. (See Appendix B)

CONCLUSION :

From this, it is concluded that Chemical degradation at STP conditions (273°K, 1atm) with an optimum time of 6 hours is the best way to remove the brominated epoxy resin, and centrifugation with an optimum time of 10-15 minutes at 1000 rpm is to separate the plastic and metal particles

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NOMENCLATURE :

PCBs	-	Printed Circuit Boards
WPCBs	-	Waste Printed Circuit Boards
BER	-	Brominated Epoxy Resin
NaOH	-	Sodium Hydroxide
DMF	-	Dimethyl formamide
H_2SO_4	-	Sulphuric Acid
SEM	-	Scanning Electron Microscope
EDS	-	Energy Dispersive spectroscopy
H_2O_2	-	Hydrogen Peroxide
AAS	-	Atomic Absorption Spectroscopy
XRF	-	X-ray Fluorescence Spectroscopy
α-CD	-	α-cyclodextrin
PBDDs	-	Poly brominated di-benzo di-oxins
PBDFs	-	Poly brominated di-benzo di-furans

Appendix :

Appendix A

Table.02 SEM-EDS analysis data of sample before BER and Plastic removal.

Element	Wt.%	Atomic %
C	72.55	79.92
O	19.68	16.28
Other metals	7.76	3.81
Total:	100.00	100.00

Appendix B

Table.03 SEM-EDS analysis data of sample after BER and Plastic removal.

Element	Wt.%	Atomic %
C	5.05	26.62
O	3.80	15.05
Cu	40.51	40.40
Sn	10.73	5.73
Pb	39.91	12.20
Total:	100.00	100.00