Recycling of Electronic Waste II

Proceedings of the Second Symposium

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Edited by

Lifeng Zhang
Gregory K. Krumdick

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Foreword

Production and use of electrical and electronic equipment, such as TV sets, computers, mobile phones and many other daily-life items, are dramatically increasing over years, while the lifespan of many products becomes shorter- for instance for CPUs from 4–6 years in 1997 to 2 years in 2005. It is estimated that 20-50 million metric tons electronic wastes per year are generated worldwide. For example, in the U.S., it was estimated that over 500 million computers between 1997 and 2007 became obsolete, and only 20% of them was collected, treated and recycled. The electronic wastes scrap represents a complex mixture of three major material fractions: (i) metals, (ii) polymers and (iii) ceramics. The metal fraction including iron, copper, aluminum, gold and others in electronic wastes is over 60%, while pollutants comprise 2.70%. Five hundred million personal computers contain approximately 2,872,000 t of plastics, 718,000 t of lead, 1363 t of cadmium and 287 t of mercury. Not surprisingly, electronic wastes today constitute 2-5% of municipal solid wastes and they are growing 2–3 times faster than any other components in municipal solid wastes. These numbers should attract our attention by the following points:

- Need for recycling: Recycling of electronic wastes is necessary and even vital to our society because of their big amount and quick increasing;

- New potential energy source and renewable materials: The large amount of plastics in electronic waste are potential energy source. The conversion of waste plastics into fuel through pyrolysis represents a sustainable way for the recovery of the organic content of the waste and also preserves valuable petroleum resources in addition to protecting the environment. The worlds limited reserve of coal, crude oil and natural gas places a great pressure on mankind to preserve its existing non-renewable materials. The combustion of the plastics in electronic waste can also used for heating sources for cement industries and metal industries.

- Economic motivation for recycling: The fact that electronic contains precious metals is a major economic driver for its recycling. For cell phones, calculators and printed circuit board scraps, the precious metals make up more than 70% of the value, and for TV boards and the DVD player they still contribute to about 40%.

- Environmental issues: Special attention should be paid to toxic components in the electronic wastes during recycling process, such as polycarbonate materials, bromine and chlorine, and heavy metals like lead, cadmium and mercury. During pyrolysis of electronic powders, toxic gas will be emitted. These toxic materials may enter our water and air system. Green recycling of electronic wastes to prevent the toxic materials from entering our living system is of importance to the environmental sustainability.

The current symposium on the Recycling of Electronic Wastes will highlight materials management and technologies to address sustainable approaches to recycle electronic wastes, including

- Mechanical recycling of Electronic Wastes
- Recycling of plastics from Electronic Wastes
- Recovery of metals from Electronic Wastes
- Hydrometallurgical recycling (leaching) of Electronic Wastes
- Combustion or pyrolysis of Electronic Wastes

Lifeng Zhang
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December 05, 2010

Organizing Committee

Dr. Lifeng Zhang currently is an assistant professor at the Department of Materials Science and Engineering at Missouri University of Science and Technology. Lifeng received his Ph.D. degree from University of Science and Technology Beijing in 1998 and had 13 years teaching and research work at different universities - Norwegian University of Science and Technology, University of Illinois, Technical University of Clausthal and Tohoku University. Lifeng has compound backgrounds in primary production, refining, casting, and recycling of metals, recycling of electronic wastes, and modeling for metallurgical processes. Lifeng has published over 200 papers and made over 150 presentations at meetings and conferences. He is a Key reader (Member of Board of Review) for three journals and a reviewer for over twenty-five journals.

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Technologies for the Recycling of Electronic Wastes

Session Chairs:
Lifeng Zhang
Jaan Kers

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MECHANICAL RECYCLING OF ELECTRONIC WASTES FOR MATERIALS RECOVERY

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Keywords: Printed Circuit Boards, Mechanical Recycling, Material Recovery

Abstract

In this paper, the mechanical milling of the Printed Circuit Boards (PCB) was carried out. First goal of the work was to examine the management of the WEEE, in particular the re-use of PCB. Firstly, recycling methods of PCBs were summarized. During the study mechanical separation methods (magnetic-, density- and air separaton), electrical, and chemical methods were examined. Secondly the optimal particle size for air-classification was determined. Several tests were carried out to find the most effective separation method for separation of different material groups from PCB scrap. The new air classification stand was developed for testing the separation of lightweight particles like tinfoil stripes and plastics. The test results showed sufficiently good separation of heavier Al and Cu. For milled materials characterization the SA, IA, laser diffraction analysis and SEM were used. The chemical composition of the PCB powders was studied by means of energy dispersive X-ray microanalysis (EDS).

Introduction

Technological innovation and intense marketing is accelerating the update rate of electric and electronic equipment (EEE) and shorten the average lifespan. As a result, the amounts of wastes of electric and electronic equipment (WEEE) containing 3% of printed circuit boards (PCB) are dramatically increasing. The UN Environment Program estimates that the world generates 20–50 million tones of WEEE each year and amounts are rising three times faster than other forms of municipal waste [1]. The typical composition of PCB is non-metals (plastics, thermosets, glass fibre, ceramics) >70%, copper ~16%, solder ~4%, iron, ferrite ~3%, nickel ~2%, silver 0.05%, gold 0.03%, palladium 0.01%, others (bismuth, antimony, tantalum, etc.) <0.01% [2] Significant quantities of nonmetallic materials in PCBs (up to 70 wt.%) present an especially difficult challenge for recycling [4]. The nonmetallic materials of PCBs mainly consist of thermosetting plastics (TS), thermoplastics (TP), glass fibers and ceramic fractions. Thermosets cannot be remelted or reformed because of their cross-linked polymeric structure. Incineration is not the best method for treating nonmetallic materials because of the presence of inorganic fillers such as glass fiber, which significantly reduces the fuel efficiency [2]. Disposal in landfill is the main method for treating non-metallic materials of PCBs, but it may cause secondary pollution and resource-wasting [3]. Since the metallic elements are covered with or encapsulated by various plastic or ceramic materials on printed circuit boards, a mechanical pre-treatment process allowing their liberation and separation is first needed in order to facilitate their efficient extraction with acid or alkali by hydrometallurgical methods [4]. Electronic scrap from printed circuit board can be processed by mechanical methods like stamp, hammer or cutting mill [4, 5, 6]. Particle size, shape and liberation degree play crucial roles in mechanical recycling processes [7]. Almost all mechanical recycling processes have a certain effective size range for material separation [5-8].

Some recent research has been done for recovery of nonmetallic fraction of powderized PCBs in molding electronic components [7], phenolic compounds [9] and as a substitute for wood fillers in thermoplastic matrix composites [10]. In [11] the recycled epoxy resin powder from electronic industry was used as filler for epoxy resin products, such as paints, adhesives, decorating agents, and building materials, and this improved the mechanical and thermal expansion properties of the products when compared to the usual fillers (talc, calcium carbonate). The amount of PCB nonmetals used in these products is varying from 10 to 40 wt. %, so these applications will not promote large scale recycling.

It has been indicated that the non-metallic fraction of PCB powder has following advantages: is lighter than mineral fillers for the composites; has finer granularity which makes the microstructure more reliable, and contains coarse glass fibers which improve mechanical strength of the composite material [12]. These superior properties of the non-metallic fraction of PCB powder can be used for development of new composite materials for engineering applications. A number of these applications are concentrated on tribological components, such as gears, cams, bearings, sliders and seals, where the self-lubrication of polymers is of special advantage [13]. In particular, short fiber reinforcements, such as carbon, glass and aramid fibers, have been successfully used to improve the strength and therefore the load carrying capacity of polymer composites subjected to various wear modes [13, 14].

The value of metals contained in PCB scrap is economic incentives for the recyclers. Recyclers use different methods (pyro- and hydrometallurgy) to reclaim metals with high purity, which can be sold at a high price. However the remarkable amount of (up to 70 wt. %) nonmetallic materials are generated inevitably, which are not recovered because of lack of proper materials separation and product characterization methodology. Mechanical recycling and air separation technology enables to recover both metallic and non-metallic fractions of milled PCB powders.

Materials and Methods

Preparation of PCB powders for classifying and materials separation

The fracture of particles in collision with the milling component of one of the rotating rotors is called disintegration. The theoretical studies on milling by the collision method, which were conducted at Tallinn University of Technology (TUT), were followed by the development of the appropriate devices, called disintegrators [15, 16]. Depending on the design of the disintegrator systems the direct, separative and selective types of milling are available and useful in powder production. Milling by collision means that the mechanisms of the particle size reduction of the ductile and brittle materials are different. The milling of brittle materials by collision results in a direct fracture [17]. During milling of ductile metallic materials, the metal will be hardened and the fatigue fracture will occur [18].

The Disintegrator Technology Laboratory of TUT has several disintegrator milling equipment (preliminary crushing, continuous milling and final milling) for production powders in different size from 1-2 mm into powders 5-10 micron. This laboratory equipment was used with pre- and after processing of powders – sieving into fractions, analyzing and measuring the particle size distribution and shape. For size reduction of the PCB scrap the different disintegrator mills (DSA-158, DSA-2, DSL-115, DSL-160 were used in direct and selective

milling conditions to prepare the powders for classification into fractions. For the air separation the developed inertial-centrifugal air-classification stand was used (see Fig.1). For the magnetic separation of ferrous fraction the several types of magnets were used.
The fraction sizes of high-energy milled PCB powders were validated to obtain the best air-separation results of metallic and organic fraction.

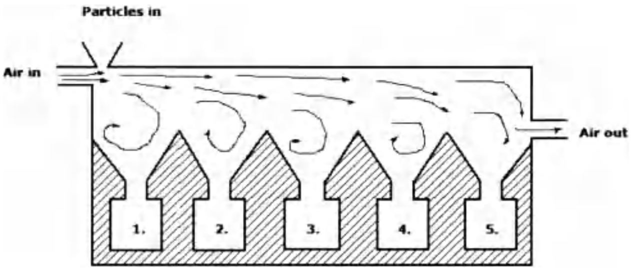

Fig.1. Principal scheme of air.separation stand with 5 separation pockets

Characterization of the milled PCB powders

Following the milling and separation processes (air, magnetic) of heavy fractions (metallic materials) and light fractions (organic an inorganic materials) particle size and shape, powder morphology properties were identified.

- For milled and air-separated materials characterization, sieving analysis (particle size more than 100 μm), laser diffraction particle-size distribution analyzer (Analyzette 22 Compact) and the stereomicroscope *Zeiss* Discovery V20 with image analysis software Omnimet and scanning electron microscope (SEM) JEOLJSM-840A was used. For evaluation of chemical composition of metallic materials the materialographic devices for preparation micropoliches (*Struers, Bühler* sample preparation system for cutting, encapsulation and poliching), the energy dispersive X-ray microanalysis (EDS) with the Link Analytical AN10000 system were used. The X-ray mapping technique will be used to evaluate element (metallic, nonmetallic) distribution inside powder particles.

Experimental

PCB scrap was recycled by using mechanical methods. The reprocessing technology of the PCBs by disintegrator milling devices consisted of the following stages:

- the preliminary size reduction of the PCB plates by the experimental DSL-158 disintegrator (up to 2 times);
- the intermediate milling for the size reduction in the semi-industrial disintegrator DSA-2 (up to 8 times);
- the final milling by the DSL-115 disintegrator system

After intermediate milling the milled product was classified by sieving with vibration into three different fractions $d_{50}>10$mm and $2 < d_{50} < 10$mm and fraction $d_{50} < 2$mm.

Results and Discussion

Size reduction of the PCB powders

The results of the preliminary size reduction, intermediate and final milling are given in Fig 1. The medium particle size of the plastic component from PCB after a 2-stage milling is about 5-10 mm, after 1-2 times of milling in the disintegrator DSA-2 it is around 1 mm. The subsequent continuous milling (6 times) in DSA-2 reduced the medium particle size to 0.45 mm. As the medium particle size and mass distribution were similar after 6th and 8th times of milling in DSA-2, the new equipment DSL-115 for further size reduction was used. Next remarkable size reduction occurred after the 4 times milling in DSL-115 the medium particle size was 0.12mm.

The powder particles from PCB after the preliminary size reduction were mainly lamellar after preliminary milling and they stay lamellar after the multi stages milling (up to 8 times). The mechanism of the fracture of PCB particles was the same after preliminary and final milling.

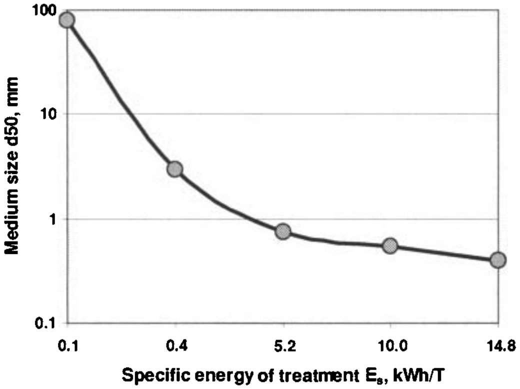

Fig. 2. Dependence of the particles medium size of PCBs on the specific energy of treatment

The particle size and distribution of the fine material (70 wt. %) obtained from 8th milling in DSL-115 (0-0.3 mm) was determinated by Laser Granulometry (see Fig. 2). The arithmetic mean diameter of the particle is 74 μm (see Fig.2).

Air separation of metallic and organic fractions

The air separation of milled PCB powder fraction d_{50}>10mm was not effective due to the large diversion of fraction size and high content of metallic inserts in organic fraction. During the first separation the light-fraction of tin-foil stripes were collected in fifth pocket of the air separation stand. The following separation tasks were performed with material collected from the first pocket of the air-separation stand. After the two times air separation the metallic and organic materials were still mixed in the first and second pockets of the stand.

The air separation of milled PCB powder fraction 2mm<d_{50}<10mm was also not so effective due to the large diversion of fraction size and particles shape. Most obstructing were the Cu-wires with 10-35mm length. During the first separation the light-fraction of tin-foil stripes were collected in fifth pocket of the air separation stand. The following separation tasks were performed with material collected from the first pocket of the air-separation stand. After the three times air separation the colour of the metallic fraction collected into first pocket was turning to similar to light-red colour of Cu, but still containing the organic particles with black colour. The second and third pockets of the stand contained mostly organic particles, so for the last step the separation of metals was quite effective.

The best air separation results gave the milled PCB powder < 2mm. After the first separation he colour of the metallic fraction collected into first pocket was turning to similar to light-red colour of Cu. The light-fraction of tin-foil stripes were collected mostly in pockets 3-5.

The colour of the material in the first pocket was similar to the Cu and only few plack and grey organic particles were detected. After the three times air separation the separated metallic and organic materials were weighed. The obtained powder (See Fig. 3.) had 80 wt.% of metallic content and 20 wt.% of organic materials.

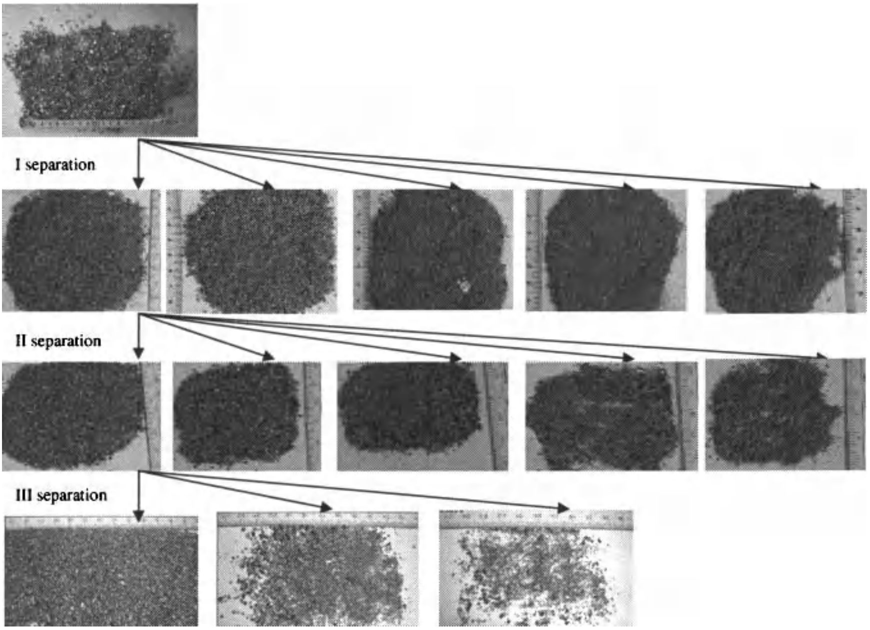

Fig. 3. Results of air separation of fine fraction d_{50}< 2mm

The air separaton results of the milled PCB powder are promising. In order to reduce the manual labour and energy consumption the air separation tests should be continued. the 5-pocket air separation stand should be re-designed to obtain two fractions of organic and metallic fractions with one processing step.

EDS study of PCB milled powders

The sample of the PCB milled powder was separated into plastic and metallic fractions and weighed. The powder contained 29 wt.% of metallic content. The micro polish of the non-metallic fraction sample was made for further EDS analysis. Then the X-ray microanalysis was performed. Oxygen was calculated by the difference of 100% with the results given in weight percentages. Most of the plastic particles contained different metallic crystals or grains inside the matrix.Samples of the separated plastic particles are in Fig 4 and prepared probes for EDS analysis are in Fig 5.

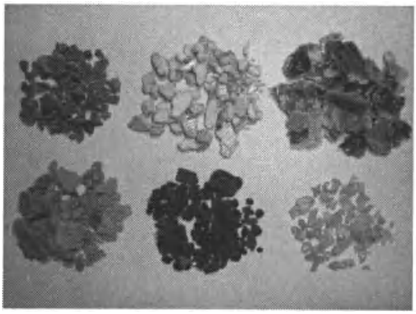

Fig 4. Separated organic fractions

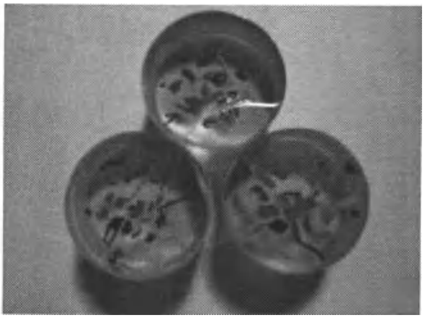

Fig 5. Probes of material for EDS analysis

In Fig. 6 PCB powder particle with red plastic matrix and 5-10 μm BrO4 crystals inside is presented. In Fig. 7 PCB powder particle with black plastic matrix containing Al, Si, Ca and fibers is presented. Plastic particles reinforced with fibres contained mainly carbon (60%) and oxygen (35%) and metals (5%). As it can be seen the plastic particles from PCB powder are composite materials containing different type of filler and fibrous reinforcement materials in polymer matrix.

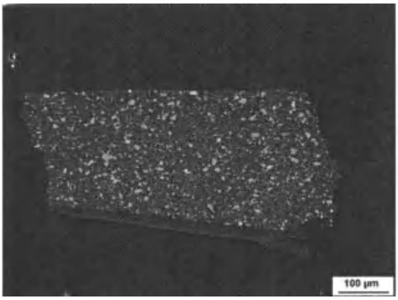

Fig. 7. Black plastic matrix with fibers

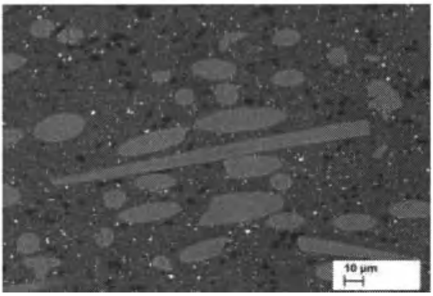

Fig. 8. Red plastic matrix with 5-10 μm BrO4 crystals

EDS analysis showed that most of the separated organic particles are composite materials, with plastic matrix and metallic, ceramic or fibre reinforcements (see Table I).

Table I. The composition of the milled PCB powder particles

Object No.	Composition, wt %	Description
11	Ca-38; Mg-0.4; O-61.4	Green plastic matrix , 5-10 µm CaCO3 crystals inside
19	Al-33; O-67	Blue plastic matrix,10-100 µm Al particles inside
23	Si-45; O-55	Black plastic matrix, 10-100 µm SiO_2 grains inside
25	Al-7; Si-24; Ca-15; Ti-0.4; O-53.6	Black plastic matrix with Al-7; Si-24;Ca-15 fibres
	Cu-65; Zn-35	CuZn35 brass, on the edge Sn-90; Pb-10
32	Sn-84; Pb-15,8; Al-0,2	Sn80-Pb20 solder
41	Cu-98	20 µm thick Cu stripe with white plastic particle
61	Pure Al	5-10 µm thick Al stripe

The precious metals like Au, Ag and Pt were not detected in milled PCB powders. The milled PCB powders consisted in larger amounts of non-metallic elements C, O Cl. S followed by metals (Cu, Al, Zn, Fe, Sn). In minor amounts alkali earth metals (Mg, Ca, Ba), alkali metals (K, Na) and non-metallic elements (Br, P, F, S) were detected. EDS analysis is useful for determining the elementary consistence of milled PCB powders.

Summary

The developed air separation stand is useful for separation of smaller than 2mm fractions of the metallic and organic particles. These tests are good basis for determining the optimum milling parameters and designing of new air or classifiers accounting for the densities of plastic and metallic particles.

The study of the chemical composition of the PCB powder particles showed that organic particles (polymers) are having metallic grains or crystals in the matrix and because of that they are difficult to be separated by air-classification system. EDS analysis is useful determining the elementary consistence of the selected particles, but for analyzing the powdered material consistence other methods should be considered. One of the methods to be considered is image analysis (IA) technique. IA enables to analyze the shape and the colour of the particles to estimate separation effectiveness by calculating the surface area of the metallic and organic materials.

The developed PCB powder milling, separation technologies and powder characterization methods are economical by enabling the competitive solutions in practice. The recycling companies can recover the organic materials into new products, by reducing their waste management costs. The experimentally obtained data of this study will be the input for numerical modeling of the particle filled composite properties to determine the influence of the filler content, resin properties and etc. to the properties of composite material.

The further experimental studies of PCB organic product recovery in thermosetting resin matrix composite will provide feasible solution in future industrial applications to use the developed material in demanding conditions. This development is the significant win for WEEE recycling companies and for environment by reducing amount of hazardous wastes in sent to landfill.

Acknowledgements

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PROCESSING OF DISCARDED LIQUID CRYSTAL DISPLAY FOR RECOVERING INDIUM

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Keywords: Indium (In), Liquid Crystal Display (LCD), Vaporization, Indium Tin Oxide, (ITO)

Abstract

Different materials are used for manufacturing various parts of a cellular phone. Considering that a great number of mobile phones are being discarded every year, it is important to recover these materials and then recycle them in order to save resources. The primary objective of this work is therefore to find and suggest ways on how to recover various materials from discarded cellular phones for recycling. Much effort, for example, has been put in recovering and recycling tin oxide (ITO), a mixture of indium (III) oxide, (In_2O_3) and tin(IV) oxide from the discarded liquid crystal displays (LCDs). Here we report a simple and cost-effective process, which includes a HCl treatment process for altering the structure of the indium (III) compound into a chloride-induced indium compound, in order to facilitate the vaporization of indium at a relatively low temperature. The experimental results indicated that 96.2 % of indium can be recovered from ITO, when the sample was heated at 973 K for 90 minutes. In addition, some thermodynamic calculations were also carried out in order to better understand the mechanism for chloride-induced vaporization of indium.

Introduction

The liquid crystal display (LCD) is about 4.4 % of the entire telephone's weight, if organic materials (for example film, etc.) are removed. Moreover, LCD of the cellular phone contains several electro-conductive electrodes, which are sandwiched between two glass planes. These electrodes are made mainly of indium tin oxide (ITO), also known as tin-doped indium oxide. ITO is a mixture of indium(III) oxide (In_2O_3) and tin(IV) oxide (SnO_2), typically 80 to 90% In_2O_3, and 10 to 20% SnO_2 by weight. [1, 2] The LCD contains approximately 1400 g/t indium (In), if the parts made of organic material are removed in advance. Thus, considering the average weight of a cellular phone, it can be found that one cellular phone contains about 6.2 mg indium. Much effort has been put in recovering and recycling indium from the discarded LCDs. There are several reports describing how to recover indium by a hydrometallurgical process, [3]. The hydrometallurgical process is efficient in dissolving ITO and recovering indium, after the large-size LCD panels used in the manufacturing process of TV sets are split. Nevertheless, in case of the small-size LCD of cellular phones, it is difficult to split the LCD panels. Moreover, a large volume of the aqueous solution of hydrochloric acid (HCl) is also required for leaching. Other researchers, on the other hand, have reported the pyrometallurgical treatment of LCDs at about 1473 K [4], in order to extract ITO by using melted silver and then recover the indium.

Nevertheless, the amount of the product recovered from this process is relatively low (i.e. recovery is about 50 %), whereas the energy consumption is relatively high.

Strictly speaking, the indium (III) chloride has a lower (s.p.) sublimation point (s.p. of $InCl_3$: 573K [5]) than indium(III) oxide (s.p. of In_2O_3: 2273K [6]). Thus, in an attempt to increase the recovery of In from ITO as well as reduce the energy consumption, the authors are putting forward a chloride-induced vaporization process. The process includes a HCl treatment process for altering the structure of the indium(III) compound into a chloride-induced indium compound, in order to facilitate the vaporization of indium at a relatively low temperature (i.e. lower than 1473 K). The chloride-induced indium compound is then vaporized, condensed and recovered.

Sample

A pure ITO sample was used in this experimental work, since indium in LCDs is the form of ITO. The fine powder of ITO was first analyzed by using a X-ray fluorescence (XRF) spectrometer, (Fischer X-RAY system XAN-FD). The results of the XRF analysis revealed that concentration of indium(III) oxide (In_2O_3) and tin(IV) oxide (SnO_2) in the sample was 95.65 % and 4.35 % respectively.

Experimental

During each test, the ITO sample was placed in a ceramic boat. The sample was first pretreated by using a HCl aqueous solution. In other words, the sample was soaked for 10 minutes in a small container filled with a known amount of 6N HCl aqueous solution. Then, it was dried at 373 K in nitrogen atmosphere for 60 minutes. The sample was then heated in nitrogen atmosphere (gas low rate: 2 L/min) by using an electric furnace. It should be noted that the vaporization of the sample was carried out after the temperature in the electric furnace reached the desired value. After each treatment, the residue of the sample remaining on the boat was dissolved, by using 6N HCl aqueous solution, and the amount of remaining indium was analyzed by using an inductively coupled plasma atomic emission spectrometer, (ICP-AES). By knowing the initial amount and the remaining amount of indium, the vaporization rate was then calculated. In other words, the efficiency of the process was expressed in term of the vaporization rate (V_r) of indium, which is calculated by the following equation, Eq. (1):

$$V_r = \frac{M_0 - M}{M_0} \cdot 100 \quad , \quad \text{(wt\%)} \qquad (1)$$

where M_o and M are the initial amount and the remaining amount of indium, respectively.

Results and Discussions

Recovering Indium from ITO: Effect of Heating Temperature and Heating Time

Figure 1 shows a quantitative relationship, which describes the relation between the heating temperature (in K), heating time (in min.) and the vaporization rate (in %) of indium in nitrogen atmosphere. The experimental results indicated that the vaporization rate of indium increases with increasing the temperature or with elongating the time of heat treatment. Figure 1 shows that when the ITO samples were heated at 673 K for 90 minutes, the vaporization rate of indium was 86.5 %. In addition, when the ITO samples were heated at 973 K for 90 minutes, the vaporization rate of indium was 96.2 % (Figure 1).

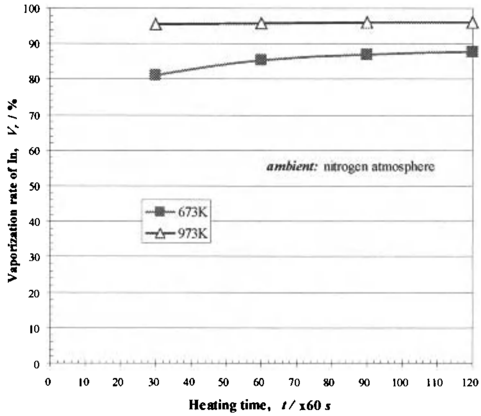

Figure 1. Vaporization rate of indium (In) from a pure ITO sample, as a function of heating time and heating temperature. (*Experimental conditions* - Sample: 1 g of pure ITO; Volume of 6N HCl: 5 mL; ambient: N2 flow rate: 2 L/min).

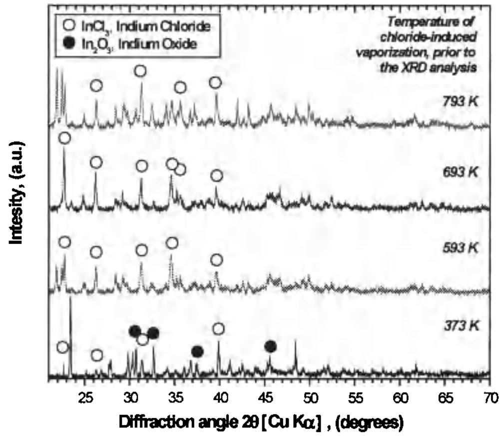

Figure 2. XRD patterns of a pure ITO sample, after chloride-induced vaporization at various temperatures for 90 minutes.

Moreover, Figure 2 shows the XRD patterns of the residue that remained on the boat after heating a pure ITO sample at various temperatures for 90 minutes. Prior to the XRD analysis each ITO sample was treated with 6N hydrochloric acid for 10 minutes and then dried in nitrogen atmosphere at 373 K for 60 minutes. All XRD analyses were performed at room temperature. It can be seen that indium(III) chloride, InCl3 is main crystalline phase of the sample. However, indium(III) oxide (In_2O_3) is also observed (at 373 K), (Figure 2).

Thermodynamic Considerations

In order to better understand the mechanism for vaporization of indium, some thermodynamic calculations were carried out by using the DATA BASE MALT software for Windows. Figure 3 shows the Gibbs energy as a function of temperature for the following chlorination reactions of indium (In) by using HCl, (Eqs. (2 - 5)).

$$1/6In_2O_3 + HCl = 1/3InCl + 1/2H_2O + 1/3Cl_2 \tag{2}$$

$$1/6In_2O_3 + HCl = 1/3InCl_2 + 1/2H_2O + 1/6Cl_2 \tag{3}$$

$$1/6In_2O_3 + HCl = 1/3In_2Cl_6 + 1/2H_2O \tag{4}$$

$$1/6In_2O_3 + HCl = 1/3InCl_3 + 1/2H_2O \tag{5}$$

Since the values of ΔG_o for the reactions (2) and (3) are positive at within the temperature range of 273 to 1273 K, these reactions would not occur at these temperatures (Figure 3). Comparing the value of reaction (4) with that of reaction (5), one can point out that the reaction (4) will proceed up to 850 K, while the reaction (5) may occur even beyond 850 K, (Figure 3).

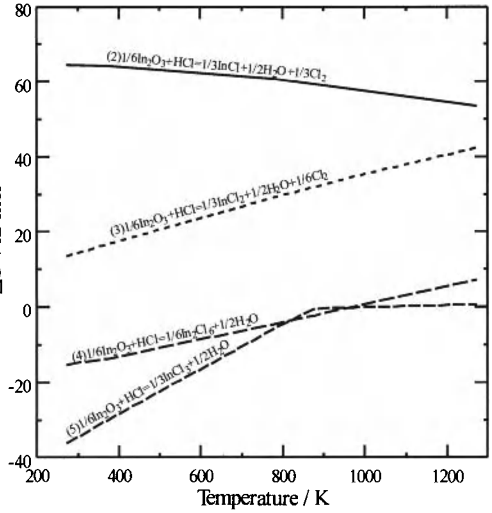

Figure 3. Gibbs free energy for the chlorination reactions of In_2O_3 by HCl.

Since, tin oxide also exists in the ITO, following is a set of another reactions indicating the possible chlorination of tin oxides:

$$1/4SnO_2 + HCl = 1/4SnCl_2 + 1/2H_2O + 1/4Cl_2 \quad (6)$$

$$1/2In_2Cl_6 + 3/4SnO_2 = 1/2In_2O_3 + 3/4SnCl_4 \quad (7)$$

$$1/4SnO_2 + HCl = 1/4SnCl_4 + 1/2H_2O \quad (8)$$

$$1/6In_2O_3 + HCl = 1/6In_2Cl_6 + 1/2H_2O \quad (9)$$

The reactions (6) and (8) indicate the possible chlorination of SnO_2 by HCl and the formation of $SnCl_2$ and $SnCl_4$, respectively. However, these reactions may not proceed, since the free energy values are positive, (Figure 4). Nevertheless, the chlorination of In_2O_3 seems to start with the formation of In_2Cl_6 (Eq. (4)). At this stage, the chlorination of SnO_2 does not proceed by adding HCl. Then, the reaction of SnO_2 with In_2Cl_6 vapor may occur (Eq. (7)), one can argue, however, its positive value of free energy (Figure 4) indicates that such a reaction does not occur spontaneously. From the above thermodynamic considerations, the reaction of In_2O_3 with HCl seems to proceed as follows: (1) $InCl_3$ is formed at relatively low temperature by adding HCl, (Eq. 5); (2) volatilization of indium as In_2Cl_6 takes places even at 773K, since In_2Cl_6 is more stable than $InCl_3$ in vapor phase; (3) $InCl_3$ volatilizes at relatively high temperature; (4) Volatilization of indium chloride in air is suppressed due to the formation of a stable oxide species.

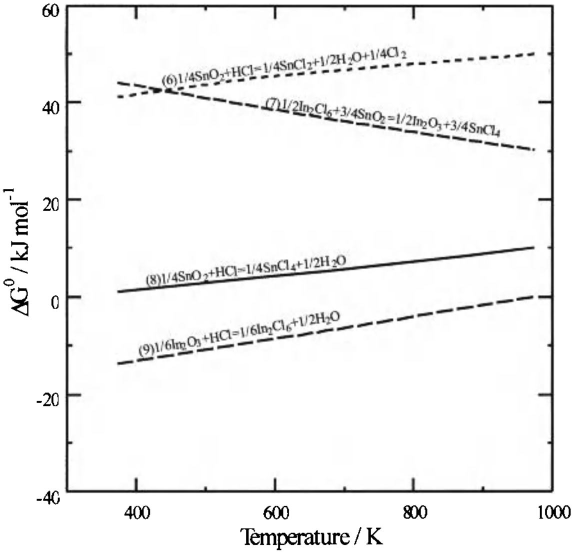

Figure 4. Gibbs free energy for the related chlorination reactions of SnO_2 and In_2O_3 by HCl.

Conclusions

The experimental results showed that when the ITO sample was heated at 673 K for 90 minutes in nitrogen atmosphere, the vaporization rate of chloride-induced indium compound was 86.5 %. When the ITO sample was heated at 973 K for 90 minutes, on the other hand, the vaporization rate was 96.2 %. In addition, the thermodynamic calculations suggested that the reaction of In_2O_3 with HCl seems to proceed as follows: (1) $InCl_3$ is formed at relatively low temperature by adding HCl; (2) Volatilization of indium as In_2Cl_6 takes places even at 773K, since In_2Cl_6 is more stable than $InCl_3$ in vapor phase; (3) $InCl_3$ volatilizes at relatively high temperature; (4) Volatilization of indium chloride in air is suppressed due to the formation of a stable oxide species.

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GREEN PYROLYSIS OF USED PRINTED WIRING BOARD POWDERS

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Abstract

Rapid technological innovation has propelled the use of electronic equipment leading to the generation of more and more waste electrical and electronic equipments (WEEE). Printed wiring board (PWB) is a component made of one or more layers of insulating material with electrical conductors. To investigate an environmentally friendly process to recycle PWBs, PWB samples with and without additives were pyrolyzed. Liquid, gas and solid products were achieved with different conversion fraction. Analysis of the exhaust gases from the experiments using GC-MS and MS showed that without $CaCO_3$ additives poisonous gases such as C_6H_6 and HBr were produced which were adequately controlled if $CaCO_3$ was added.

Introduction

Pyrolysis is one of the best methods for treating complex mixtures of waste polymers and to recover the material and energy content. The process consists of thermal decomposition at moderate temperatures in total absence or small amount of oxygen in which the structures of polymers break down into smaller intermediate products [1)]. The decomposition temperature of a substance is the temperature at which the substance breaks up into smaller substances or into its constituent atoms [2)]. Thermal treatment of PWBs were reported using DC Arc Plasma furnace [3)], and fixed bed reactor [4)]. One drawback in dealing with thermal treatment of PWB scraps is the likely production of super-toxic halogenated dibenzodioxins and dibenzofurans from the bromine containing structures. Pyrolysis of organic materials contained in waste PWBs leads to the formation of gases, oils, and chars which can be used as chemical feedstock or fuels [5-6)]. Dehalogenation of the pyrolysis product of electronic scraps is essential to make it commercially acceptable. It would be obviously the most advantageous solution as pyrolysis and dehalogenation are carried out simultaneously. Reported pyrolysis investigations are at experimental stage and have been carried out in vacuum, molten salt, fluidized bed, rotary kiln, entrained, stationary, and moving bed reactors [7)]. Comparing to the incineration and combustion of PWBs, the pyrolysis process has several characteristics: [8-10)] 1). Converting the organic solid substance into fuel gas, fuel oil and carbon-black as storage energy; 2) Emitting toxic substances such as sulfur, bromine and heavy metals in wastes; and 3) Keeping metals from being oxidized. Although many researches into the pyrolysis of PWB wastes have been reported, most of the works have been carried out using analytical pyrolysis techniques or very small batch reactors [11-15)]. Also, most of the works for the pyrolysis of PWBs haves concentrated on the composition of the organic products, particularly the brominated organics. The current study is to investigate the pyrolysis of PWB powders in a small TG-DTA scale and a 50-gram tube furnace scale.

Small Scale Pyrolysis Experiments Using TG-DTA-MS System

Experimental Methods

The powders of Printed Wiring Boards (PWBs) with size of 100-500 μm were pyrolyzed in a TG/DTA-MS machine. Argon gas was used as carrier gas. The evolved gases were measured using a MS. The initial mass, heating rate, carrier gas type and its flow rate, terminal temperature (T_m) and the holding time at T_m were varied in the experiments. Pre-purging of gases was carried out for 60 min in order to keep the initial mass, temperature and atmosphere in a steady condition process. After reaching T_m, samples were held there for some time, and then the system was naturally cooled down to room temperature.

Pyrolysis of PWBs without Additives

TG, DTG and DTA curves showed that the sample temperature followed the heating procedure exactly and no temperature jump as observed in the case of combustion 16-17). The DTA curves of pyrolysis are plotted in **Figure 1**. DTA curve during pyrolysis was very complicated, the peak lasts very long temperature range from 300-900 °C, which means that pyrolysis reaction occurred within a big temperature range. Since the PWB is made of mixture of polymers, the degradation reaction for different polymers occurs at different temperature, thus the entire degradation lasts over a very long temperature range. For example, epoxy resin degrades at ~280 °C, while brominated flame retardant degrades above 390 °C 18-19). It was reported that the pyrolysis temperature of PWBs is ~300-600 °C 20-21). For current the case, the pyrolysis reaction starts at ~330°C no matter the conditions of gas flow rate and heating rate, with the following special features: 1) With 10 °C/min heating rate, there is a small peak before at ~250 °C with 50-75 ml/min, and a peak at ~700 °C with 100-150 ml/min gas flow rate; and 2) With 50ml/min gas flow rate, there is a peak ~250 °C for 10-20 °C/min heating rate, and a peak at ~700 °C for 30 °C/min heating rate.

The TG and DTG curves with different flow rate and heating rate are also shown in **Figure 1**. The final remaining mass fraction was somehow independent of gas flow rate, especially >100 ml/min. To some extent, larger heating rate accelerated the pyrolysis process. For TV PWB samples, with the same gas flow rate, the final mass fraction with heating rate of 10, 20 and 30°C/min is 20%, 22% and 14% respectively. The degradation reactions still continued during the holding period at T_m and the period of temperature declining. The final remaining mass fraction depended on the holding time at the top temperature. Longer holding time degraded more PWBs. The final mass fraction of PWBs by pyrolysis was 15-25% of the initial mass, far larger than the combustion process (~3-13% for combustion process 16-17)).

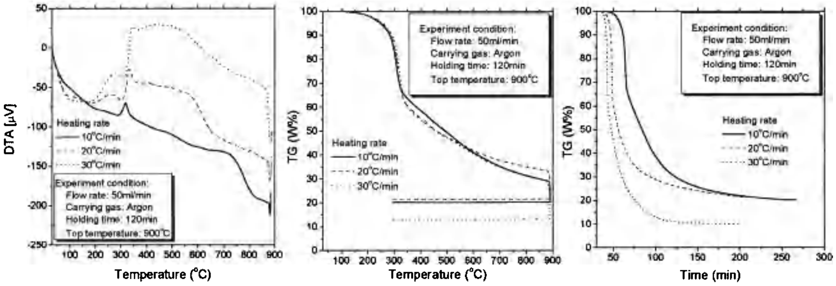

Figure 1 DTA and TG and DTG curves for the pyrolysis of TV PWB powders

Pyrolysis of PWBs with Additives

Pyrolysis experiments of PWB and "PWB+additives" were done using TG/DTA-MS machine. Additives were used to control toxic substances evolving from the pyrolysis process, and to enhance the pyrolysis reaction. Samples were heated at 15 °C/min heating rate with 150 ml/min gas flow rate. The top temperature was 900 °C and the holding time was 2 hours. Five additive powders were used: $CaCO_3$, CaO, ZSM-5($Na_nAl_nSi_{96-n}O_{192}\bullet 16H_2O$ ($0<n<27$)), Y-zeolite ($Na_xAl_YSi_ZO_m$) and Fe_2O_3. The additives were mixed with PWB powders with a mass ratio 5:1 (5 PWB : 1 additive).

Figure 2 shows the mass loss fraction with temperature and time. The temperature reached the top temperature of 900 °C at 60 min. **Table 1** shows the remaining materials after pyrolysis. The pyrolysis of the pure PWB sample stopped at 77 min with a final mass fraction of ~36%. The pyrolysis of PWB+$CaCO_3$ samples stopped at 100min with 43% residue remained in the crucible. Since Bromine component in PWBs is ~6.5% Br component in PWB materials [22)], considering the decomposition of $CaCO_3$ and the reaction between $CaCO_3$ and HBr, there was ~35% residue after subtracting CaO and $CaBr_2$. For the mixture of PWB+CaO, the final residue subtracting the additives and the inorganic products was ~41%. For ZSM-5 + PWB and Y-zeolite + PWB mixtures, the residue fraction subtracting the additives and the inorganic products with these two additives was ~46%. Thus, ZSM-5 and Y-zeolite mainly acted as catalyst to accelerate the pyrolysis reaction but not as reactants. The pyrolysis of PWB+Fe_2O_3 stopped at 113min with a ~28% final residue fraction subtracting the additives and the inorganic products. Thus, compared to other four additives, the effect of Fe_2O_3 on the pyrolysis of PWB was the best. DTA curves for different pyrolysis experiments are shown in **Figure 3**. There were many peaks of endothermic and exothermic reactions during pyrolysis.

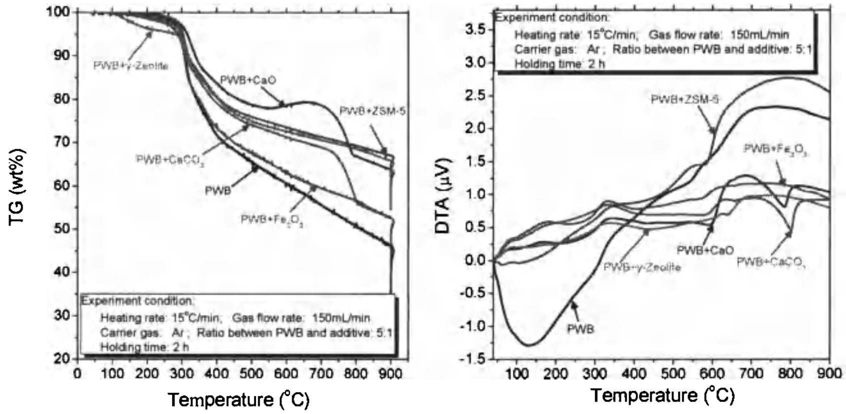

Figure 2 TG curves for the pyrolysis of "PWB+ additives"

Table 1 The Final Mass Fraction during pyrolysis experiments

	PWB	With additives				
		$CaCO_3$	CaO	ZSM-5	y-Zeolite	Fe_2O_3
Solid fraction, %	35.56	42.85	54.98	55.04	55.02	39.79
Fraction of residue subtracting additives, %	35.56	35.02	40.78	46.05	46.02	27.75

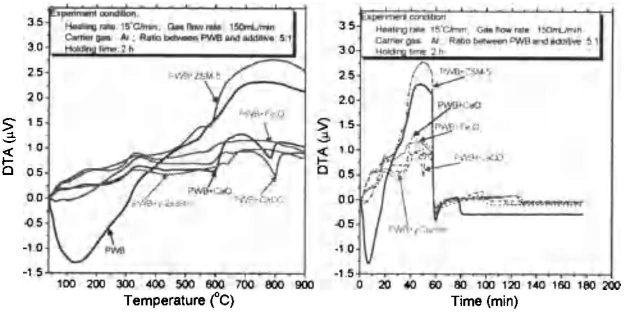

Figure 3 DTA curves of pyrolysis of PWB+additive

For the pyrolysis of PWB+$CaCO_3$, signals of CH_4, CO, C_2H_6, C_3H_4, C_2H_3O, C_3H_6 or C_2H_2O, CO_2 or C_2H_4O, C_2H_5O, Cl_2, C_6H_6, H_2O and HCl were stronger than that of PWBs without additives, which means that $CaCO_3$ has a certain effect on enhancing the pyrolysis process. $CaCO_3$ could also control HBr emission. CaO had a big effect on promoting the signal intensity of C_2H_2, CO, C_2H_6, HCl, C_3H_4. ZSM-5 could increase the peak of CH_4, HCl, C_3H_4, C_2H_3O, 1st peak CO_2 or C_2H_4O, C_2H_5O and C_6H_6, and lower the peak of HBr and H_2O signals. Y-Zeolite could perform very well on producing CH_4, H_2O, C_2H_2, CO, HCl, C_3H_4, 1st peak C_2H_3O, 1st peak CO_2 or C_2H_4O, Cl_2 and C_6H_6, and lowers HBr. Fe_2O_3 helps pyrolyze more PWB samples than other additives. MS signal from the pyrolysis of PWB+Fe_2O_3 had very strong intensity of CH_4, H_2O, C_2H_3O and 1st peak CO_2 or C_2H_4O. **Figure 4** shows that signal intensity of HCl, Cl_2, C_6H_6 and HBr could be controlled to a lower level by Fe_2O_3 than other additives.

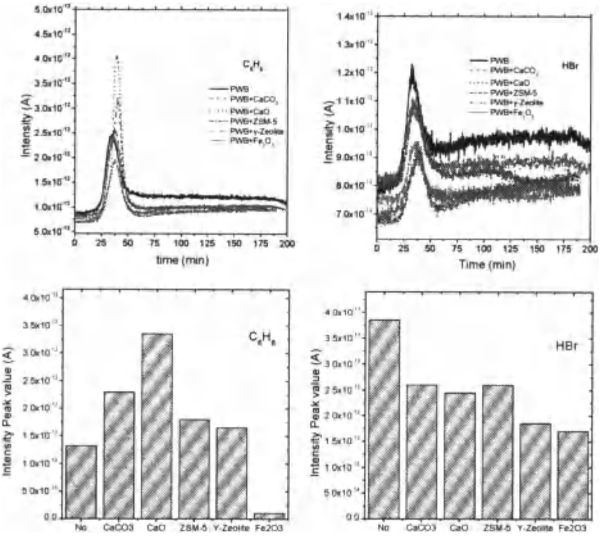

Figure 4 MS signal of exhausted gases (HBr and C_6H_6) during pyrolysis process

Large Scale Pyrolysis Experiments Using a Tube Furnace

Experimental Procedure

A tube furnace was used to perform the big scale pyrolysis experiments of PWBs. **Figure 5** is the schematic of the experimental setup. Argon gas as a carrier was used to push out the gas emitted during the pyrolysis process at a certain flow rate and to prevent oxidation reaction. Fifty grams PWB powders were used in each experiment with a 15 °C/min heating rate and a 900 °C top temperature. The holding time at the top temperature was 120 min. The emitted gases from the furnace were condensed. Both gas samples and liquid samples were collected. Finally, the tail gas passed a 5% NaOH solution and entered the venting system. The samples were analyzed using FTIR and GC-MS.

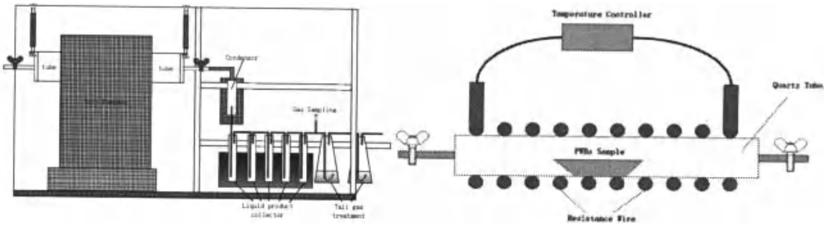

Figure 3 The schematic of pyrolysis experiment using a tube furnace system (left: experimental setup; right: heating unit in the tube furnace)

Pyrolysis of PWBs without Additives

Three types of products - solid product, liquid product and gas product-were produced. Solid products mainly consisted of glass-fiber, metals and carbon. As shown in **Table 2**, the solid product produced without additives was ~24 g, and ~47% of the original mass, implying that ~53% of PWBs were converted to liquid and gas. While, the pyrolysis experiments through TG/DTA results showed that the solid products was 36% of the original mass, indicating that PWB powders in tube furnace were not completely pyrolyzed.

Table 2 Solid, liquid and gas products produced in pyrolysis experiments

Experiment	Heating rate, °C/min	Solid product		Liquid product		Gas product	
		g	%	g	%	g	%
#1	10	23.7	47.4	7.3+2.4	19.4	16.6	33.2
#2	10	23.3	46.6	8.2+2.4	21.2	16.1	33.2
#3	5	25.2	50.4	7.05+2.4	18.9	15.35	30.7
#4	15	22.5	45	8.0+2.4	20.8	17.1	34.2
Mean		23.68	47.35	10.00	20.08	16.29	32.57

As liquid products, the pyrolysis oil obtained during PWB pyrolysis was a mixture of organic compounds, also containing aqueous products. Similar results for the pyrolysis of different plastics were reported [23-24)], indicating that water and hydrocarbon by-products could either be a product formed in the process (derived from the oxygen-containing functional groups, -COO-, OH-, -COOH-, etc.) or due to the original moisture in the samples. As shown in **Table 2**, the current pyrolysis experiments produced 9.5-10.6 g of liquid products, averaging 20% of the original PWB mass. The collected oil from experiment #1 (Table 5.1) was analyzed using FTIR and the spectrum is shown in **Figure 4**. The wide adsorption peak between 3600-3200 cm^{-1} was caused by the stretching vibration of free O-H band. For alkane functional groups, several stretching vibration of alkane C-H band could be found at 3000-2850 cm^{-1}. Bending vibration of alkane C-H band could be found at 1465-1340 cm^{-1}. There was stretching vibration of olefin C-H at 3100-

3010 cm^{-1}, stretching vibration of olefin C=C bond at 1675-1640 cm^{-1}, and bending vibration of olefin C-H bond at 675 cm^{-1}. A peak occurred at 2250-2100 cm^{-1} stand for alkyne stretching vibration. Stretching vibration of C-H at aromatic ring might occur at 3100-3000 cm^{-1}. At 1600 cm^{-1}, 1580 cm^{-1}, 1500 cm^{-1}, 1450 cm^{-1}, there are four peaks standing for aromatic compounds. For alcohol and phenol functional groups, stretching vibration of C-O took place at 1300-1000 cm^{-1}, and the out-of-plane bending of hydroxy O-H could be found at 769-659 cm^{-1}.

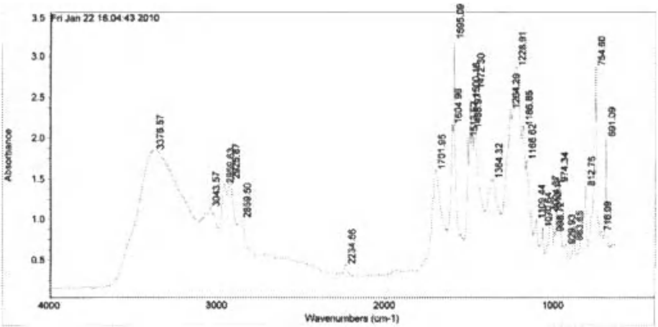

Figure 4 FTIR Spectra of heavy oil from liquid product (#1 Experiment).

For #1 experiment, heavy oil, water and light oil could be separated from liquid products, and the FTIR spectrum is shown in **Figure 5**, indicating a big difference between the heavy liquid product and the light liquid product. For example, there were two strong absorption peaks at 1550-1400 cm^{-1}, and 1050-800 cm^{-1} for the light liquid product, but not for the heavy liquid product. Around 1500 cm^{-1} C=C stretching bond vibration for aromatic rings could be found. C-H bend vibration for alkenes was at 1050-800 cm^{-1}. Consequently, the liquid products for the PWB without additives mainly consisted of aromatic compounds with phenol and substituted phenol, but few alkane chains.

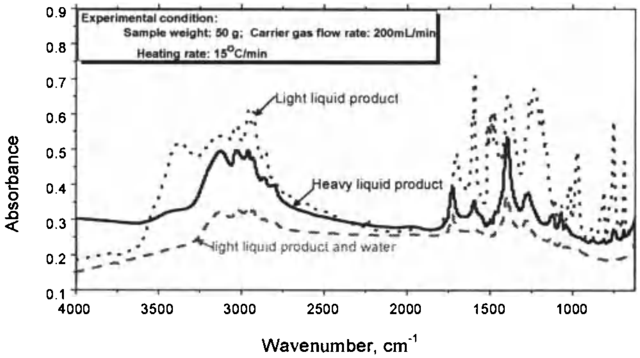

Figure 0 FTIR Spectra of heavy oil, water and light liquid (Experiment: #4)

Pyrolysis of PWBs with Additives

CaCO$_3$ powders were added into PWB powders to control the toxic substance like HBr emitted during pyrolysis. PWB sample mixed with CaCO$_3$ sample in the ratio of 5:1. In the current study, 10 g CaCO$_3$

powder was used to mix with 50 g PWB powders. The solid product mainly consisted of the pyrolysis residue (coke, tar, etc.) and products of CaO and $CaBr_2$. For PWB powers with larger range sizes, there were 26.75 g solid products, 9.76 g liquid products and 13.49 g gas products, and the yield was approximately 53.5%, 19.5% and 27.0% respectively. For screened PWB powders (150-250 μm), there were ~ 70.0% solid products, 12.9% liquid products and 17.1%) gas products. Smaller size powders implied more metals and thus there were more solid products after pyrolysis. Again, the pyrolysis of PWB in the tube furnace experiment was incomplete compared to TG-DTA experiments.

Summary

For small scale pyrolysis of PWB powders using TG-DTA-MS equipment, the reaction occurred within a big temperature range, and there were a few sub-peaks at 350, 500, and 700 °C respectively. The sub-peak temperature slightly increased with increasing gas flow rate. Longer holding time degraded more PWB. The final mass fraction of PWB during pyrolysis was 15-25% of the initial mass. Larger heating rate accelerated the pyrolysis process, while the final mass fraction were the same no matter what heating rate was used. The best pyrolysis conditions were: 15-20 °C/min heat rate, >100 ml/min gas flow rate, >900 °C top temperature, and long holding time. Fe_2O_3 is the most effective additive to help control HBr and C_6H_6 during the pyrolysis of PWB. MS signal from PWB+Fe_2O_3 experiment had very strong intensity of CH_4, H_2O, C_2H_3O and 1st peak CO_2 or C_2H_4O. Signal intensity of HCl, Cl_2, C_6H_6 and HBr were controlled at a lower level than by other additives.

For large scale pyrolysis process in a tube furnace, three types of pyrolysis products (solid product, liquid product and gas product) were produced by the pyrolysis process. The mass of the solid products depended on the size of PWB powders and the additives. The pyrolysis liquid products mainly consisted of aromatic compounds with phenol and substituted phenol, but few alkane chains. Addition of $CaCO_3$ into PWB powder was rarely beneficial to enhance the pyrolysis of PWB, but controlled the emission of the toxic gas like the toxic gas like HBr and C_6H_6.

Acknowledgements

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LEACHING OF LEAD FROM SOLDER MATERIAL USED IN ELECTRICAL AND ELECTRONIC EQUIPMENT

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Keywords: Lead, Tin, Solder, Leaching

Abstract

Present work is a part of developing novel recycling technique for waste printed circuit boards (PCBs) i.e. the liberation of metals from PCBs by organic swelling followed by the treatment of resin to remove/ recover hazardous soldering materials. In order to recover the hazardous metallic constituent lead from the liberated resin, initially the leaching studies were made using fresh solder containing 63.9% Pb and remaining tin. Experimental results obtained in different conditions viz. time, temperature and acidity showed ~97.20% of lead dissolution with 6M HNO_3 at solid to liquid (S:L) ratio 1:10 (g/mL) and temperature 90°C in 75 minutes. The result of the studies validated with crushed PCBs shows that almost total lead and tin was leached out with 6M HNO_3 and 6M HCl respectively at S:L ratio 1:10 (g/mL) and temperature 90°C within 50 minutes. The results will be useful for the treatment and safe disposal of PCBs resin.

Introduction

Global economical growth and technological advancement resulted in the incredible increase in the volume of electrical and electronic equipments (EEE) being procured by the consumers with replacement of used EEE [1]. Therefore, huge amount of waste EEEs generation takes place globally, specially in industrialized countries such as India, China, Greece etc. India is one of the fastest growing economies countries of the world and the growth in PC ownership per capita during the period 1993 - 2000 increased to the extent of 604%, compared to a world's average of 181% [2]. As India is the second most populous country with over 1 billion population, the quantity of e-waste generation is also high, respectively. These electronic products are made up of variety of components. Printed Circuit Boards (PCBs) are essential component in advanced EEE, and its recycling is one of the major challenges. The surface of the PCBs mainly contains the Cu metal circuits which is usually covered by a layer of epoxy resin and solder material, which is an alloy of lead and tin. Direct leaching of metallic fractions encapsulated with plastics, reinforced resins and ceramic rarely accomplishes effective extraction of metals from these waste PCBs [3]. Metal recovery using hydrometallurgical technique readily involves the leaching process in order to reduce the volume of the waste material and to recover selectively valuable as well as the perilous metals. In pyrometallurgical recycling processes, traditional methods such as incineration, melting etc are employed to recover precious and non ferrous metals from e-waste at high temperature. In this process a considerable amount of metals loss takes place with high energy consumption, therefore it is not suitable for the recycling of valuable, noble, rare metals etc. In other hand, PCBs components also contain plastic and brominated flame retardants, which produce toxic gases and carcinogenic compounds during incineration. Therefore, it is necessary to develop an environmental and economically feasible technique for recovery of metals from electronic scrap. Among the several extraction processes, hydrometallurgy is a suitable route for recycling of valuable metals of high commercial value following leaching, solvent extraction, ion-exchange etc. Therefore, sincere efforts have been made world wide to develop an eco-friendly process using mechanical pretreatment in combination with hydrometallurgical technique [4]. Lee et al. [5] have reported that the metal liberation from these waste PCBs could be achieved up to 95-100% using swing hammer type impact mill or stamp mill, but those pretreatment processes are not applied in the commercial plant yet. Liberation of metals from PCBs is difficult due to its complex material of construction and lack of appropriate grinding/ mechanical pre-treatment processes. A series of hydrometallurgical processes, including leaching, separation and recovery has been employed for the recovery of valuable metals from the metallic concentrate. Some technologies are under lab scale investigation for leaching of the valuable metals from waste PCBs using electro-generated chlorine leaching [6, 7], ammoniacal leaching [8, 9] and bacterial leaching [10, 11]. The development of individual process or hybrid processes, including precipitation, cementation, solvent extraction, ion exchange and supported liquid membrane is underway. Developments of eco- friendly and energy-saving processes are necessary to comply with stringent environmental regulations.

The paper is a part of novel recycling technique, which is going to be developed under joint collaboration of NML, India and KIGAM, South Korea. The process consists of 1) organic swelling of waste PCBs, 2) liberation of thin layer of metals, 3) removal of solder material from epoxy resin for its safe utilization. Waste PCBs consist of several layers of resin, thin glass fiber, reinforced epoxy resins and interconnecting metal wires and plates. Aim of the study is to optimize the leaching parameters for recovery of lead and tin from the solder materials used in PCBs. The data will be useful to recover lead and tin from the liberated epoxy resin obtained after the separation of metals from the organic swelled PCBs. The data will also be useful to develop and simulate the leaching process in continuous mode.

Experimental

Solder material purchased from local market was used for the experimental purposes. Solder wire of diameter 0.7 mm was cut to 25.4 mm length. The solder contained 63.89% Pb and remaining Sn. The leaching experiment was carried out in a temperature controlled leaching reactor. The samples were taken at particular interval of time to see the leaching behavior of the metals for particular acid. After leaching the residue was dried in oven and weighed to see the material balance. Good material balance was obtained for each set of experiment. Lead and tin present in the leach solution were analyzed using Atomic Absorption Spectrophotometer instrument. Based on the result of leaching of the solder, the removal of lead and tin from waste printed circuit boards were also validated. The crushed PCBs of size ~7 mm used for experimental purposes contained 1.5% Pb and 1.23% Sn. The obtained leaching result for lead and tin from PCBs was validated with its leaching from solder wire. Good validation was observed between both the results. All the reagents used were of AnalaR/LR grade chemical without any further purification.

Results and Discussion

Leaching studies were carried out for the extraction and separation of the lead/ tin from the solder material of PCBs. Initially, some batch experiments were carried out with freshly purchased solder. The solder contained 63.89% lead and remaining tin. The effect of process parameters viz. time and acid concentration was studied to examine the leaching behavior of lead and tin. After getting the data from solder leaching, the experiments were carried out to leach lead and tin from crushed PCBs.

Leaching of Pb and Sn from solder in HNO_3 medium

Leaching experiments were carried out by taking 25 grams of solder wire (diameter 0.7 mm and size ~25.4 mm) in 250 mL of dilute HNO_3 (1-6 M) at solid to liquid ratio 1: 10 i.e. pulp density 100 g/L and temperature 90°C. The leaching of lead was found to increase with increase in reaction time. The Fig. 1 indicates that in 75 minutes the maximum percentage leaching of lead obtained was 51.93, 55.98, 84.98 and 97.20 with 1M, 2M, 4M and 6M nitric acid, respectively. In all cases the leaching of tin was found very poor. Fig. 2 indicates that the percentage leaching of lead with 6M HNO_3 was increased from 85.64 to 97.20 with increase in time from 10 to 75 minutes at pulp density 100 g/L and temperature 90°C, however in same set of experiment very little amount of tin was found to be leached out due to salt formation.

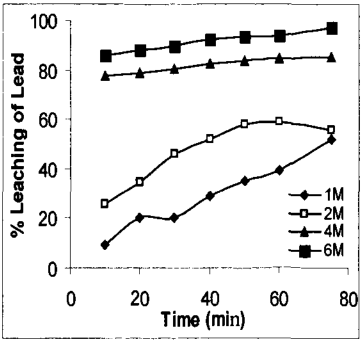

Fig. 1. Leaching of lead from solder with different nitric acid concentration [Pulp density = 100 g/L, Temp. = 90°C]

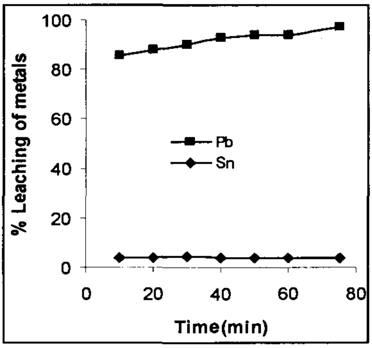

Fig. 2. Leaching of metals from solder with 6M HNO_3 [Pulp density = 100 g/L, Temp. = 90°C]

Leaching kinetics of lead from solder

An attempt has been made to study the kinetics of dissolution of lead from solder material using shrinking core models. All standard equations of the shrinking core models were tested for reaction kinetics [12, 13]. The calculated data was tested to fit with all standard kinetics core equation but these value most suitably fitted with "Chemical reaction control dense constant size cylindrical particles, $1-(1-X)^{1/2} = Kct$", where Kc = reaction rate constant (min^{-1}), t = time (min) and X = fraction reacted of lead (% extraction/100) kinetics rate equation. The kinetics model (Fig. 3) is selected on the basis of constant value of Kc and regression coefficient i.e. higher the regression coefficient close to 1 among all kinetics core equation.

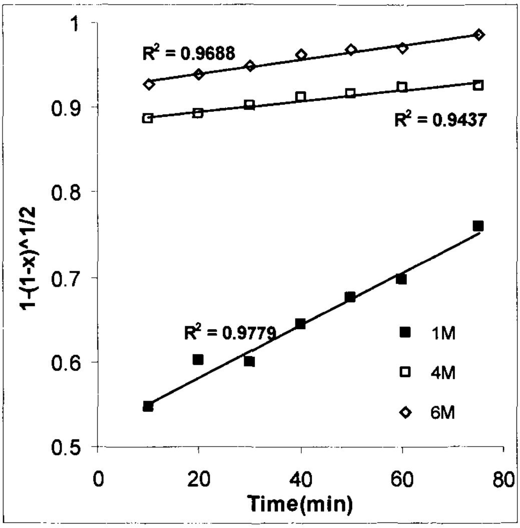

Fig. 3. Kinetics of leaching of lead from solder with HNO_3

Leaching of Pb and Sn from solder in HCl medium

The leaching studies were carried out with HCl to study the leaching behavior of lead and tin from solder having diameter 0.7 mm and size ~25.4 mm. The solder wire (25g) was leached with HCl (1-6 M) at solid to liquid ratio 1: 10, pulp density 100 g/L and temperature 90°C in 500 mL flask. The leaching was found to be increased with increase in reaction time. Fig. 4 indicates that maximum leaching of tin could be achieved up to 26.97% with 6M HCl in 75 minutes. As the acid concentration increases from 1 to 6M, the leaching of tin also increases from 7.77 to 26.97% in 75 minutes. The results of leaching studies for lead and tin from solder using 6M hydrochloric acid are presented in Fig. 5. As the leaching time increases from 10 to 75 minutes the percentage leaching of lead and tin also increases from 2.51 to 9.13 and 9.86 to 26.97, respectively.

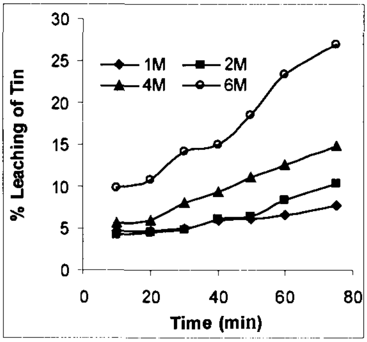

Fig. 4. Leaching of tin from solder with different hydrochloric acid concentration [Pulp density = 100 g/L, Temp. = 90°C]

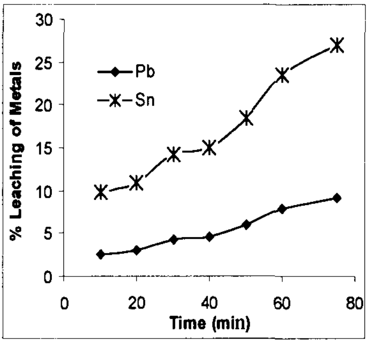

Fig. 5. Leaching of metals from solder with 6M HCl [Pulp density = 100 g/L, Temp. = 90°C]

Leaching results of solder with HCl and HNO_3, show that nitric acid is suitable leachant for lead recovery whereas hydrochloric acid is effective for tin. Therefore, the leaching experiments for the removal and recovery of lead and tin from PCBs were carried out with both the acids using crushed PCBs of size 7 mm containing 1.5% lead and 1.23% tin. The result for the leaching of lead from PCBs in nitric acid medium at S:L ratio 1:10 i.e. pulp density 100 g/L is presented in Fig.6.

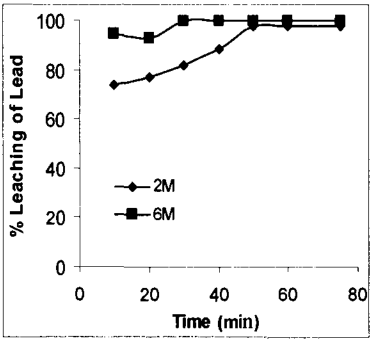

Fig. 6. Leaching of lead from crushed PCBs with different concentration of nitric acid [Pulp density = 100 g/L, Temp. = 90°C]

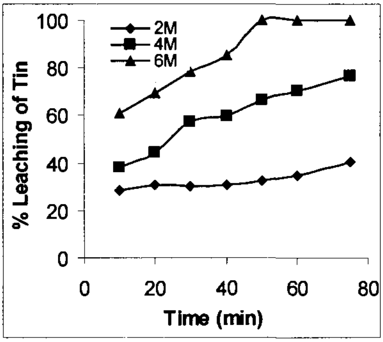

Fig. 7. Leaching of tin from crushed PCBs using different hydrochloric acid concentration [Pulp density = 100 g/L, Temp. = 90°C]

The result indicates that 99.99% lead could be leached with 6M nitric acid at 90°C in 30 minutes maintaining the above experimental condition. The NO_x gas generated during nitric acid leaching can be scrubbed in suitable scrubbing solution. After recovery of lead from PCBs the effort were made to leach out the tin from the waste PCBs. The experiments were carried out by varying the acid concentration from 2M to 6M. As the concentration of hydrochloric acid increases, the leaching efficiency of tin also increases. The results presented in Fig. 7 indicates that 32.31%, 66.33% and 99.99% of tin could be recovered with 2M, 4M and 6M HCl, respectively in 50 minutes at solid to liquid ratio 1:10, pulp density 100 g/L and temperature 90°C. Further leach liquor can be purified by solvent extraction process, and from the purified solution salt/ pure novel, valuable and precious metal can be obtained using suitable hydrometallurgical techniques.

Conclusions

Leaching of lead and tin from solder / crushed PCBs were performed using hydrochloric and nitric acid. Nitric acid is suitable leachant for dissolution of lead from solder as well as PCBs. The leaching of lead increases with the increase in the nitric acid concentration. Maximum leaching of lead from solder was found to be 97.20% with 6M HNO_3 at pulp density 100 g/L and temperature 90°C. In nitric acid medium tin dissolved significantly but precipitated due to the salt formation. The recovery/ leaching of tin was found very poor with HNO_3. Kinetics of the leaching of lead from solder follows the model "Chemical reaction control dense constant size cylindrical particles, $1-(1-X)^{1/2} = Kct$" in all concentration of nitric acid. The experimental results for the leaching of lead from PCBs in nitric acid medium at S:L ratio 1:10, pulp density 100 g/L indicates that 99.99% of lead could be leached with 6M nitric acid. The recovery of tin could be obtained 99.99% with 6M HCl in 50 minutes time at solid to liquid ratio 1:10, pulp density 100 g/L and temperature 90°C. The NO_x gas generated during nitric acid leaching can be scrubbed in suitable scrubbing solution. Further leach liquor can be purified by solvent extraction, and from the purified solution salt/ pure novel, valuable and precious metal can be obtained using suitable hydrometallurgical techniques.

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COPPER RECOVERY FROM PRINTED CIRCUIT BOARD OF E-WASTE

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Keywords: Carbonization, Printed Circuit Board, Recycling

Abstract

In an attempt to raise the copper grade of Printed Circuit board (PCB) by removing other components, carbonization treatment was investigated. The crushed PCB without surface-mounted parts was carbonized under nitrogen atmosphere. After screening, the char was classified by size into oversized pieces, undersized pieces and powder. The copper foil and glass fiber pieces were liberated and collected in undersized fraction. The liberation of copper foil from the oversized pieces was also investigated. The copper foil was liberated easily from glass fiber by stamping treatment. Liberation rate of copper foil was high at high carbonized temperature. The experimental results indicated that 90% of oversized char was liberated and the copper foil recovery from PCB carbonized at 1073K was 110kg/t. The copper recovery from char powder by flotation was also investigated. 15% of the copper grade and 80 % of the copper recovery were obtained, whereas the removal rate of silicon was 55%.

Introduction

Waste Electrical and Electronic Equipments (WEEEs) should be recycled because they have many kinds of valuable materials and most WEEEs include Printed Circuit Boards (PCBs). In Japan, about 30 km^2 per year of Printed Circuit board (PCB) has been produced [1]. PCBs are normally separated from WEEEs and picked up by hand and sold to non-ferrous metal market because PCBs include high grade of copper and other precious metal such as gold, silver and palladium [2]. However, PCB also has impurities such as silicon, aluminum and calcium which are slag materials in non-ferrous smelting process, and other harmful elements such as lead, bromine and antimony. Low grade PCBs are sold after removal of invaluable parts or sometimes land filled without any treatment.

Recovery of metal from PCB has been studied by several methods such as crushing, separation method and leaching method [3-7]. Glass fiber recovery has also been studied [8].

In this paper, carbonization treatment was studied to remove glass fiber from low grade PCBs. Carbonization is a pyrolysis treatment of solids in low amount of air. Pyrolysis of PCB has been studied but these studies were mainly investigated about the pyrolysis gas and char constituent [9-12]. Resin in PCB is pyrolyzed and metal is not oxidized by carbonization. It is therefore expected to recover copper efficiently in post process.

Experiments

Carbonization and separation

PCBs of 3-20 mm in size, which were crushed by using a biaxial shear cutter and rotor crusher, were used for experiment. Surface mounted parts were removed from crushed PCBs. 100 g of crushed PCB was spread over a stainless tray made of SUS430 and set in an electric furnace with 17 L of furnace volume. PCBs were heated with 50 K/min. of heating rate and carbonized at 673, 873, or 1073 K for 1hour. 15 L/min. of nitrogen gas was blown into the furnace to keep 2.5 % of oxygen concentration due to air leakage into the furnace. PCB char was air-cooled after carbonization. PCB char was screened by sieves and weight ratio with each particle size was measured. From char pieces with size over 4 mm, copper foil, glass fiber and other parts were hand-picked and recovery of copper foil was measured.

Separation tests were conducted for parts in which copper foil and glass fiber keep multi-layered form to liberate copper foil with cutter mill, ball mill and stamp mill. 20 g of multi-layered parts was tested with each test. Parts with the size over 4mm were screened after separation test and liberated copper foil and glass fiber were hand-picked to measure each weight.

Flotation

For the powder of PCB char carbonized at 1073 K with size under 0.5 mm, copper upgrade was investigated by flotation. Char was ground with pestle and mortar to prepare powder of particle size under 150, 75 and 44 μm. Flotation reagents were 0.5 mol/L sulfuric acid and 1mol/L sodium hydroxide as pH adjustor, sodium hydrogen sulfide (NaHS, purity 70 %) as surfactant, Potassium Amyl Xanthate (PAX, purity 90%) as collector and Methyl Isobutyl Carbinol (MIBC) as frother. The dosage of MIBC was 1.4kg/t. NaHS and PAX are dissolved in ionic exchange water to obtain 5 wt% and 1 wt% solution.

Denver type flotation cell of 200 cm^3 was used. 5 g of powder was added in 150 cm^3 of deionized water while stirring by impeller at 350 rpm. Next, NaHS solution was added. After 15 minutes, PAX was added and pH was regulated by pH adjustor. After 15 minutes, MIBC was added and 1.5 mL/min. of air was introduced under the cell. The floated froth was collected for 10 minutes. The froth and tailing were filtered and dried at 363 K for 12 hours. After measuring the weight, several elements such as copper, silicon and calcium were analyzed with X-ray Fluorescence Analyzer and copper grade and recovery were calculated. Figure 1 shows the experimental flow.

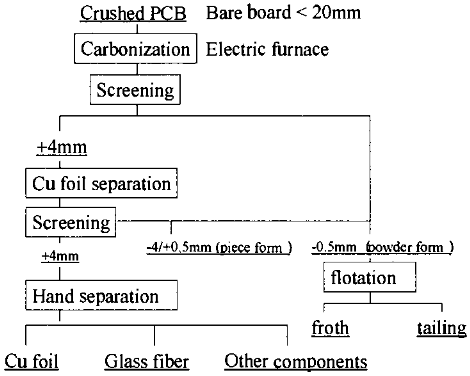

Figure 1. Experimental flow sheet

Results and Discussions

Carbonization condition

Char with size over 4 mm was composed of copper foil, glass fiber, other parts, and multi-layered parts at any carbonized temperature. On the other hand, copper foil and glass fiber were liberated with a size smaller than 4 mm. It is expected to recover copper foil efficiently from char with size under 4 mm with eddy current separator or electrostatic separator. As a result of separation tests for multi-layered parts, both copper foil and glass fiber were pulverized with cutter mill. Most parts kept multi-layered form with ball mill. Multi-layered parts decreased gradually with back and forth shaker, but most parts were pulverized by abrasion and copper foil hardly increased. On the other hand, copper foil and glass fiber were liberated by stamping. Table I shows the result of separation test by stamping with pestle at a rate of 150 times per minute.

The authors suggest that stamping treatment was the best way for copper foil liberation. Copper foil liberation of char carbonized at each temperature was compared. Table II shows the breakdown of the char after stamping treatment. Parts with size over 4mm were classified with copper foil, glass fiber, other parts and multi-layered parts. Most parts keep multi-layered form for char carbonized at 673 K. Glass fiber was liberated most from char carbonized at 873 K. Copper foil was liberated most from char carbonized at 1073 K. Especially, multi-layered parts were broken down most and glass fiber was selectively crushed to powder for the char. Copper foil yield was 110 kg/t-PCB and copper recovery was 55 % in case of carbonization at 1073 K. More copper foil was liberated from char carbonized at higher temperature. Carbonization at high temperature was effective to recover copper foil.

Table I. Results of stamping treatment: relationship between stamping time and recovery of copper foil for char carbonized at 873 and 1073 K.

Carbonized Temperature, K	Stamping Time, min.	Products, wt%			
		Multilayered plates	Cu foil	Glass fiber	Fine powder, -4mm
873	0	100	0	0	0
	5	34	6	32	27
	10	19	8	36	35
1073	0	100	0	0	0
	5	38	9	10	41
	10	4	17	5	74

Table II. The yield and breakdown of char at each carbonized temperature after stamping treatment for 10min.

		Carbonized temperature, K		
		673	873	1073
Products ,kg/t	-0.5 mm	80	110	230
	-1+0.5 mm	20	15	70
	-2+1 mm	30	40	80
	-4+2 mm	25	70	80
	Multilayered plates	300	110	20
	Cu foil	45	80	110
	Glass fiber	105	190	20
	Other components	110	30	55

Flotation for powder of PCB char

Copper grade of char carbonized at 1073 K with size under 0.5 mm was 10 % and copper distribution in the char was 12 %. Figure 2 shows the X-ray diffraction pattern of PCB char carbonized at each temperature. The peak of Cu, Pb, SiO_2 and Sb_2O_3 were observed. So it is expected that copper is separated from SiO_2 by sulfurization and flotation.
Figure 3 shows the grade and recovery of copper in froth as a function of NaHS dosage. The flotation tests were carried out for the powder grounded to particle size under 150 µm by adding 10 kg/t PAX and adjusting pH at 6. NaHS dosage in the 5 to 50 kg/t range has little effect on copper grade and recovery. So it is concluded that 5kg/t of NaHS is enough.
The flotation tests were carried out for the powder grounded to particle size under 150 µm by adding 5 kg/t NaHS and 10 kg/t PAX. The recovery was highest and the grade increased from 10 to 12 % at pH 10. No pH adjuster was added at pH 6. Considering the grade, recovery and reagent dosage, it is concluded that optimum pH is 10. Optimum dosage of PAX is 10 kg/t.

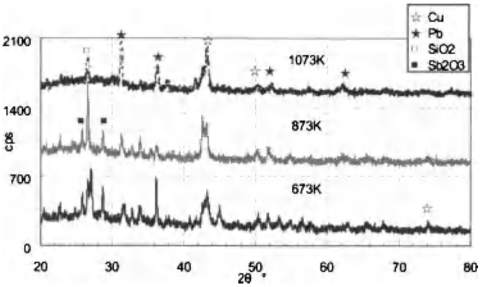

Figure 2. X-ray diffraction pattern of PCB char with size under 0.5 mm

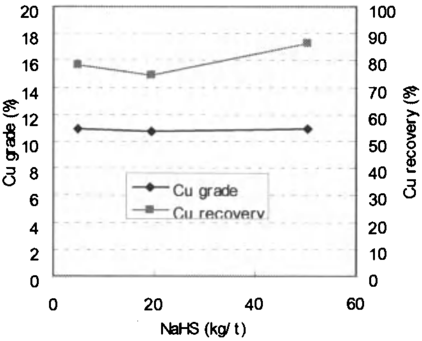

Figure 3. Effect of NaHS dosage on the flotation (particle size under 150 µm, pH 6, 10 kg/t PAX)

Figure 4 shows the grade and recovery of copper in froth as a function of particle size. The flotation tests were carried out by adding 5 kg/t NaHS and 10 kg/t PAX adjusting pH at 10. The grade increased with the smaller particle size, but the recovery decreased. Considering the grade and recovery, under 75 μm was optimum grinding size. At this optimum condition, the copper grade increased from 10 to 15 %, the copper recovery was 80 % and silicon and calcium removal rate was both 55 %. Though this copper grade was not enough for copper smelting material, the flotation was effective for the recovery of copper from the powder of PCB char.

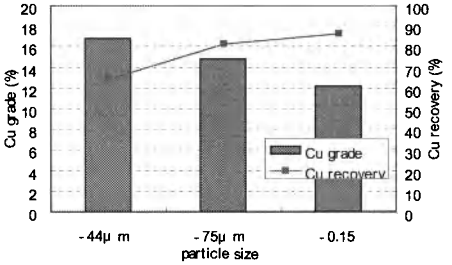

Figure 4. Effect of particle size on the flotation (pH 10, 5 kg/t NaHS, 10 kg/t PAX)

Conclusions

Copper with foil form can be liberated from carbonized PCB by stamping treatment. Glass fibers were pulverized selectively by stamping treatment and 110 kg/t of copper foil was liberated from PCB carbonized at 1073 K.

Copper grade was raised from 10 to 15 % by flotation for char powder carbonized at 1073 K with size under 0.5 mm and 80 % of the copper recovery was obtained on the condition: particle size under 75 μm, 5 kg/t of NaHS, 10 kg/t of PAX and pH 10.

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RECOVERY OF NICKEL FROM LEACHING LIQUOR OF PRINTED CIRCUIT BOARD BY SOLVENT EXTRACTION

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Keywords: Solvent extraction, Cyanex 272, Nickel, Printed circuit board

Abstract

The aim of the present work is to investigate the recovery of nickel from obsolete cell phones printed circuit boards. The printed circuit boards were firstly submitted to a grinding process and then leached in sulfuric acid. Nickel was extracted from aqueous solution using Cyanex 272. Aqueous/organic ratio was 1/1. The effect of both pH and modifier addition on selectivity of extraction was investigated.

Introduction

Currently, electric and electronic equipments (EEE) have become a necessity to the modern life. Associated with this necessity comes the continuous and increasing replacement of those equipments by new ones. The accelerated technology advances are responsible for the generation of electric and electronic waste. This waste can be dangerous not only to human health but also to the environment. Waste of electric and electronic equipments (WEEE) has a variety of components and metals in its composition becoming a potential pollutant to the environment when not properly discarded[1,2]. Its wrong disposal causes a loss of materials that could be recovered and reused. Therefore WEEE treatment is an important matter because it can assist the reduction of waste generated and the recovery of valuable metals[3].

Printed circuit board (PCBs) is an essential component of EEE and is typically very complex from a chemical point of view. Several metals may be present in its composition, such as cooper, nickel, iron, zinc, lead, tin and silver[1]. This characteristic hinders the development of a simple treatment, making it necessary the application of chemical and mechanical processing for their recycling[4]. The UN estimates that approximately 20 to 50 million of tonnes of WEEE are generated worldwide each year[2,5].

However, there are different processes that can be used to recover the metals present in PCBs waste, these processes are based on: pyrometallurgy, hydrometallurgy and bio-hydrometallurgy or even the combination of the previous processes[5,6]. Hydrometallurgical processes consist, essentially, in three steps: leaching, purification of the leach solution and reclamation of the desired metals. The purification can be carried out by solvent extraction, adsorption or ion-exchange, for example[6]. Hydrometallurgical processes are widely used for metals recovery from WEEE, these processes are based on the dissolution of the desired metals into the leaching liquor both in acid or alkaline media. Leaching studies and solvent extraction regarding metals reclamation from printed circuit board scrap has been conducted[7,8]. Solvent extraction technique has been used broadly for the separation of various metal ions[9]. The recovery of nickel from sulphate solution containing Fe, Cu, Co, Zn, Cr, Pb and Mn as contaminants separately or mixture was studied using extractants such as Cyanex 272, D2EHPA, LIX 84, LIX 984N[10-16].

The aim of this paper is to study nickel recovery from leaching liquor of PCBs containing iron and zinc by solvent extraction process using Cyanex 272 as extractant evaluating the influence of pH and temperature.

Experimental Procedure

Aqueous Solution

The studied aqueous solution was obtained through the sulphuric leaching at pH 0,5 of printed circuit boards from obsolete mobile phones. This leaching was conduced for 4h at 75°C and under constant stirring. The chemical analysis of the leach liquor was carried out with atomic absorption spectrophotometer (AAS). The principal components of leach solution are shown in the table 1.

Table 1. Metal composition of the leach liquor

pH	Concentration mg/L		
	Ni	Zn	Fe
0.5	3609.7	2585.3	11238.3

Organic Solution

Nickel recovery from leach liquor of PCBs, was investigated using CYANEX 272 (bis(2,4,4-trimethylpentyl) phosphonic acid) 17% (v/v) as extractant diluted in kerosene and 5% (v/v) TBP was used as modifier phase, the metals are extracted through of cation exchange mechanism, where the hydrogen ions of the extractant are exchanged for the metal ions present in the aqueous phase, the metal extraction is given by the following reaction[17]:

$$M^{n+} + \overline{nHA} \leftrightarrow \overline{MA_n} + nH^+ \qquad (1)$$

Solvent Extraction

Solvent extraction experiments were carried out using Cyanex 272 as extractant with equal volume of the aqueous and organic phases, the two phases were contacted at room temperature and under constant stirring, the contact time was 20 min in order to ensure that the equilibrium has been reached with and the pH was adjusted and controlled with 2M ammonium hydroxide addition then at the end experiment, the aqueous and organic phases are separated with a separator funnel, during the separated the aqueous phase was filtrate through a 7.5µm filter paper, the metal concentrations in the aqueous phase was determinate by AAS and the metal ions in the organic phase was calculate by mass balance, the pH was measured with Quimis pH meter, model Q400MT. The distribution ratio *(D)* was calculated as the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium, the percent extraction (%E) was calculated with these results through following equation.

$$D = \frac{\text{Concentration of metal in the organic phase}}{\text{Concentration of metal in the aquaeous phase}} \qquad (2)$$

$$\%E = \frac{100D}{D + \frac{V_a}{V_o}} \qquad (3)$$

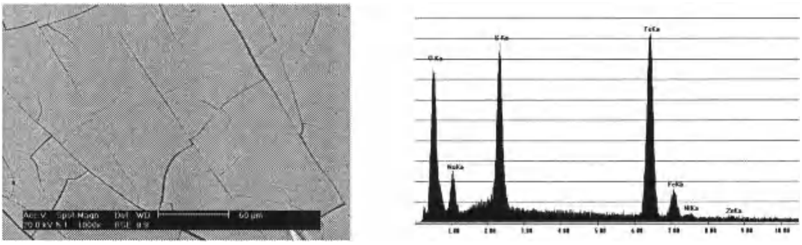
where V_a and V_o be the volumes of the aqueous and organic phases respectively.

Results and discussion

The iron can be the main problem during the extraction, wherefore methods as precipitation[18,19] or solvent extraction[10] are used for iron and nickel separation. The iron removal was carried out through of both techniques (precipitation and solvent extraction), Thus it was possible to determinate the most efficient technique for iron removal from aqueous solution. So the first step was iron removal of the aqueous phase, to after perform the nickel recover.

Removal of Iron of Feed Solution

Precipitation. the precipitation technique was performed through of addition 5M NaOH, the pH values used ranging from 3.0 to 7.0 under constant agitation, with the results it was decided to precipitate the aqueous solution at pH 4 to remove the greatest amount of iron without lost the other metals. In the current study. the feed solution after to precipitation process was analyzed by AAS for determinate the chemical composition. The results showed that with increasing of pH values the amount of iron removal increased, but also confirmed the co-extraction of Ni and Zn, so the pH value at which it was the largest iron removal without lost considerable amount of metallic ions in the solution was pH 4. The precipitate was analyzed in EDS (Energy Dispersive Spectroscopy) and the morphology by SEM are presented in Figure 1. The iron content in the final solution is several g L^{-1}.



(a) (b)

Fig 1. (a) SEM image of the precipitate morphology at pH 4.0 and (b) EDS analysis of precipitate in pH 4

Solvent extraction. Solvent extraction using Cyanex 272 dissolved in kerosene and TBP as modifier. At A/O ratio of 1:1, for iron removal the pH ranged from 2.0 and 2.5 using 2M NH_4OH for the pH control in two contacts. The aqueous phase presented a stable emulsion near of pH 3.0 as a result of reaction between iron and ammonium hydroxide added for the control of pH, which resulted iron III hydroxide $Fe(OH)_3$, due to the iron hydrolysis, the reaction of the precipitated is shown in the equation 4.

$$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3 \qquad (4)$$

Nickel Purification from Feed Solution

Influence of equilibrium pH. The purification of nickel contained in the aqueous phase was studied at different pH values, ranging from 1.5 to 4, using Cyanex 272 17% (v/v), the extraction behavior in the pH function is shown in figure 2.

Addition of modifier influence. The tests were conducing using Cyanex 272 17% (v/v), the A/O ratio 1:1, was studied the influence of the addition a modifier on the extraction of metals in the feed solution, the solvent extraction was carried out with two organic solutions, one with the addition of 5% (v/v) TBP as modifier, and one without addition of modifier.

Conclusions

The nickel of the liquor leach containing zinc and iron were purified employing both precipitation and solvent extraction techniques, the iron removal trough precipitation and solvent extraction processes allowed decreasing of iron, therefore the bulk of the iron was removed through. With the use of modifier not variation was observed on the extraction process, so due to the difference of cost isn´t necessary to be used it.

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RECOVERY OF COPPER FROM PRINTED CIRCUIT BOARDS WASTE BY BIOLEACHING

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Keywords: Bioleaching, Printed circuit boards, Acidithiobacillus ferrooxidans, Shake flasks, Copper.

Abstract

The present work investigated the influence of Fe^{+2} initial concentrations in the bioleaching of copper from printed circuit board using Acidithiobacillus ferrooxidans-LR. Printed circuit boards were collected from obsolete computers and mechanically processed through size reduction followed by magnetic separation. The bacteria Acidithiobacillus ferrooxidans-LR were grown and adapted in presence of printed circuit boards. A shake flask study was carried out on the printed circuit boards samples (non-magnetic fraction) using a rotary shaker under the following fixed conditions (185 rpm, 30°C). The bioleaching efficiency was evaluated by comparison between the concentration in the initial sample and in the leached liquor, pH of the medium and concentration of ferrous iron produced. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the metals concentration. The results showed that Acidithiobacillus ferrooxidans-LR leached 63% copper from printed circuit boards using supplemented medium with Fe^{+2}.

Introduction

The waste of electric and electronic equipment is generated by discarding of equipment such as obsolete computers and cell phones which is stimulated by the technology innovations and it has been growing each year. Because of the amount that has been accumulated it has become a prominent environmental problem but also can be a source of valuable materials, such precious and base metals [1,2] The printed circuit boards are found in almost all electric and electronic equipment being composed of polymers, ceramics and metals and can be an alternative source to recover base and precious metals. The precious metals are used in the printed circuit boards to protect against oxidation and base metals because of its conducting properties [3]. The heterogeneous composition of printed circuit board is a limiting factor in the recycling processes and the metals concentrations also range.

The bioleaching can be an alternative method to recover base metals such as copper inside the printed circuit boards [4]. The bioleaching works at room temperature and normal atmospheric pressure, not needing high temperature and pressurization, which reduces the energy cost and avoids the emission of gas pollutants [5]. Advances in knowledge about bioleaching as an economically viable process to recover metals are also attributed to the depletion of high grade ores [6]. Today, bioleaching is applied on a commercial scale for the recovery of copper and uranium from low levels ores and sulfide minerals [7,8].

Studies [6,9,10] about metals extraction such as copper from refuses, for subsequent recovery of precious metals, used the bacterial leaching as a pretreatment. Bioleaching can be an alternative to conventional methods in the recovery of base metals contained in the printed circuit boards. Experiments can use percolation columns, leaching columns, shake flasks and bioreactors [10].

Solubilization of copper from printed circuit boards using *Acidithiobacillus ferrooxidans* isolated from acid mine drainage can reach 75% copper leaching rates [11]. The mechanism of copper leaching from printed circuit boards by *A. ferrooxidans* is similar to bioleaching from metal sulfide. For example, the $Fe_2(SO_4)_3$ formed by *A. ferrooxidans* oxidizes elemental copper contained in the printed circuit board to copper ion resulting in the copper solubilization. The regeneration of $FeSO_4$ suggests that the bioleaching process is cyclic [12]. Ilyas et al. [13] demonstrated that metals can also be recovered from electronic scrap by bacterial leaching using thermophilic bacteria such as *S. thermosulfidooxidans.* Choi et al. [12] and Yang et al. [4] studied the bacterial recovery of copper from printed circuit boards scrap computers using *Acidithiobacillus ferrooxidans* in shake flasks getting copper extraction rates higher than 70%.

The aim of this work was to investigate the influence of Fe^{+2} supplementation on bioleaching process to recover copper from non-magnetic fraction of printed circuit boards of obsolete computers using *Acidithiobacillus ferrooxidans*-LR bacteria.

Materials and methods

Printed circuit boards

The printed circuit boards from obsolete computers was comminuted (<2mm) in hammer mill and taken in the magnetic cross-belt separator. Samples obtained through quartering of non-magnetic fraction from magnetic separator were used in bioleaching experiments and analysis of metals' concentration.

To determine the initial metals concentration, the sample was dissolved in aqua regia in 1:20 [14] (1g of printed circuit board sample to 20ml of aqua regia solution). The contact between the printed circuit boards waste and aqua regia was 24hours; follow by simple filtration with quantitative filter paper. The fraction leached was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).

Cell cultures

The bacteria *Acidithiobacillus ferrooxidans* strain LR, isolated from uranium mine effluents [15] was used in this work. *A. ferrooxidans*-LR was initially adapted through several subcultures with gradual increase of printed circuit boards' concentration (non-magnetic fraction samples) and successive replacement of Fe^{+2}. The *A. ferrooxidans*-LR grew in 200ml T&K medium in 250ml shake sterilized flasks with 15g L^{-1} printed circuit boards' samples (non-magnetic fraction) at 30°C and 185rpm.

Culture conditions

T&K medium that was adopted for the growth of bacterial inoculums [16] was composed from two solutions (A and B), being:

Solution A: $(NH_4)_2SO_4$: 0.625g L^{-1};$MgSO_4.7H_2O$: 0.625g L^{-1};K_2HPO_4: 0.625g L^{-1}.
Solution B: 166.5g L^{-1} $FeSO_4.7H_2O$

For the preparation of T&K medium, the solutions A and B were prepared, acidified with H_2SO_4 10N to pH 1.8 and sterilized separately. The solution A was sterilized by autoclaving at 120°C for 30min and 1atm. The solution B was filter-sterilized (0.45μm). Finally, the solutions A and B were mixed at proportion 4:1 respectively.

Bioleaching experiments

Bioleaching experiments were carried out in 200ml T&K medium in 250ml shake flasks containing printed circuit boards samples (15g L^{-1}) and inoculate with 5% (v/v) adapted *A. ferrooxidans*-LR. The cultures were incubated at 185 rpm and 30°C.

The water evaporation was replenished at each sampling with sterile water acidic (pH 1.8) and the medium pH was adjusted with H_2SO_4 10N to 1.8-2.0. All conditions were performed in triplicate. The experiments evaluated the influence of pH and ferrous iron initial concentration on copper bioleaching of non-magnetic fraction samples from printed circuit boards. Two conditions were evaluated. In the first condition a bioleaching experiment was carried out with T&K medium complete inoculated with adapted bacteria and in the second condition the experiment was performed with solution A (culture medium without ferrous iron) inoculated with adapted bacteria. Control conditions uninoculated also run in parallel.

Analytical methods

Leach samples were periodically withdrawn for chemical analyses (1, 2, 3, 4, 5, 6, 7, 10, 15, 20, 30, 40° days) and centrifuged during 20min at 5000rpm. 10ml from supernatants was used to determine Fe^{+2} and 5ml was preserved with 1m HNO_3 concentrate at 4°C for metal analyses (Cu and total Fe). The metals concentration (Cu and Fe_{total}) were determine by inductively coupled plasma optical emission spectroscopy (ICP-OES). For measurements of pH, a bench pH meter was used (an $Ag^0/AgCl$ reference). The determination of Fe^{+2} concentrations was performed by titration with potassium dichromate ($K_2Cr_2O_7$). 10ml samples were acidified with 20ml acid mixture (H_2SO_4/H_3PO_4) and diluted to 50 ml. 3 drops of indicator (1% barium diphenylamina sulphonate) were added and the this solution was titrated with potassium dichromate until it turned from green to purple.

Results and discussion

Printed circuit boards characterization

The non-magnetic fraction (82% w/w) of printed circuit boards containing (w/w) 18.3% copper was used in this work. The elemental analyses (%w/w) of this fraction are showed in Table 1.

Table 1 - Elemental analyses (%w/w) of non-magnetic fraction of printed circuit boards

Metals									Polymers and ceramics
Cu	Sn	Pb	Al	Zn	Fe	Ni	Ag	Au	41,8
18,3	7,8	4,9	4,5	3,9	0,4	0,2	0,1	0,1	

The non-magnetic fraction of printed circuit boards consists of 40% metals and 42% other materials (ceramics and polymers). Copper is the metal of the highest percentage in the printed circuit boards; this is because the printed circuit boards of computers are type FR2, which is a fiberglass layer or cellulose paper and phenolic resin. The surface contains copper layer to connect electrical contacts. Small amounts (0.2% w/w) of precious metals were also present. Studies [2,3,14] demonstrate that the printed circuit boards composition changes probably due to different methodologies applied in the works or because the composition has changed over time. Ilyas et al. [13] also suggested that analytical methods and origin of the material can be attributed to this difference.

Bioleaching experiments

The results of copper extraction are presented in Fig. 1.

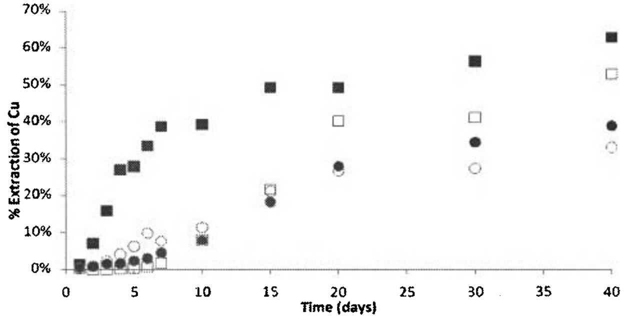

Fig. 1 – Cu^{+2} extraction vs time. Symbols: (□) abiotic control with complete T&K medium and printed circuit boards, (■) adapted *A. ferrooxidans* LR growing with printed circuit boards in complete T&K medium, (○) abiotic control with T&K medium without Fe^{+2} and printed circuit boards, (●) adapted *A. ferrooxidans*-LR growing with printed circuit boards in T&K medium without Fe^{+2}.

As can be seen in Fig. 1, the results show that the copper extraction percentage with inoculated complete T&K medium was higher compared to inoculated T&K medium without Fe^{+2}, due the bacterial action is based on Fe^{+2} oxidation to Fe^{+3} which is an oxidant. Similar results were obtained in studies without addition of Fe^{+2} in the bioleaching process using shake flasks [17,18]. The Fig. 1 also shows that the extraction is more pronounced in the first seven days of experiment in the inoculated complete T&K medium probably due the bacterial growth to be in exponential phase, resulting in exponential increase in the bacterial cells number by increasing the bacterial metabolic activity (oxidation of Fe^{+2} to Fe^{+3}) and consequent copper dissolution, as show in reaction 2:

$$Cu^0 + 2Fe^{+3} \leftrightarrow 2Fe^{+2} + Cu^{+2} \qquad (2)$$

From the 8th day, bacterial growth in the inoculated complete T&K medium enters in the stationary phase and the copper extraction becomes less intense because, at this stage, the number of bacterial cells remains constant until the death phase.

With the complete T&K medium, the bacteria leached about 60% more than in medium without iron supplementation. Similar result was obtained in the biooxidation of chalcopyrite, in which the culture of *A. ferrooxidans* with additional iron leached twice as much copper as in the culture without additional iron [19]. Furthermore, the non-magnetic fraction of printed circuit boards did not have a high iron concentration (0.4% w/w), therefore the largest source of iron for the bacteria was the solution of ferrous sulphate (solution B of T&K medium).

The solution A (control and inoculated) presented less than 40% copper extraction. Although copper be insoluble in dilute sulfuric acid, the aeration of the medium introduce oxygen in the solution which can to promote some solubilization [20].

The bacteria *A. ferrooxidans* is obligatorily aerobic and therefore chemolithotrophic with CO_2 as carbon source for growth, the medium should be agitated in order to provide aeration of the medium [21] The medium even without iron showed solubility of copper, probably due shaking (185rpm) has favored the chemical leaching of copper, thus a decrease in the agitation could be applied as a way to suppress the effect of chemical leaching. The results obtained in the inoculated solution A suggest that bacterial activity was not significantly increased the extraction of copper (<5%) compared with control in the same condition indicating that copper was primarily solubilized by chemical leaching.

The Fig. 2 shows the changes in pH before the adjustments to the range 1.8 to 2.0. The pH stability was needed because the CO_2 is a limiting factor in bacterial growth and acid pH is fundamental in the solubility of CO_2 [21].

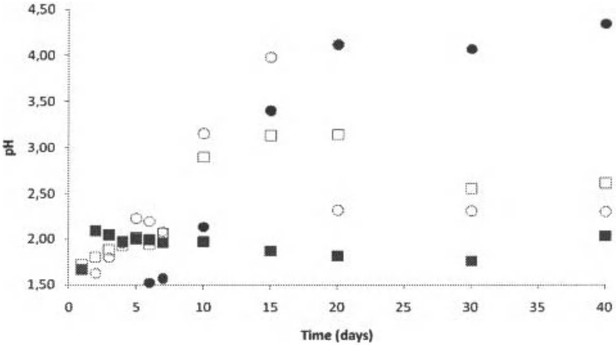

Fig. 2 – Changes in pH vs time. Symbols: (□) abiotic control with complete T&K medium and printed circuit boards, (■) adapted *A. ferrooxidans* LR growing with printed circuit boards in complete T&K medium, (○) abiotic control with T&K medium without Fe^{+2} and printed circuit boards, (●) adapted *A. ferrooxidans* LR growing with printed circuit boards in T&K medium without Fe^{+2}.

In the inoculated T&K medium without Fe^{+2} the pH increased (above 3.5) until the 15th day, suggesting the acid consumption during the oxidation of other metals from printed circuit board, such as Zn, Sn, Al and Pb and partially of copper. The pH values lower than 1.3 or greater than 3.5 strongly inhibit bacterial growth [22] which probably inhibited the bacterial activity after the 20th day of experiment, corroborating the fact that the rate of copper extraction obtained in the inoculated medium without Fe^{+2} was not affected by bacteria. In the control T&K medium without Fe^{+2} there was an increase of pH showing the consumption of acid during the oxidation process of printed circuit boards. Another factor that could explain the higher pH values of control even with the adjustments is the H^+ consumption from metals oxidation which was not reset through the Fe^{+2}/Fe^{+3} cycle. The pH of inoculated complete T&K medium remained steady between 1.8 and 2.0 after 8th day, possibly due to the combinations of reactions that consume acid, such as chemical and microbiological oxidation of Fe^{+2} and the reactions that produce acid, as the hydrolysis of ferric ion [13,14]. After 20 days was observed a pH decrease in both complete T&K medium (control and inoculated) probably because of jarosite precipitation, which produces acid.

The pH of control complete T&K medium presented values higher than inoculated (Fig. 2), probably because the consumption of H^+ and O_2 (promoted by shaking) in the Fe^{+2} oxidation, as show in reaction 3:

$$O_2 + 4H^+ + 4\ Fe^{+2} \rightarrow 4\ Fe^{+3} + 2H_2O \qquad (3)$$

This also explains the copper leaching rate in the control complete T&K medium (Fig. 1) by Fe^{+3} produced (Eq. 3). The Fig. 3 presents the results of changes in Fe^{+2} concentrations.

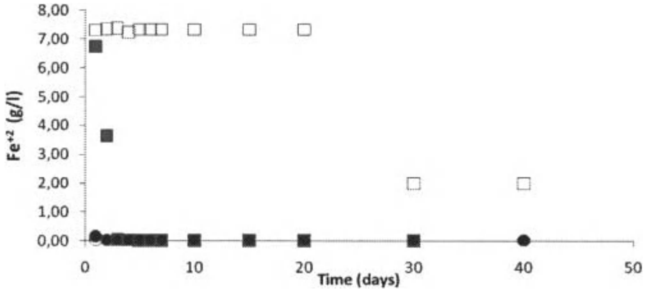

Fig. 3 – Changes in Fe^{+2} concentrations vs time. Symbols: (□) abiotic control with complete T&K medium and printed circuit boards, (■) adapted *A. ferrooxidans* LR growing with printed circuit boards in complete T&K medium, (○) abiotic control with T&K medium without Fe^{+2} and printed circuit boards, (●) adapted *A. ferrooxidans* LR growing with printed circuit boards in T&K medium without Fe^{+2}.

The ferrous iron concentrations obtained in the T&K medium without Fe^{+2} (control and inoculated) were insignificant (Fig. 3). In the inoculated complete T&K medium was observed consumption of Fe^{+2} until the 10th day indicating that the bacterial activity was intense in this period. Same behavior observed in the chalcopyrite bioleaching [19]. This behavior occurs due to the exponential phase of bacterial growth because of the increase in the number of bacterial cells while there is Fe^{+2} available. In copper recovery study [12] from printed circuit board using *A. ferrooxidans*, was concluded that the addition of ferrous ion to the bioleaching process helps to promote the copper dissolution. In the control complete T&K medium, the Fe^{+2} concentrations starts to decline after the 20th day (Fig. 3). Similar behavior was observed in bacterial leaching of complex mineral sample containing pyrite, pyrrotite and molybdenite, which suggested that this fact may have occurred by natural oxidation of Fe^{+2} [22].

Conclusion

The results demonstrate that addition of Fe^{2+} in the leaching medium increases the percentage of copper extraction in the bioleaching process of non-magnetic fraction of printed circuit boards which strengthens the relevance of oxidation mechanism promoted by Fe^{+3}. The changes in Fe^{+2} concentrations of inoculated complete T&K medium suggests that exponential phase of bacterial growth occurs until 5° day. Based on the high values of pH observed in the T&K medium without Fe^{+2}, other metals can be oxidized by sulfur acid, consuming H^+ which increase the pH.

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Recycling of Electronic Waste II

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STATE OF THE ART IN THE RECYCLING OF WASTE PRINTED WIRING BOARDS

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Keywords: Printed Wiring Boards, Recycling, Pyrolysis

Abstract

Printed Wiring Board (PWB) is a platform upon which microelectronic components such as semiconductor chips and capacitors are mounted. It is also called printed circuit board (PCB). In the PWBs, the organic substances are approximately 72%. The main composition of organic substances in PWBs is ethoxyline resin bromide or ethoxyline resin chlorinate. Depending on the different application and design of the PWB, various metals may be used in the manufacturing process, including precious metals such as copper, lead, silver, gold, platinum, and toxic metals such as mercury, cadmium, barium, gallium, cadmium, lead, bismuth. The current paper reviewed the recycling process for waste PWB materials, including mechanical recycling, combustion for energy recovery and different pyrolysis processes, such as vacuum pyrolysis, atmospheric inert pyrolysi and flux pyrolysis process, and hydrometallurgical recycling process.

Backgrounds of Electronic Scraps

Production and use of electrical and electronic equipment (EEE), such as TV sets, computers, mobile phones and many other daily-life items, have dramatically increased over past decades, while the lifespan of many products becomes shorter[1)]. The rapid innovation in technology in past decades has resulted in availability of cheaper and better electronic products in the market. Thus the production of waste electrical and electronic equipment (WEEE) is also increasing, with estimates of 20-50 million tons per year being generated worldwide [2)], and it is a problem that governments and policy makers have to handle [3-4)]. WEEE is also called “E-wastes” or “E-scraps”. From the points of view of recycling and the valuable materials in the used EEE, “E-scrap” is more appropriate than “E-waste” since the used EEE are not real wastes to be dumped but had much benefit to recycle. In the US, it was estimated that over 315 million computers between 1997 and 2004 and 185 million computers between 2004 and 2007 would become obsolete [5)]. E-scrap is the fastest-growing part of the U.S. garbage stream [6)]. It is estimated that only 20% of the E-scrap generated within the US is currently collected and treated, with as much as 80% being unaccounted for [7)].

In the past 10 years, there have been many literature reviews on the recycling of E-scraps, as summarized in Table 1, such as the mechanical recycling by Cui and Forssberg [8)] and the recovery of metals from E-scraps by Cui and Zhang [9)] However, the state of the art in the combustion and pyrolysis treatment for the plastics and polymers in E-scraps is still not well reviewed.

E-scrap represents a complex mixture of two major material fractions: (i) metals (and alloys) and (ii) polymers. An example composition of Printer Wiring Boards (PWBs) is as follows: 28% metals, 72% plastics (epoxy resins) [10)], in details: C (22.5%) H (2.7%) O (5.4%) S (0.04%) Br (N6.5%)+ Pb, Zn, Sb, Ni, Cd, Ga, or As. Metals, particularly heavy metals, represent the quantitatively dominating fraction.

PWB is a platform upon which microelectronic components such as semiconductor chips and capacitors are mounted. PWB consists of three basic parts: a insulator substrate or laminate, conductive circuits printed on or inside the substrate, and mounted components. PWBs are estimated to be ~3wt% of the total electronic appliance and are the core components of many electronic systems installed in martial and demotic electronic appliances [11]. PWBs consist ~72% of organic substance and ~28% of metals. The main composition of organic substances in PWBs (as exampled in **Figure 1**) is ethoxyline resin bromide or ethoxyline resin chlorinate. Many PWBs contain polymer films such as polyimides, polyethylene terephthalate, polyethylene naphthalate (less frequently), and glass fiber composites bonded with a thermoset resin. Typical density of a raw PWB is 2.15 g/cm^3 (an average value with no components) [12]. Metals in PWBs include Cu, Al, Sn, etc. Depending on the different application and design of the PWB, various metals may be used in the manufacturing process, including precious metals such as copper, lead, silver, gold, platinum, and toxic metals such as mercury, cadmium, barium, gallium, cadmium, lead, bismuth, as shown in **Table 2** [13]. These metals are from the electrical components and the solder used to attach them to the boards. Many of these metals have negative impacts on the environment and human health [11, 14-16]. The purity of precious metals in PWBs is more than 10 times higher than that of rich-content minerals [4, 17]. The main motivation to recycle the used PWBs is the value of the precious metals in them [9].

Table 1 Literature Reviews on the Recycling of E-scraps in Recent Years

Authors	Article name and main purpose	Year	Ref.
Sum	Overview pyro- and hydrometallurgical methods to recycle metals from E-scraps	1991	18)
Menad et al.	Overview combustion methods to recycle plastics contained in electronic scrap	1998	19)
Gao et al.	Review the current industrial and laboratory research in PWB recycling	2002	20)
Goosey et al.	Review technologies and processes to recycle materials from end of life PWBs.	2003	21)
Cui et al	Review mechanical methods of recycling E-scrap.	2003	8)
Levchik et al.	Overview the recent literature on combustion and flame-retardancy of epoxy resins.	2004	22)
Shuey et al.	A survey of pyrometallurgical processes of E-scraps.	2004	23)
Kang et al.	Various recycling technologies for the glass, plastics, and metals from E-scrap.	2005	24)
Hilty	Overview the development of electronic technology and the risk of E-scrap.	2005	25)
Wong et al.	Review the level of persistent organic pollutants and heavy metals/metalloid concentrations of at Guiyu, China, an intensive recycling site of E-scrap.	2007	26)
Babu et al.	Overview of E-scrap recycling, including the source, type of E-scrap, strategies and technologies to recover materials.	2007	27)
Gupta	Overview the effect of E-scrap recycling on environment and human healthy.	2007	28)
Susan	Correlations between the environmental and financial performance of existing E-scrap systems operating in different countries.	2008	29)
Huang et al.	Current status of waste PWBs mechanical treatment in China technologies.	2009	30)
Cui and Zhang	Title: Metallurgical recovery of metals from electronic waste: A review Purpose: Recover precious metals from E-scraps by pyrometallurgical processing, hydrometallurgical processing, and biometallurgical processing.	2008	9)
Guo et al.	Recover non-metallic fractions from the PWBs using physical methods.	2009	31)
Guo et al.	The effect of E-scrap recycling activities at Guiyu, China on heavy metal pollution in the surrounding waterway system.	2009	32)
Yu et al.	Comparing different technologies available for PWBs recycling and discovering the limitations of different recycling methods.	2009	33)

Recycling of PWB scraps includes mechanical recycling that roughly separates different sections or parts (such as plastics, metals), and metallurgical recycling that recovers metals or high value materials from the products of mechanical recycling and controls the pollution through some exhaust gases treatment. Combustion or burning is a complex sequence of exothermic chemical reactions between a fuel(usually a hydrocarbon) and an oxidant accompanied by the production of heat or both heat and light in the form of either glow or flames, appearance of light flickering [34]. Pyrolysis is the chemical decomposition of organic substances by heating. Pyrolysis, which occurs spontaneously at high temperatures, is a special case of thermolysis, and is most commonly used for organic materials [35]. Thermal treatment of PWBs were reported using DC Arc Plasma furnace [36], fixed bed reactor [37]. PWBs scraps also represent a significant quantity of energy in terms of the energy consumed in processing petroleum. Recover part of this energy content in a form with the highest possible value, i.e., fuel oil, would be economically and environmentally attractive. However, there is a limited Br content in product oil and emissions.

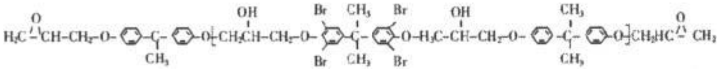

Figure 1 An Example Chemical Structure of PWBs [38]

Table 2 Main elements within PWBs [13]

Elements	wt% in PWB	Annual tonnage worldwide	Elements	wt% in PWB	Annual tonnage worldwide
Cu	9.7	97,000	Ag	0.06	600
Fe	9.2	92,000	Cr	0.052	520
Al	5.8	58,000	Au	0.023	230
Pb	2.24	22,400	Cd	0.014	140
Sn	2.15	21,500	Pd	0.01	100
Zn	1.16	11,600	Be	0.003	30
Ni	0.69	6,900	Hg	0.0009	9
Sb	0.35	3,500	Br	6.5	65,000
Cr	0.24	2,400	Cl	0.24	2,400

The main drawback of the thermal treatment of E-scrap is the toxic products. Pollutants from PWB incineration include heavy metals, organic compounds, particulate and acid gas (Br_2, Cl_2, HBr, HCl, HCN, NH_3). The main toxic substances in PWBs are Brominated Flame Retardants (BFRs) such as TBBPA and PBDEs and heavy metals such as lead and mercury [13, 39]. Researchers have claimed that BFRs, cadmium, chloro-paraffins, chromium, copper, lead, mercury, nickel, and silver compounds are the main toxic substances detected in PWBs [19, 40]. They can cause serious environmental problems if not properly disposed. The open burning of PWBs stripped of metal parts can produce toxic fumes and ashes containing polycyclic aromatic hydrocarbons and polychlorinated biphenyls [5], and induced emission of heavy metals as well [5, 41-42]. The volatile heavy metals are also a problem [43]. For the hydrometallurgical process, the leaching solution used in this process will enter into the environment like the water and air system. About 70% of the heavy metals (mercury and cadmium) in US landfills come from electronic wastes. Consumer electronics contribute 40% of the lead in landfills. These toxins can cause brain damage, allergic reactions and cancer. As an example, at Guiyu, China, many tons of E-scrap materials and process residues were dumped into workshops, yards, roadsides, open fields, irrigation canals, riverbanks, ponds, and rivers. It was reported that the blood lead levels of children in Guiyu ranged from 4.40 to 32.67 μg/dL with a mean of 15.3 μg/dL, exceeding the "elevated blood lead level" of 10 μg/dL in children [44]. PWBs incineration plants need contribute significantly to the annual emissions of cadmium and mercury. In addition, heavy metals not emitted into the atmosphere are transferred to slag and exhaust gas residues and can reenter the environment on disposal.

Combustion of Waste PWBs

Combustion is a gas phase reaction involving a fuel source and oxygen. Energy recovery is a key option for waste plastics, as their basic raw material, is derived from oil. Plastics have high energy potential. The heat value of plastics like PP and PET is even higher than the fuel, as shown in **Figure 2** [19]. PS is similar to the fuel in heat value. Moreover, during the complete combustion of organic materials simple molecules such as CO_2, H_2O, N_2, SO_2 and hydrogen halide will form. The heat energy recovery from plastics has been studied for industries such as electric power making, iron making, and steam supplying. While in the past, there were much oppositions — justified by concerns around the poor environmental performance of old incinerators — today energy recovery is more widely required as an environmentally sound option. Incinerating and combusting the plastic directly in order to utilize the heat energy released, and producing steam or electricity have received increased attention nowadays, since conventional energy sources are declining sharply. [17, 45-47) 48)] The use of incineration, together with the associated energy recovery, plays a complementary role for recycling and can reduce the amount of PWBs going to landfill by as much as 70%. Plastic contains as much energy as petroleum and natural gas, and much more energy than other types of garbage since plastics are made from fossil fuels. For instance, the PVC found in PWBs, cables and connectors holds in store 140kJ/mol and 290kJ/mol energy respectively, as shown in Table 3. Waste plastics are particularly interesting due to their high caloric value and the gate fee; hence the recycling industry is willing to invest in this field [49-51)]. As an alternative to oil and pulverized coal, the injection of high caloric plastics into the tuyere zone in blast furnaces has been accomplished by several ironmaking companies [49-50, 52-54)]

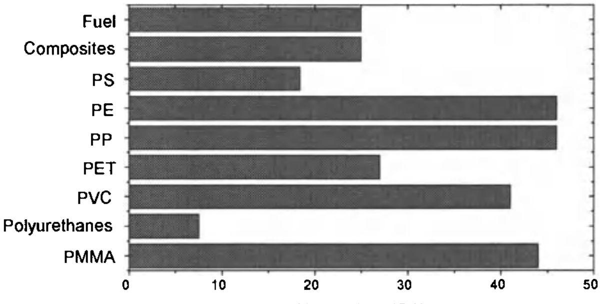

Figure 2 Heat Values of Fuel and Different Plastics [19)]

Table 3 Kinetic Data of the Combustion of Plastics in E-scraps

Type of resin	Decomposition temperature range (°C)	Maximum rate of decomposition temperature (°C)	Store energy (kJ/mol)	Ref.
PA 6	310-450	415	211	55)
PS	320-415	355	172	
PVC	210-350(in PWBs)	250-280(in PWBs)	140	
	350-500(in cable and connectors)	425(in cable and connectors)	290	
HDPE	340-500	475	262	
PP	340-460	425	190	
PET	360-410	400	322.3-338.98	56)
Epoxy resins	280-500	375	230.4	57)
TBBA	180-270	250	179.1	58)

Pyrolysis of Waste PWBs

Pyrolysis is one of the best methods for treating complex mixtures of waste polymers and to recover the material and energy content. The process consists of thermal decomposition at moderate temperatures in total absence or small amount of oxygen in which the structures of polymers break down into smaller intermediate products [59)]. The pyrolysis process, provided that the temperature is high enough, will melt the solder used to attach the electrical components to the PWBs [4)]. Although many researches into the pyrolysis of PWB wastes have been reported, most of the works have been carried out using analytical pyrolysis techniques or very small batch reactors [60-64)]. Also, most of the works for the pyrolysis of PWBs haves concentrated on the composition of the organic products, particularly the brominated organics. Pyrolysis of organic materials contained in waste PWBs leads to the formation of gases, oils, and chars which can be used as chemical feedstock or fuels [30, 65)]. Reported pyrolysis investigations are at experimental stage and have been carried out in vacuum, molten salt, fluidized bed, rotary kiln, entrained, stationary, and moving bed reactors [66]. Comparing to the incineration and combustion of PWBs, the pyrolysis process has several characteristics: [12, 55, 67] 1). Converting the organic solid substance into fuel gas, fuel oil and carbon-black as storage energy; 2) Emitting toxic substances such as sulfur, bromine and heavy metals in wastes; and 3) Keeping metals from being oxidized.

Vacuum Pyrolysis of PWBs

The vacuum pyrolysis method, with the sample being pyrolysed in a closed furnace with vacuum, has been used in recycling waste car tires. The vacuum could help reduce the apparent activation energy of the PWBs pyrolysis, and increase the volatile of pyrolytic products and decrease the secondary pyrolytic reactions [68-69]. The vacuum is beneficial to raise the yield of liquid products. Results from the vacuum pyrolysis indicates a liquid oil yield of 20–36%, a gas yield of 2–35% and a solid yield of approximately 40-60% were obtained, as shown in **Table 4**. Heating rate is a significant factor affecting the yield of products. At a certain top temperature under a certain vacuum, the biggest yield of liquid products will be at about 15-20 °C/min. At a lower heating rate the PWBs powders will reside at a certain temperature for a longer time so that the secondary pyrolysis reaction will take place. Some weak oxygen-bridge bond and side-chain in benzene ring are easy to break to form free radical to decrease the oil yield and increase volatiles [70]. The terminal temperature can also greatly affect the yield of pyrolysis products. Generally, at same heating rate under same vacuum, lower terminal temperature will have a lower oil yield.

Table 4 The Yield of Oil/Gas from Different Vacuum Pyrolysis Experiments

Yield of / product, wt%.		Experimental conditions			Year	Ref.
oil	gas					
25.33	8.76	10 °C/min, 30 min, 500 °C, Vacuum			2006	68)
21	2	10 °C/min, 30 min, Vacuum, 5 kPa		200 °C	2008	71)
31	2.5			300 °C		
36	2.5			400°C		
35	3			500 °C		
34.5	3			600 °C		
35	2.5			700 °C		
34.37	3.05	20 °C/min, 30 min, 400 °C		Vacuum, 3 kPa		
34.67	2.25			Vacuum, 10 kPa		
35.05	2.14			Vacuum, 15 kPa		
34.36	2.24			Vacuum, 20 kPa		
34.25	2.29			Vacuum, 25 kPa		
34.05	2.34			Vacuum, 30 kPa		
32.30	-	30 min, 400 °C Vacuum, 15 kPa		5 °C/min		
34.30	-			10 °C/min		
34.32	-			15 °C/min		
34.37	-			20 °C/min		
33.80	-			25 °C/min		
33.65	-			30 °C/min		
34.37	30.52	15-20 °C/min, 30 min	300 °C	Vacuum, 5 kPa	2009	72)
35.05	34.92		400 °C	Vacuum, 15 kPa		
34.05	34.78		500 °C	Vacuum, 30 kPa		
26.32	34.38		600 °C	Atmosphere		

Table 4 shows that the oil yield is 35% at the temperature of 400-550 °C and 20-30% at the temperature of 200-300 °C. With the increase of the terminal temperature the high molecular polymer like epoxy resin will be broken to some long bond compound so that more oil products will be obtained. However, if the terminal temperature is too high, secondary pyrolysis reaction of pyrolysis gases will happen to break the long bond to short bond, the amount of gaseous products will increase but not oil products [70-71]. Peng et al. [68] investigated the pyrolysis of waste PWBs in a bench-scale pyrolysis reactor under low vacuum and

nitrogen, indicating that the apparent activation energy under vacuum became smaller than that in nitrogen, vacuum helped to increase the volatility of pyrolysis products, and weakened the secondary reaction, so the liquid yield under vacuum was increased at the expense of gas and solid yields. Wu et al. 71) investigated the pyrolysis of epoxy resin in waste PWBs in a pyrolysis oven. The experimental results showed that the optimal condition was obtained as follows: pyrolysis terminal temperature at 400-550 °C, heating rate of 15-20 °C/ min, pressure of 15 kPa, holding time of 30min. Hall et al. 65) recycled the organic compounds and metals from scrap PWBs by pyrolysing in a fixed bed at 800 °C, and found that different gases release at different temperature from the mobile phone boards. Qiu et al. 72) pyrolysed waste PWBs in vacuum oven and investigated the products of liquid, solid and gas yield by FT-IR, GC-MS, and SEM. The results showed that the density and component of the liquid changes with different pressure. The oils mainly consist of phenol, substituted phenols, bisphenol-A and bromides of them

Atmospheric Inert Pyrolysis of PWBs

The waste PWBs can be pyrolysed in an inert gas (such as N_2, Ar, etc.) under atmospheric pressure, which mainly uses fixed bed as a reactor. The yields of pyrolysis products (oil and gas) are listed in **Table 5**. The main pyrolysis process takes place between 350-500 °C. As temperature increases above 600, there is little change in the yield of products. The flow rate of nitrogen has a certain effect on the mass loss. Higher flow rate could take the pyrolysis gas away more quickly, thus the secondary reaction is hard to happen so the gas products decrease. The pyro-oil obtained during the pyrolysis process is a mixture of organic compounds (usually termed oils), and also contains some aqueous products. Water and hydrocarbons by-product could either be a product formed during the process (derived from the oxygen-containing functional groups, –COO–, OH–, –COOH–, etc.) or due to the original moisture in the samples, as shown in **Tables 6** and **7** 73-74).

Table 5 Yield of oil/gas in Vacuum and Inert Atmosphere Pyrolysis Experiments

Yield of product, wt%.		Experimental condition		Year	Ref.
oil	gas				
40.6	24.9	5°C/min, 30min, 540°C, Nitrogen, 100ml/min. Fixed-bed reactor		2000	43)
	17-23/13-23	155°C/min, 30min, 1000°C, Nitrogen 100ml/min.		2003	75)
	49/31(TBBA)	10°C/min, 600°C, Nitrogen 60ml/min		2004	76)
0	0.33	15°C/min, 30min, Nitrogen 200ml/min	200°C	2005, 2002	77-78)
14.99	20.22		300°C		
19.42	14.79		400°C		
20.79	14.99		600°C		
19.63	19.86		800°C		
22.47	10.75	10°C/min, 30min, 500°C, Nitrogen		2006	68)
22.7	4.7(PC PWBs)	10°C/min, 135min, 800°C, Nitrogen, Fixed-bed reactor		2007	65)
28.5	6.5(TV PWBs)				
15.2	2.3(Cell PWBs)				
28.29	35.94	20°C/min, 900°C, Nitrogen, 10L/h-15L/h		2007	79)
9.85±0.38	5.21±1.55	10°C/min, 30min, Nitrogen 200ml/min, A tubular oven,	300°C	2008	80)
13.56±1.46	6.90±2.00		400°C		
12.93±1.55	9.06±0.23		500°C		
13.18±1.55	9.13±0.80		600°C		
13.90±1.55	8.87±1.19		700°C		
16.2±1.1	7.3±0.7	15°C/min, 30min, 500°C, Nitrogen 1000ml/min		2008	81)
7.9, 14.4	-	10°C/min, Nitrogen, 0.19m/s, 0.48m/s, Fluidized bed reactors	400°C	2009	82)
11.7, 15.2	-		450°C		
15.1, 20.1	-		500°C		
17.8, 23.5	-		550°C		
18.1, 24.5	-		600°C		
18	19	800°C, Nitrogen, 20min, Muffle furnace		2009	83)

Pyrolysis oil obtained during the pyrolysis process under atmospheric inert condition is also a mixture of organic compounds (usually termed oils), and also contains some aqueous products. Similar results in the pyrolysis of different plastics have been reported 43, 73, 80, 84). They all agree that water and hydrocarbons by-product could either be a product formed during the process (derived from the oxygen-containing functional groups, -COO-, OH-, -COOH-, etc.) or due to the original moisture in the samples 85).

Guan et al. 80) pyrolyzed the PWB sample (2.0 cm×2.0 cm) under nitrogen atmosphere, at 300-700 °C in a tubular type oven. Peng et al. 86) also pyrolyzed PWBs under nitrogen atmosphere. Sun et al. 75) investigated the pyrolysis kinetics of PWB scraps under various conditions with TG. Sun et al. 78) also analyzed the pyrolysis products for different particle size of PWB powders (0.2-15 mm) at 600 °C. Li et al. 87) reported that the yield of products at higher heating rate was more than at lower heating rate. Xiong et al. 88) investigated the characteristics of PWB pyrolysis and its kinetics using a tubular furnace and TGA. Guo et al. 89) pyrolysed waste polytet rafluoroet hylene (PTFE)-PWBs in a fixed bed at different heating rates (5-50 °C/min) under 50 ml/min N_2. Guo et al. 90) also analyzed the composition of the pyrolysis oil products from the pryolysis of PWBs using GC-MS. Hall et al. 65) used a fixed bed reactor to pyrolyze three types of PWBs (from computers, televisions and mobile phones) at 800 °C. The pyrolysis products were analyzed using GC–FID, GC–TCD, GC–MS, GCECD, ICP-MS, and SEM–EDX. Wang et al. 82) used a fluidized bed reactor to pyrolyze scrap PWB particles under inert gas. Zhou et al. 91) studied the pyrolysis characteristic of waste phenolic-resin-based PWBs by TG and DSC. The composition of pyrolysis products were analyzed by pyrolysis gas charomatography mass spectrometry (Py-GC-MS).

Table 6 Major Products in the Pyrolysis Oil Resulting from the Pyrolysis of PWBs

The main products in the oil	Composition percentage, %	The main products in the oil	Composition percentage, %	Experimental information	Ref.
Phenol	25.23/10.06/38.49	*p*-Hydroxydiphenyl	1.47/0.08/2.87	10°C/min, 800°C Nitrogen Fraction of pyrolysis oil: PC 42.1% TV 21.4% Cell phone 60.7%	65)
2-Methylphenol	1.04/1.60/1.07	Bisphenol A	1.38/0.11/0.67		
4-Methylphenol	1.45/2.20/0.31	Triphenyl phosphate	0.92/4.25/0.09		
2,6-Dimethylphenol	0.27/0.50/0.15	*o*-Cresyl phosphate	0.55/0.00/0.00		
2-Ethylphenol	0.22/0.20/0.24	*m*-Cresyl phosphate	0.10/0.00/0.00		
4-Ethylphenol	0.47/0.26/0.61	2,4-Dibromophenol	0.03/0.35/0.01		
4-(1-Methylethyl) phenol	8.61/1.26/16.11	2,6-Dibromophenol	0.34/0.56/0.10		
TBBPA	0.0006/0.0013/0.00				
Acetonitrile	2.48	2H-1-benzopyran-3ol	1.98	10°C/min, 500°C Vacuum, 10 kPa Nitrogen gas was pumped in the reactor for 20min.	68)
Phenol	46.37	Dibromophenol	0.93		
Methylphenol	0.84	Dibenzofum	0.63		
2-bromophenol	1.45	p-hydroxybiphenyl	4.06		
Ethylphenol	0.58	1,3-dibromo-propanol	0.78		
4-(1-methylethyl) phenol	12.73	Bis(4-aminophenyl)-metylene	0.21		
Isoquinoline	0.11	Biphenol A	21.07		
Bromobiphenol A	0.57	2,6-dibrom-4-(1,1-dimethylethyl)-phenol	4.05		
Phenol	1.0	bromobisphenol A	2.3	10°C/min, 600°C Nitrogen, 60ml/min	76)
2-bromophenol	2.0	dibromobisphenol A (1)	10.5		
4-bromophenol	3.3	dibromobisphenol A (2)	2.1		
2,4-dibromophenol	6.9	tribromobisphenol A	24.7		
2,6-dibromophenol	8.7	Others	6.6		
2,4,6-tribromophenol	8.1	TBBA	23.8		
Phenol	49.4917	2,4-dimethylphenol	6.3818	Microwave 700W Microwave reactor	92)
2-Methylphenol	13.2910	2,6-dimethylphenol	1.4397		
Methylphenol	13.7923	Isopropylphenol	5.2259		
2,3-dimethylphenol	3.3293				

Table 7 Major Products in the Pyrolysis Gas Resulting from the Pyrolysis of PWBs

The main products in the gas	Composition percentage, %	The main products in the gas	Composition percentage, %	Experimental condition	Ref.
H_2	4.6/3.2/5.7	Propene	2/1.1/2.7	10°C/min, 800°C N_2, and fraction of pyrolysis oil: PC 42.1% TV 21.4% Cell phone 60.7%	65)
CO	27/21.8/36.1	Propane	1/1.6/0.4		
CO_2	51/51.5/45.8	Butene	0.8/1.8/1		
Methane	10.3/14/6.4	Butane	0.5/1.2/0.2		
Ethene	0.6/1.1/0.5	Cl	0/0/0.1		
Ethane	1.9/2.7/0.6	Br	0.3/0.1/0.5		
H_2	38.52	C_1–C_4	15.23	10°C/min, 500°C Nitrogen/200 A tubular oven	80)
CO	7.23	O_2	12.03		
CO_2	7.93	N_2	9.50		
CH4	9.55				

Summary

The current paper briefly reviewed the recycling process for waste PWB materials, including mechanical recycling, combustion for energy recovery and different pyrolysis processes, such as vacuum pyrolysis, atmospheric inert pyrolysi and flux pyrolysis process, and hydrometallurgical recycling process.

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OVERVIEW OF ELECTRONICS WASTE MANAGEMENT IN INDIA*

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Keywords: electronics waste, PCB recycling, metal recovery

ABSTRACT

Growth of electronics waste (e-waste) and lack of appropriate disposal mechanism are the great concern for developing countries like India. The domestic generation of e-waste in India is rapidly growing with the development. The imported substance is also substantially contributing to the e-waste inventory. Recycling of e-waste is mainly carried out in unorganized units in India. The primitive recycling technique used by the unorganized sector is a great threat to the environment and the health of the operators involved in these profession. Therefore, improvement of technology used by these units towards a cost effective, environmental friendly alternative could be the solution to the present crisis. Few initiatives of recycling have, however, come up in recent years in organized units. The precious metals are still recycled in the developed countries. This report discusses the inventory, technology status, legal legislative and existing practices of e-waste management in India.

1. INTRODUCTION

Innovation, research and development in the field of electronics and information and communication technology (ICT) lead to convenient, independent human life. Consumption of electronics and hardware products has enhanced by manifold. Electronics and hardware sectors have, thus, become the fastest growing sector in the world. Faster obsolescence of these products is forcing users to replace products with an advanced technology. Life cycles of these products are few years. Discarded electronics products are, therefore, accumulating alarmingly in our society. Electronics waste (e-waste) is a crisis not only due to its volume but also for presence of its toxic ingredients, like heavy metals (e.g. lead, mercury, cadmium, hexavalent chromium) and flame retardants such as poly brominated biphenyles and poly brominated diphenyles ether. These substances create potential occupational and environmental health hazardous.

Six million of e-waste was generated in 1998, which was 4% of the municipality waste. E-waste grows nearly 5%, which is nearly 3 times faster than municipality waste [1]. Like other parts of the world, India is also facing serious crisis due to e-waste. Main challenges in the society are awareness of the environmental, social and economic aspects of e-waste among the public, consumers, producers and policy and law makers. India does not have safe, environ-friendly, e-waste disposal technology. India generated, disposed and recycled 3, 32, 979 Metric Tonnes (MT, 1MT= 1000Kg)), 1, 44, 43 MT and 19,000 MT of e-waste respectively in 2007 [2].

Import of e-waste is banned by Supreme Court of India. It is against the Basel Convention. Large quantities of discarded hardware equipments are still arriving India for disposal through non-official channels. Imported e-waste is contributing significantly in the total inventory. The 50, 000 MT of e-waste was imported in India during 2007 [2]. Developed

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* *The views expressed in the article are those of the authors and do not represent the official views of the Department of Information Technology, Ministry of Communication & Information Technology, Government of India.*

countries find it financially profitable to send e-waste for re-use /recycling in developing countries. Cost of recycling of a single computer in the USA is US $ 20, whereas in India the cost is only US $ 2 [3]. Western countries are thus compelled to find out alternative destinations for disposal. Large volume of e-waste is, therefore, exported to developing countries, where labour cost is low, environmental laws are not enforced strictly and market is available for secondary components and materials. Major e-waste recycling in India is done in the unorganized sector, using non-scientific, non-environment-friendly methods, violating prevailing laws of the land. The present article describes the status of generation of e-waste, existing laws to monitor its management, practices employed reusing, reducing and recycling of e-waste in India.

2. INDIAN ICT GROWTH

Indian ICT sector has established its supremacy in world market and consistently maintained its growth in last two decades. After economical slowing down in 2008-09, India has shown 7.2 % of growth in 2009-10 as compared to 6.7% in 2008-09. Revenue aggregate of IT Business Process Outsourcing (IT-BPO) industry had grown at 5% to US $ 73.1 billion in 2009-10. Exports of software and services exports grew at 5.5% to US $ 49.7 billion in 2009-10. IT services exports grew at 5.8% to achieve US $ 27.3 billion in 2009-10. ITeS-BPO exports had reached to US $ 12.4 billion in 2009-10, with a 6% of growth [4]. Electronics hardware production grew from US $ 11 billion in 2004-05 to US $ 23 billion in 2009-10, with a cumulative annual growth of 20%. Demand for electronics hardware in the country reached US $ 45 billion in 2009 and has a potential to grow US $ 125 billion by 2014 and US $ 400 billion by 2020. Electronics hardware production would reach US $ 100 billion by 2014 and US $ 400 billion by 2020, whereas, the export would reach US $ 15 billion by 2014 and US $ 80 billion by 2020 [4]. ISA-Frost & Sullivan had indicated that the market size of electronics equipment manufacturing sector will reach to US$ 160 by 2015 [5]. ICT penetration is given at Table I.

Table: I ICT Penetration

ICT Indicator	Number in million	Percentage (%)
Fixed Telephones - main lines in use	37.05	3.16
Cellular Telephones	525.16	44.73
Total Tele-density	562.21	47.89
Televisions	176	15
Cable TV connections	140	12
Internet users	81	7.1
Internet Connections	3.611	0.31
Broadband Connection	7.83	0.67
PC Population	30	2.55

***Source: Annual Report, DIT*[4] *and DOT*[6], *CIA*[7]**

3. E-WASTE INVENTORY IN INDIA

Increase in usages, faster obsolescence and subsequent up-gradation have resulted in discarding of electronics products, which adds large volumes of e-waste to the solid waste stream. Actual data on generation of e-waste is not available in India. Several studies have, however, been conducted to find out the inventory of e-waste generation in the country. One such study carried out by MAIT/GTZ in 2007, projected that the total quantities of generated e-waste in India per annum was 3, 32, 979 MT. Recyclable and recycled e-waste per annum were estimated to 1, 44, 43 MT and 19,000 MT respectively. Total processed e-waste during 2007 was categorized as 12000 MT of computers and 7000 MT of televisions. The 2.2 million computers were become obsolete in 2007. India had 20 million computers in 2007, which grew to 75 million by 2010. Around 14 million mobile handsets had been replaced in 2007 [2]. Growth of e-waste in India is projected as 10% and the volume would reach 467098 MT by 2011 [2]. Considering 10% growth, the inventory of the e-waste is estimated to cross 1 million MT by 2020 (**Figure1**). Import of e-waste has created complex scenario for e-waste management in India. India is becoming a big market for discarded electronics and hardware products. Import of e-waste was estimated in 2007 around 50000 MT per annum [2]. Another study indicated that PCs imported to Delhi during 2003 was nearly 3,600 tonnes/year [8].

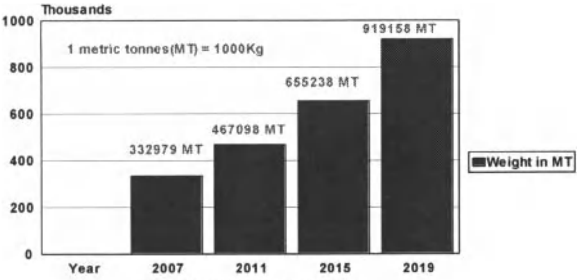


Fig.1: Growth of Ewaste in India

4. INDIAN LAWS ON E-WASTE MANAGEMENT

Trade and management of e-waste are dealt in India under the regulatory framework of environment, foreign trade of central government as well as environmental rules and regulations of state government. Ministry of Environment and Forests (MoEF) is the nodal agency at the central level for policy, planning, promoting and coordinating the environmental programs. E-waste was first introduced at the Environment (Protection) Act 1986 as a hazardous waste. Being a signatory to Basel Convention on the control of trans-boundary movement of Hazardous Wastes and Disposal in 1992, trans-boundary movement and disposal of hazardous wastes issues are addressed through international cooperation. India is committed towards waste minimization and control of hazardous wastes [9-11]. Rules/ guidelines on hazardous wastes are given below:

1. Hazardous Wastes (Management and Handling) Rules, 1989/2000/2002
2. MoEF Guidelines for Management and Handling of Hazardous Wastes, 1991
3. Guidelines for Safe Road Transport of Hazardous Chemicals, 1995
4. The Public Liability Act, 1991
5. Batteries (Management and Handling) Rules, 2001
6. The National Environmental Tribunal Act, 1995
7. Bio-Medical Wastes (Management and Handling) Rules, 1998
8. Municipal Solid Wastes (Management and Handling) Rules, 2000 and 2002
9. Hazardous Waste (Management and Handling) Amended Rules, 2003
10. Guidelines for Environmentally Sound Management of E-waste, 2007
11. Hazardous Wastes (Management, Handling & Transboundary) Rules, 2008

12. E-waste (Management and Handling) Rules, 2010 *(yet to be enacted)*

Hazardous Wastes (Management and Handling) Rules, 1989 provides the guidelines for the control of generation, collection, treatment, transport, import, storage and disposal of wastes. This rule was amended in 2002 to widen the definition of hazardous waste as per Basel Convention. MoEF had issued a guideline in 1991 for management and handling of hazardous wastes for generators of waste to ensure safe transportation of hazardous waste, responsibility of owners and operators of hazardous waste storage, treatment and disposal facilities, reporting system for the movement of hazardous waste and the procedures for closure and post closure requirements for landfills. E-waste was covered under the Environment (Protection) Act, 1986 under stipulated Hazardous Wastes (Management, Handling & Transboundary) Rules, 2008. MoEF amended the Environment and Forests Hazardous Wastes (Management and Handling) Rules in 2008 to elaborate its ramification to include e-waste to address aspects relating to imposition of restrictions and prescribed procedures for management, handling and disposal of hazardous wastes. An exclusive legislation on e-waste (Management and Handling) Rules, 2010, drafted by MoEF on 14.06.10, aims is to ensure the responsibility of the manufacturers, vendors, and consumers of the e-waste. Financial responsibility extending beyond the sales of equipment and setting up of take-back systems for effective management and handling of e-waste are also addressed to be enacted soon [12].

5. E-WASTE MANAGEMENT

E-waste management in India is carried out by various players including collectors, traders and recyclers in unorganized sector. The business of collection, disassembly, segregation and recovery of traceable/ recyclable e-waste requires low investment so attracts many small entrepreneurs. The unorganized sector involved in e-waste management employs large manpower. One study indicates that over 10,000 numbers of unskilled workers are involved in unorganized sector alone in Delhi [13].

5.1 E-waste Recycling in Non-formal sector

The major (95%) e-waste recycling is carried out in India in small-scale units in non-formal sector, which include *kawaries* (rag-pickers), scrap dealers, whole sellers, recyclers etc. The e-waste management in non-formal sector has following major operations.

Kawaries (rag pickers), small scrap dealers collect materials from e-waste generators including manufacturers, offices, importers etc. and domestic users. Suitable incentives are paid for the collected e-wastes to encourage consumers in putting the e-waste in recycling chain instead of storing the same or throwing away in municipality garbage. Collected e-waste are dismantled and segregated by secondary handlers to various categories such as components, modules, metals frames, glass and plastics depending on their selling potential. Disassembly methods are of two types, non–destructive and destructive. Non–destructive recovers the certain disassembled parts for reuse while the destructive disassembly separates each material type for recycling processes. The disassembly of the e-waste segregates broadly following items:

- Small & large structural metal parts, heat sinks
- Small & large structural plastic parts
- PCBs with integrated circuits (ICs),Chips, electronic components and connectors

- Ferrite and ceramic components
- Cables and wires
- Glass components.

The components and modules include Cathode Ray Tube (CRT), PCB, power supply, deflection yoke, etc., have fairly good market value. Remaining items such as plastic and glass are sold to scrap market with suitable price. The circuit tray contains a number of condensers of different sizes, which can be sold depending on their functional condition and market value.

Computer monitor and television consist of CRT, CPU, keyboard, mouse, and printers. CRT disassemblies to components like picture tube, copper yoke, PCB, plastic casing, and plates. Functional CRTs are sold for re-gunning as re-charged tubes have a potential market value for local manufacturer. Defective CRTs are mechanically separated to recover iron frames. Copper are recovered from deflection yoke, transformers and circuit broads and stripped cables and wire. Copper and iron are sold to appropriate smelters. PCB, commonly recoverable module in all the electronic gazettes, has potential market value in recycling market. Defective condensers, ICs are also sold along with populated PCBs for recovery of precious metals.

The casing of monitors, TV, refrigerator is made of two types of plastics, PVC (polyvinyl chloride) or ABS (acrylonitrile-butadiene styrene). The insulator of copper wire and cable are also consists of PVC. The PVC is not recyclable due to presence of high percentage of silicate to make it fire retardant. ABS is recycled into or High Impact Plastic, used in toy industry. Plastic enclosures are sold to plastic reprocesses. Glasses contain high lead content. Cullet of glasses are used as glass parts (panels, funnels) manufacturing units.

Main objective of non-formal units are to recover gold from the ICs, gold plated terminals of connectors and PCBs and other components etc. Gold rich components are removed by loosening of the lead solder by surface heating, which causes air pollution. Stripped PCBs are subjected to open burning to recover copper. The boards are heated to extract the thin layer of copper foils in the PCBs. In the acid bath process, the circuit boards are dipped in acid for few hours for de-soldering. The used chemical solutions are drained to the ground causing soil pollution. Lead sludge that collects in the bottom during the process is recovered and sold. After a water bath the de-soldered PCBs are boiled with a caustic soda solution and manual scrubbing is done to remove the paint. The boards are again dipped in an acid solution for few hours, which results in copper sulphate formation. Iron wires are added to the solution and the sludge contained copper settles in the bottom. The acid solution is drained out to recover the sludge, which is dried, grounded to power and sold in the market. This is one of the most hazardous processes in e-waste recycling and creates occupational and environmental hazards.

5.2 E-waste Recycling in Formal Sector

India does not have end-to-end e-waste recycling plant. The authorized units carry out few mechanical operations to segregate PCBs at suitable stage. The facility for the treatment of the PCBs to recover precious metals is still not available in India. The shredded PCBs of suitable size is exported to the developed countries for final recovery of precious metals. India has 16 organized recyclers, authorized by MoEF and CPCB. The recycling method of the e-waste in the formal units includes following major processes.

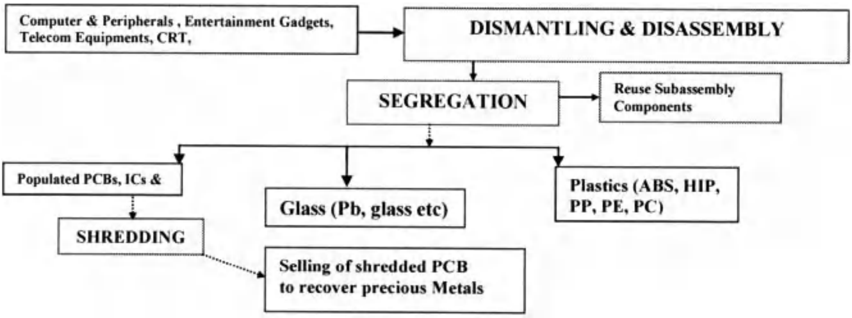


Fig. 2 Block Diagram of E-waste Recycling in Formal

Block diagram, **Fig.2,** shows the dismantling, dissembling of discarded electronics and hardware products. Disassembly removes hazardous components like batteries and high and low grade components, part, group of parts or a sub-assembly from a products. Output steam consists of PCBs, connectors, components, modules, ICs, metal enclosures, wires, mixture of plastics, glass, etc. The segregated useful modules, components, wire, metal enclosures, plastics and glass are appropriately sold to the respective users, smelters and re-processors depending on their market demand. Re-processors and smelters of metal, glass and plastics are specialized in converting these scrap of coppers, aluminum, iron, glass and plastics for further use as virgin materials. Remaining components, PCBs connectors etc. are separated out for further process to recover precious metals. Populated PCB/ components contain valuable metals like Gold (Au), Palladium (Pd), Tantalum (Ta), Indium (In), Gallium (Ga), Beryllium (Be) etc. Some of the precious metals are present in traces and the economic value of recovery will substantially be influenced by these substances. Present recovery practices in India only include the glass, plastic, copper, aluminum, iron etc. Extraction of precious metals requires advanced technology, which is not available presently in India. PCBs are thus shredded further to the suitable size, which are then sent to the developed countries to the companies like, Umicore, Belgium etc. to extract the precious metals.

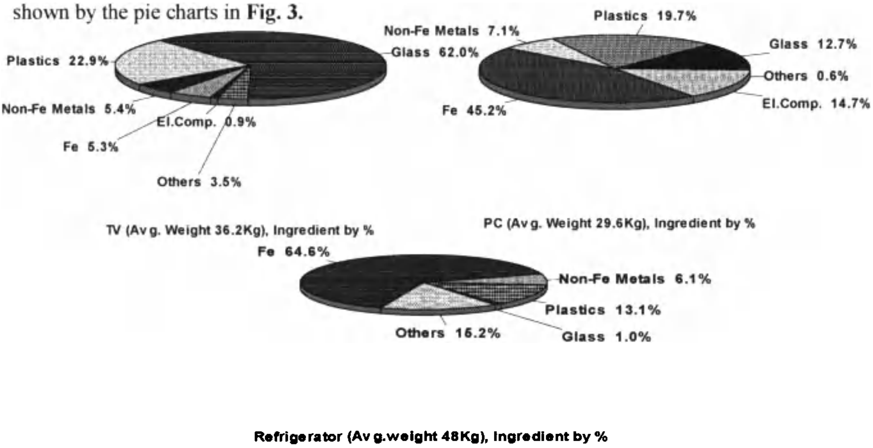
5.3. E-waste Market Potential

Motivation of non-formal units for metal recovery can be understood if one sees the quantities and qualities of the materials recovered from e-waste and their market value. Major three items, like, metals, glass and plastics are recovered. Economic value of the items varies in every appliance. Metal composition, however, depend on the design, functionality of the products and it varies with time and requirement. CPCB, India had carried out study on three main e-waste products, namely, television (TV), personal computer (PC) and refrigerator, shows the percentage (%) of comprising materials in the e-waste products [14]. Following items are broadly recovered from the e-waste products [14]:

- Iron and steel from casings and frames
- Non-ferrous metals, especially copper from cables, and aluminum
- Glass from CRT
- Plastic from casing, cables
- Electronic components

- Precious Metals (Au, Ag, Pd etc) recovered from populated PCB
- Others (rubber, wood, ceramic etc.).

The weight and percentage of the recovered materials from TV, PC and Refrigerators is shown by the pie charts in **Fig. 3.**



TV (Avg. Weight 36.2Kg), Ingredient by %

PC (Avg. Weight 29.6Kg), Ingredient by %

Refrigerator (Avg.weight 48Kg), Ingredient by %

Fig. 3 Ingredient of TV, Refrigerators and PCs

Market value of the materials recovered from e-waste in India are indicated in **Table II**

Table: II Market Value Of Materials Recovered from E-Waste *[13-15]*.

	Item	US$
Metal Parts	**Steel from yoke (100 gm)**	**0.07**
	Iron frames a color monitor (200~250 gm)	***US$ 0.15 per kg***
	Copper from yoke (colour-200gm):*(Rate: US$1.5-1.75/kg)*	**0.35**
	Copper from yoke (colour-50-60gm) *(Rate: US$1.5-1.75/kg)*	**0.10**
	Laminated gold plating at PCB (25-30 gm/ computer unit)	**1.12**
	Gold plating pin at PCB (250 gm/computer set)	**15**
	Aluminum recovered from defective ICs, capacitors and transistors	***US$1- 1.25 per kg***
Plastics Parts	**Plastic without silica (from all sources) (2-2.5Kg)**	**1.12**
	Plastic with silica (2-2.5Kg)	**0.6**
	PVC wire	**0.25**
	Plastic casings of PCs (PVC)	**0.02/kg.**
	Plastic casings of PCs(ABS)	**0.37/kg.**
	PCBs	**0.05-0.5**
	PCBs before desoldering *(included defective IC, CPU and capacitors) (1.5Kg per pc)*	***US$ 0.15 per kg***
	PCBs after desoldering *(Rate: US$ 0.12 per kg)*	-
Glass Parts: CRT glass (~3Kg) *(Rate: US$ 0.01 per kg)*		-

6. R&D INITIATIVES

Research is carried out to develop eco-friendly products so that e-waste could be made less or zero hazardous. Improved design, miniaturizing of size, replacing or reducing the hazardous chemical from electronic products are carried out worldwide to address the issue. Recycling of e-waste by primitive means is most dangerous practices and appropriate technology needs to be established. Department of Information Technology (DIT), Government of India is promoting several such initiatives in this direction. A project has developed a process technology for recycling and reuse of electronic waste with a metal recovery of 90%. Another project is carried out to recovery metals from PCB, where PCB is depopulated and segregated component wise before treating the circuit board. Green electronics are also encouraged in a various projects. Lead free x-ray absorbing coating materials are developed with phospho-silicate glass composite/ phosphate composite to use as x-ray absorbent in the apron used for medical purpose. European Commission has restricted the import of electronic goods, manufactured using hazardous substances (RoHS) such as lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyles, polybromonated diphenyl ethers exceeding certain level. DIT has, thus, created a testing and certification facility for the hazardous raw materials used for manufacturing electronic components to facilitate Indian exporters to European countries.

7. CONCLUSION

E-waste cannot be managed just by enacting stringent laws and their strict implementation in India. The bulk of the e-waste in India is recycled in the units in unorganized sector by primitive methods. It however generates significant employment for poor families. The existing laws on labour, environment protection and industry have adequate provisions to monitor their operations. However, since the issue is linked to socio-economic problem and also the availability of unemployed youths is abundance, it is becoming difficult to stop these activities only by imposing laws. It is imperative to give them proper education and awareness and most importantly to provide them alternative cost effective technology. A holistic approach is needed to address the challenges faced by India in e-waste management. A suitable mechanism needs to be evolved to include small units in unorganized sector and large units in organized into a single value chain. One approach could be for units in unorganized sector to concentrate on collection, dismantling, segregation, whereas, the metal extraction, recycling and disposal could be done by organized sector. This would create a win-win situation for the recyclers.

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PROSPECTIVE SCENARIO OF E-WASTE RECYCLING IN INDIA

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Keywords: E-waste, Scenario of e-waste, Recycling technology

Abstract

However, India is rich in ores and mineral, but E-waste recycling is necessary due to the report of national and international studies, which cautioned on the generation, treatment and accumulation of e-waste in India. Current data indicate that the total domestic e-waste generation including imports is around 382979 MT, however waste available for recycling and actually recycled are 144143 MT and 19000 MT, respectively. In which recycling by non-formal and formal sector are 95% and 5%, respectively. On the other hand, India has developed expertise in handling verities of metallic wastes in an organized and safe manner. The development of individual process or combined processes for handling the e-waste is underway. Eco- friendly and energy-saving processes are necessary to comply with stringent environmental regulations. The paper includes the recent trend of e-waste generation, recycling process and its future prospects particularly in India.

Introduction

With the development of technology, the lifespan of electrical and electronic equipments (EEE) is decreasing. The life span of computers has decreased from 4.5 to 2 years in the period 1992 to 2005, thus generating large amount of e-waste to the extent of 20-50 million tones/ year in the world [1]. In India alone, 330 thousand tones of e-waste generated in 2007, which is expected to rise 470 thousand tonnes by 2011 [2]. The e-wastes contain valuable, precious and hazardous elements viz. iron, copper, gold, silver, cadmium, mercury etc. In order to meet the environmental norms for hazardous waste disposal and conservation of natural resources around the world, there is a growing concern for the safe recycling of e-waste. Recycling of e-wastes is carried out by the formal and non-formal sectors for the recovery of valuables and disposing of wastes. In India, participation for recycling of e-wastes by non-formal sector is about 95% and that of formal sector is 5%. The greater share of unscientific handling of e-waste recycling by non-formal sector causes serious threat to the environment due the emission of dioxine, furan and other harmful gases along with element viz. lead, cadmium, mercury etc. The availability of huge amount of e-wastes and environmental concern attributed development in handling and recycling technology in India and other countries. Some operating or proposed industries for the recycling of e-waste in India are the following companies: Attero Recycling, Delhi, (www.attero.in), Trishyiraya Recycling India Private Limited, (www.ewaste.in), Ecoreco, (www.ecoreco.com), and E-Parisara, (www.ewasteindia.com) These industries are operating e-waste centers in different parts of India viz. Delhi, Meerut, Ferozabad, Chennai, Bangalore and Mumbai. Various R&D work have been proposed for the development of e-waste recycling processes. In this regard few review papers are also appearing in national and international seminars [3]. Various government organization and research centers are trying to achieve an integrated process for the recovery and separation of metals from the e-wastes including pretreatment process like cutting, shredding, grinding, air classification followed by leaching and solvent extraction process. The processes have also been proposed for the recovery of precious metals such as gold. Researchers and industrialists are integrating together to parleys small scale e-waste recycling industries into large scale industries.

Scenario of E-waste in India

Due to lack of proper technology for the recycling of waste electrical and electronic equipments (WEEE), all around the world, the amount of generation of WEEE is increasing rapidly and comprises about 5% of all the solid waste [4]. In India also demand and supply of EEE increases at a tremendous rate. Fig. 1 shows that there is rapid increase in the number of sales of desktop in the period of 1994 to 2007 and the value reaches up-to 5.52 million [5]. Fig. 2 shows that mobile subscriber in India increases from 90 million to 433 million during the period 2006-11 and expected to touch 900 million in 2015-16 [6].

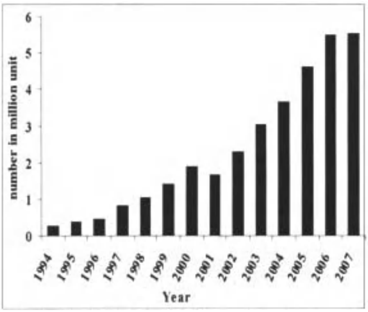

Figure 1. Domestic sales data of electronic devices in India (in million units)

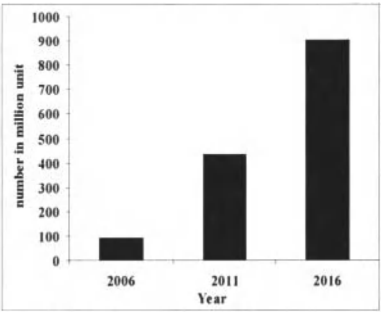

Figure 2. Number of mobile phone subscriber in India (in million units)

Based on the logistic model, it is revealed that around 41-152 million units of computers will become obsolete by the end of 2020 [5]. However, total of 2.5 million tonnes of WEEE comprising of PC, television, washing machine and refrigerators are expected to generate during the period of 2007-11 [7]. These statistics will help the recyclers in building strategy for the recycling of e-wastes.

Composition of e-wastes

The composition of e-wastes widely varies depending on the type of the products and their models as depicted in Table. 1, which shows the presence of metals such as Fe, Cu, Al, Pb, Ni and precious metals like Ag, Au etc. [8]. Older model of the e-scrap found to contain higher value of precious metals. There is wide variation in weight composition of e-scraps and the average content is 40% metals, 30% plastic and 30% refractory as shown in Fig. 3. Among the metals copper, iron, tin, lead, aluminum and nickel are found in significant amount while others metals like gold silver etc. are found in traces [9].

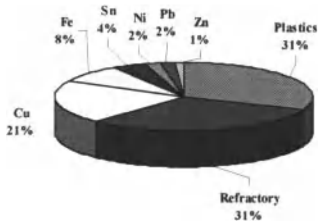

Figure 3. Composition of e-wastes

Table 1. Composition of metals for different e-scrap samples

Electronic waste	Weight (%)					Weight (ppm)		
	Fe	Cu	Al	Pb	Ni	Ag	Au	Pd
TV board scrap	28	10	10	1	0.3	280	20	10
PC board scrap	7	20	5	1.5	1	1000	250	110
Mobile phone scrap	5	13	1	0.3	0.1	1380	350	210
Portable audio scrap	23	21	1	0.14	0.03	150	10	44
DVD player scrap	62	5	2	0.1	0.05	115	15	4
Calculator scrap	4	3	5	0.1	0.5	260	50	5
PC main board scrap	4.5	14.3	2.8	2.2	1.1	639	566	124
Printed circuit boards scrap	12	10	7	1.2	0.85	280	110	NR
TV scrap (CRTs removed)	NR	3.4	1.2	0.2	0.038	20	<10	<10
Electronic scrap	8.3	8.5	0.71	3.15	2.0	29	12	NR
PC scrap	20	7	14	6	0.85	189	16	3
Typical electronic scrap	8	20	2	2	2	2000	1000	50
E-scrap sample 1	37.4	18.2	19	1.6	NR	6	12	NR
E-scrap sample 2	27.3	16.4	11.0	1.4	NR	210	150	20
Printed circuit boards	5.3	26.8	1.9	NR	0.47	3300	80	NR
e-scrap (1972 sample)	26.2	18.6	NR	NR	NR	1800	220	30
E-waste mixture	36	4.1	4.9	0.29	1.0	NR	NR	NR

NR means not reported.

Collection and Recycling of e-wastes in India

Collection of e-wastes

In India, the collection and recycling of e-wastes is largely linked among the manufacturers, distributors, consumers, collectors, traders and recyclers as shown in Fig. 4 [10].

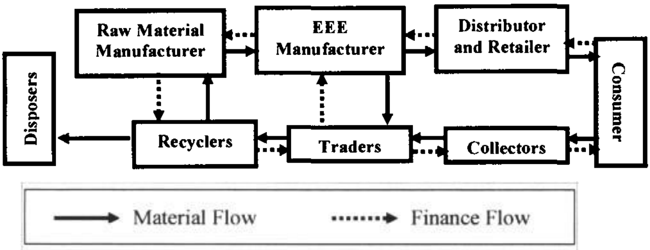

Figure 4. Flow of e-wastes collection for recycling in India

The unorganized sectors are largely involved in the collecting, trading and recycling works. Unlike developed countries, waste pickers pay price to consumers for their discarded products and there is no concept of Advance Recycling Fee (ARF) which are paid by the consumers to the retailers, retailers to manufacturers and manufacturers to the recyclers.

Recycling of e-wastes

The recycling of e-wastes in India is mainly practiced in unorganized sectors while some industries are also recycling these materials in their plants. In order to develop suitable recycling methods, R & D institutions are also developing processes to recover the valuables to conserve the resources without affecting the environment. The collaborative research in association with foreign research institutions is also being made. These details are discussed below.

a. Industrial approach of Recycling: As mentioned above, the main constituents of e-wastes are plastic, glass and metals. The recovery of metallic constituents is tedious due to presence of various valuable, precious and hazardous metals.

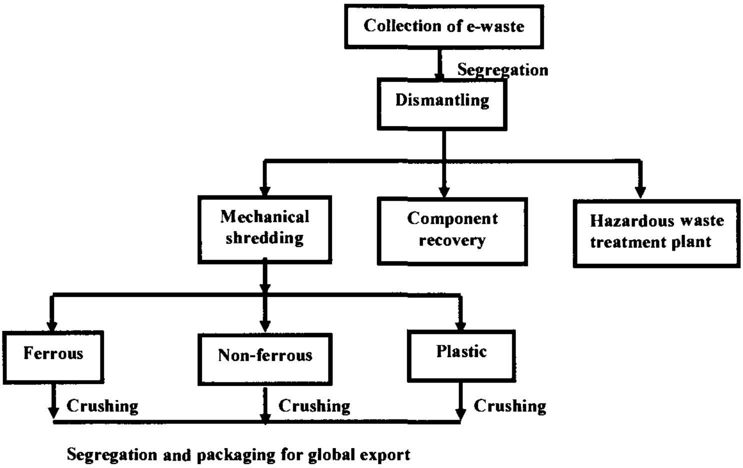

Figure 5. Schematic flow diagram for the recycling of e-wastes in Indian industry

Some of the industries like Attero, TPL, Ecoreco etc. are involved in the recycling and management of the e-wastes. Fig. 5. depicts typical flow process for recycling of e-scraps in Indian recycling plant. For the better recovery of elements, initially collected e-wastes are segregated according to their parent products followed by dismantling. Components like solder, battery, cables etc. obtained from the dismantling of e-wastes. These components are recycled for the recovery of elements like tin, lead, nickel, lithium etc. The hazardous substances that cannot be recycled are exported to hazardous waste treatment plant. Rest of the part of e-waste viz. plastic, PCBs etc obtained after component recovery undergoes for the mechanical shredding followed by the separation of ferrous, non-ferrous and plastic material. After crushing and segregation of obtained class, these are packed for the global export. Apart from the recycling of valuable and hazardous elements, the segregated constituents are also exported for the recycling of precious metals like gold and silver.

b. R&D studies for recycling of e-wastes: The studies are being made in different R&D institutions. Among them National Metallurgical Laboratory (NML), Jamshedpur is pioneer in developing processes for e-waste recycling, in India. The studies are basically concentrated on physical processing for the segregation and concentration of materials followed by their recovery by hydro/pyro-metallurgical techniques to develop eco-friendly processes. The results of salient processes are described below.

Physical processing of e-wastes: E-wastes are heterogeneous in nature and present in different physical shapes and composition. Different authors made different attempts to classify the e-waste into metallic and non-metallic form by physical processing methods. At NML, physical separation technique has been employed for the beneficiation of metals and other useable components from e-wastes as presented in Fig. 6 [9]. E-wastes after dismantling, segregation and shredding are pulverized to a size fraction of 1 to 0.5mm to dislodge the bounded part for downstream process.

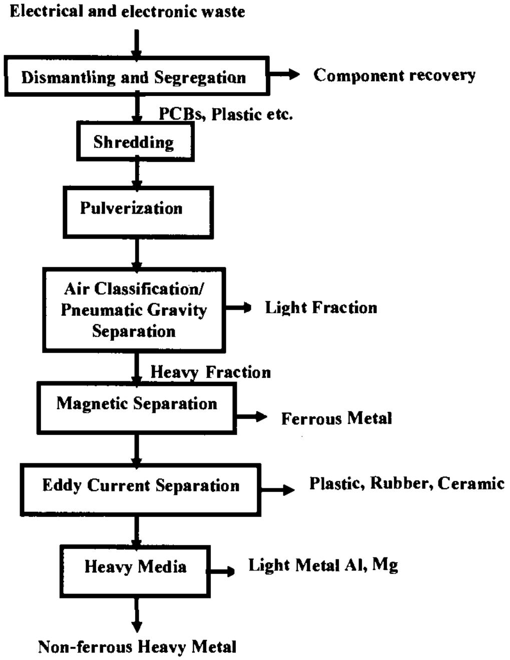

Figure 6. Schematic flow diagram of physical processing of e-wastes

Pulverized material undergoes for other physical separation techniques based on the physical properties of the material such as density, magnetic susceptibility, electrical conductivity, surface property etc. The pulverized materials are then processed following air classification, magnetic separation of heavy fraction, eddy current separation and heavy media [9]. The product obtained in the process is light fraction (rubber plastics), ferrous metals, ceramics, light metals (Al, Mg) and non-ferrous metals. These separated materials could be further processed to produce valuable products depending on their constituents for certain applications.

Hydrometallurgical Treatment: The metallic fractions obtained after physical processing are further processed for the recovery of valuables following pyro/ hydro-metallurgical routes. Several authors studied leaching, solvent extraction and electro-winning processes for the recovery of valuables in form of metals [11, 12, 13, 14, 15]. The e-scraps are leached for the dissolution of metals present using basic or acidic reagents like sulfuric acid, ammonia, nitric acid etc. Obtained leached solution containing metals undergoes liquid-liquid extraction by the use of organic extractants viz. dialkyl monothiophosphinic acid (Cyanex), di-(2-ethylhexyl) phosphoric acid (D2EPHA), 2-hydroxy-5-nonylacetophenoneoxime (LIX84) etc. for the extraction and separation of metals. Fig. 7 shows the schematic diagram for the extraction and separation of metal mixtures for example A, B and C present in the leach liquor of electronic waste using different organics. Organic enriched in metallic values are stripped by using suitable reagents and lastly the purified solution is crystallized/electro-won for recovery of salt/metal.

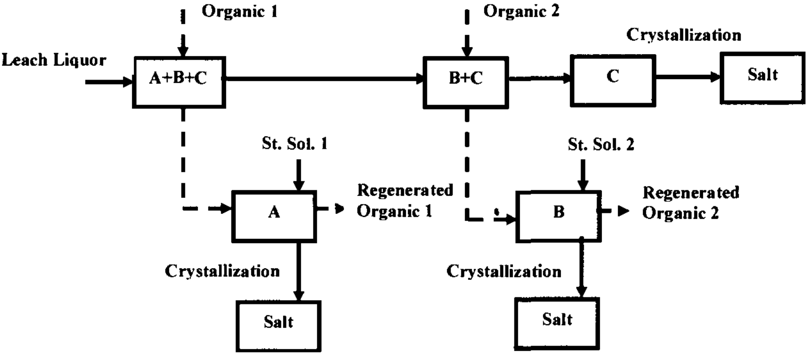

Figure 7. Schematic flow diagram for the extraction and separation of metals from the leach solution

At NML Jamshedpur work has been done for the recovery of metals like Cu, Zn, Cd and Ni from the sulfate leach solution of e-waste. Copper was selectively recovered by using LIX84 at aqueous feed pH ~2, and then Cyanex and D2EHPA were used at different feed pH for the selective extraction and separation of Zn, Cd and Ni from the Cu free leach solution. Another approach for process development to recycle metals from waste PCBs is going on under joint collaboration between NML, India and KIGAM, South Korea. Metals encapsulated between plastic layers are found poor in its effective leaching, therefore a novel pre-treatment technique i.e. organic swelling of e-waste is employed for the separation of metallic layers from the plastic layer [16] followed by selective dissolution of lead and tin in suitable reagents. The selective dissolution of lead in nitric acid followed by tin dissolution in hydrochloric acid for the recovery of metals from the organic swelled materials of printed circuit boards is carried out. Various other hydrometallurgical processes have been proposed for the recovery of precious metals like gold. Leaching of gold in cyanide medium is most beneficial route but due to hazardous effect of cyanide, thiourea might be the substitute for leaching of gold [17]. For the recovery of gold from the leached solution, cementation process may be applied using zinc and sodium borohydride from cyanide and thiourea leached solutions, respectively.

Although attempts are being made in India and abroad for the recovery and recycling of large quantity of e-wastes, there is need to develop feasible and eco-friendly technology and their enforcement for the effective recycling and management to conserve the resources. Considering the depth of problem, government is serious to implement adequate system of law, control and administrative procedure, ban on imports and export of hazardous materials, identification of components containing toxic materials collection of e-wastes from manufacturers/ consumers, incentives for their collection, awareness programs, etc.

Conclusion

E-waste is one of the fastest growing solid municipal wastes in India. Out of 20-50 million tones of e-waste being generated in the world, it is estimated that India will alone generate 4.7 hundred thousand tones by the end of 2011. E-waste collection, trading and recycling are mostly carried out by unorganized sectors. Only 5% of the total e-waste being generated is recycled by the formal sectors, while large involvement of non-formal sector may cause threat to the environment. E-wastes contain hazardous, valuable and precious metals. In general, the e-waste comprises of 30% plastics, 30% refractory, and 40% metals. Most of the Indian recycling companies are treating e-waste up-to pretreatment stages only. Considering the depth of this problem, government is serious to implement law, administrative procedure, ban on imports and export of hazardous materials, identification of components containing toxic materials collection of e-wastes from manufacturers/ consumers, incentives for their collection, awareness programs, etc. The Indian R&D work related to e-waste recycling is directed towards the development of feasible process consists of mechanical pre-treatment and pyro/ hydro-metallurgical techniques. Several researchers reported bench and pilot scale studies for recycling of e-waste using mechanical/ organic pre-treatment processes followed by leaching, solvent extraction and electro-winning. Eco- friendly and energy-saving processes are necessary to comply with stringent environmental regulations.

Acknowledgement

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METHODOLOGY FOR RECOVERY PRECIOUS METALS: GOLD, SILVER AND PLATINUM GROUP FROM ELECTRONIC WASTE

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KEYWORDS: Electronic wastes, Leaching, Electrowinning, Precious metals

ABSTRACT

Colombia produces nine tons of electronic waste per year and there are approximately 60 tons accumulation generated in the last nine years. This work aims to establish a general methodology in the laboratory to recover gold, silver and platinum group present in electronic waste, also explore other forms of recovery of metals contained in electronic waste. We selected seven types of electronic cards present in the computers, which have their parent desoldering electronic components. Initially, we characterized the components of the cards through X-ray diffraction and SEM, to identify the metal species and composition. Tests were conducted laboratory hydrometallurgical recovery of metals. This paper proposes a methodology for laboratory-scale work.

INTRODUCTION

Colombia produces nine tonnes of electronic waste per year and build there in about 60 tons generated in the last 9 years [1], Computers, TVs, audio equipment, monitors, cell phones, remote controls, printers and operated toys battery, among others are part of this inventory, which mostly comes to landfills, because the lack of legislation to control the final destination of waste electrical and electronic equipment, and lack of efficient technologies to recover materials [2]. Under these circumstances which have environmental implications, technological and economic recovery is essential metals present in the electronic cards of computers, by hydrometallurgical with subsequent base metal electrodeposition [3]. Pyrometallurgical route is discarded by major implications for economic and environmental [4]. Recovery From this perspective, the determination of the metal fraction and the relationship between the different metals, using the SEM characterization techniques - BSE and XRD is indispensable [5] It follows with electrolytic dissociation processes in the leaching and electrodeposition [6], and unit operations in the laboratory to carry out successfully these processes on a larger scale. Were randomly selected computer twenty-four postcards for nine types of cards have different functions in the computer, which, through the absorption desoldering technique, they broke the resistance (thermal, surface, photoresist, power), capacitors (ceramic, electrolytic), diodes (silicon, germanium, high frequency), transistor (NPN, PNP), processors, integrated (high, medium and low frequency), the RAM card and pin parallel port serial

CHARACTERIZATION

Materials

The materials in the current study include E-cards, copper mesh and natural rosin and solder paste.

Equipment and Procedure

Using a soldering iron absorption PACE brand SX - 90, dismantled the components of the motherboard, hard disk, network card, the switching power supply, video card, RAM card, the unit compact disk and floppy drive, as shown in Figure 1. Figure 2 shows the welding station and aspects of the dismantling of electronics. Components are grouped the 24 postcards in the categories: Integrated Surface, processors, resistors, diodes, RAM, transistors, capacitors and pin serial and parallel ports. Then the metal surface is found present in every electronic component in order to select the pairs of samples for SEM and XRD characterization. Samples for SEM are replicated for DRX. Selected samples are necessary to characterize them through the analytical techniques listed.

Figure 1. PACE soldering station 90 SX

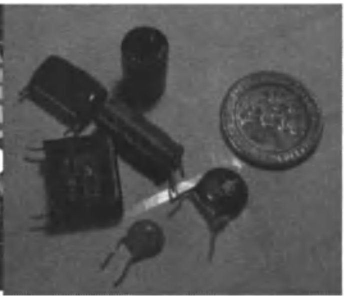


Figure 2. Ceramic and electrolytic capacitors

Analysis

Procedure SEM - BSE: This technique was used to define the chemical composition of the metal fraction and the relationships between these species, present in electronic components. SEM images were taken in a JEOL JSM 5910 equipment LV brand, with solid state detector type brand Oxford EDS micro-chemical analysis on BSE monitoring mode (electron back-projected), accelerating voltage of 20 kV and a time collection of 120 seconds. Solid samples were mounted on a slide and covered with graphite.

DRX procedure: This technique was used to determine the presence of crystalline phases on the chemical product of the insulating materials, conductors and semiconductors, which are electronic cards. Analyses were performed using an X-ray diffractometer PANalytical X 'Pert brand PRO MPD sweep of 2θ 4 to 70 ° with steps of 0.013 ° and time per step of 56 seconds and Cu radiation $\lambda = 1.540$Å, radiation generated 45kV and 40mA. The spectra were analyzed using X 'Pert software High Score Plus, using the PDF 2.0 database 2006.

Data Processing: Images are compiled, the chemical compositions and spectra thrown by SEM EDS and XRD technique.

RESULTS AND DISCUSSION

SEM images showed gold and lead in electronic component pin processor. There was a matrix is not defined by the two phases. The metal fraction by weight for Au is 0.07% (Fig. 4). SEM images also showed gold and nickel in the integrated electronic component surface and potentially platinum and nickel in the RAM card, the fractions of nickel metal by weight were 1.36 and 50.26 respectively, and the fraction of metallic gold on the surface was composed of 28.54 %. The images in these two components show well-defined phases, however in the case of intergenerational surface there is a non-homogeneous surface (Fig. 5). SEM images for the pins of parallel and serial ports introduced metal species nickel, copper, and gold. There were three phases fully identified with homogeneous surface and a ductile texture to the case of copper. It highlights the gold metal fraction by weight in 20% and 43.30% in the case of nickel (Fig 6). SEM images for electronic components germanium diode, LED and silicon diode as a whole showed metallic copper species, silver and lead. The weight fractions for copper, silver and lead were 59.70, 34.12 and 27.55 respectively. Compositional images showed definite phases, highlighting the Cu metal species on a matrix of lead (Fig 7). Electronic components photoresist resistance, heat resistance and surface resistance were observed tin metal species, copper and lead, with fractions of metal by weight of 11.72, 53.35 and 31.76 respectively. Compositional phases are homogeneous and distinct (Fig 8). Finally, SEM images showed tin and silver in the electronic component transistor (Fig 9).

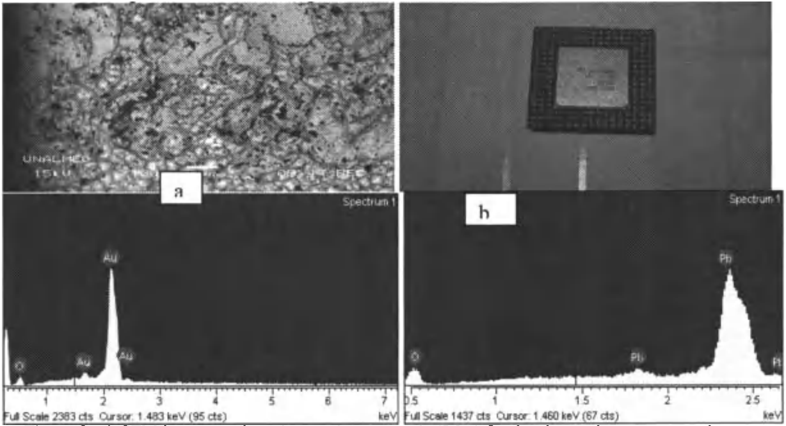
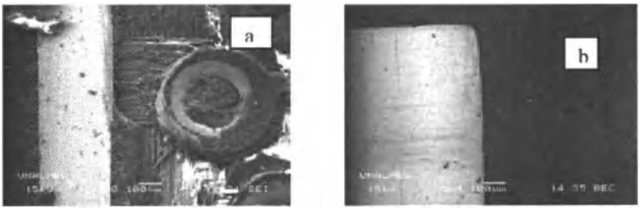


Figure 3 - 4. SEM images projected retro electron mode (BSE) for the electronic component pin processor (a), photo of a processor (b)



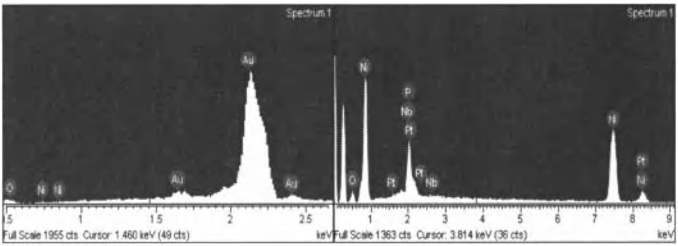


Figure 5. SEM images projected retro electron mode (BSE) for electronic components surface processor (a), RAM card (b).

The analysis of X-ray diffraction for tests show the presence of significant peaks for gold in the electronics processor pins (gold Au phase, phase gold - cadmium, Au_3Cd) (Figure 10), composed of surface (gold phase tin, $Au_{0.94}Sn_{0.06}$) (Figure 11) and RAM card (gold phase aluminum Al_2Au) (Figure 12), silver in the integrated electronic component surface (silver oxide phase, AGO) (Figure 11) for platinum in the electronic component board RAM (Pt_3O_4) (fig12) for the palladium-pin processor component (phase $Pd_{.08}Sn_{0.92}$), (fig10). The X-ray diffractometer showed different phases considered alloys, aluminum alloys, copper, nickel ($Al_{20.88}Cu_{12.14}Ni_{3.04}$) and zinc, aluminum ($ZnAl_2O_4$) in the integrated electronic component surface, nickel alloy, zinc ($NiZn_{7.33}$) electronic component in the RAM card, copper alloy, tin (Cu_3Sn) in the electronic component processor pins, and lead alloy, iron ($Al_{192.40}Fe_{46.22}$) in the electronic component pin serial and parallel ports.

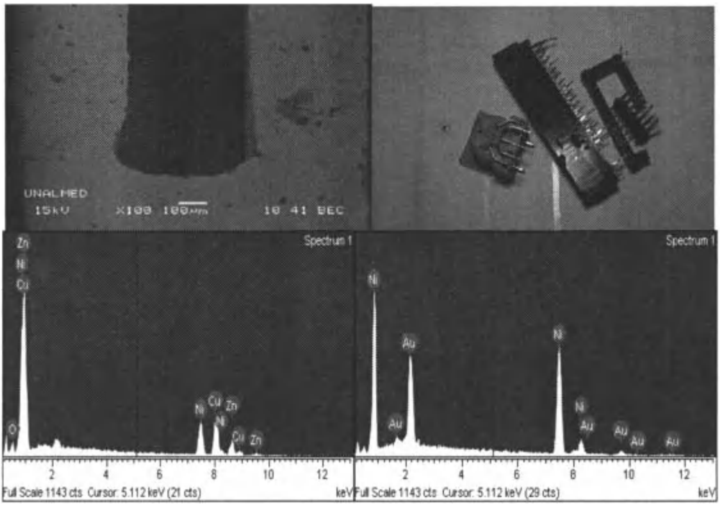


Figure 6 SEM images projected retro electron mode (BSE) for the pin Electronic components parallel and serial ports.

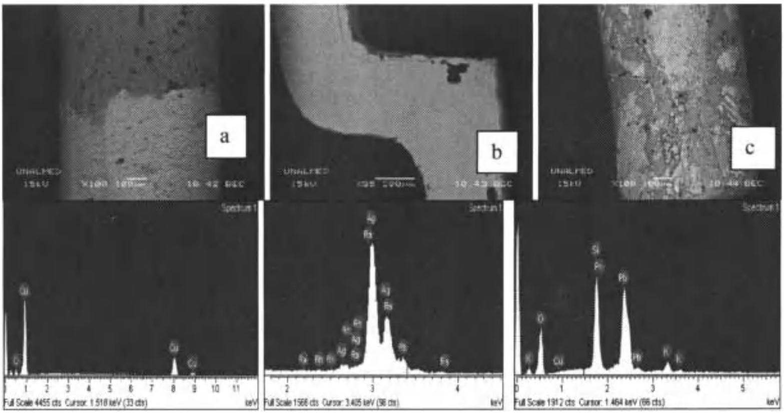


Figure 7. SEM images projected retro electron mode (BSE) for germanium diodes electronic components (a), LEDs (b) and silicon diode (c).

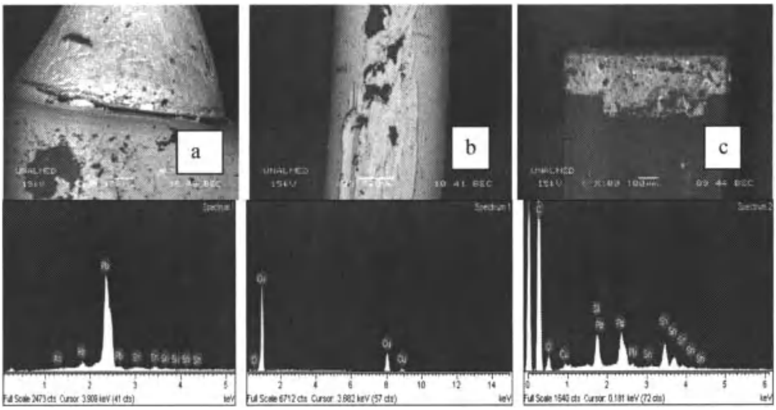


Figure 8. SEM images projected retro electron mode (BSE) for electronic components photoresist resistance (a), heat resistance (b) and surface resistance (c).

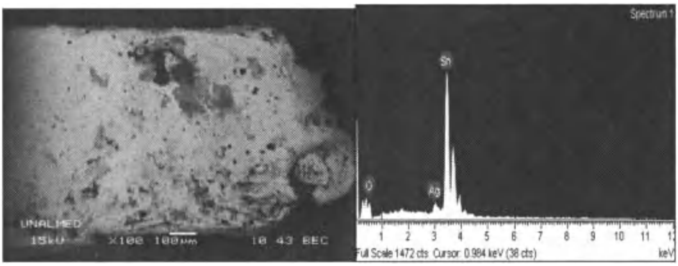


Figure 9. SEM images projected retro electron mode (BSE) for the electronic component transistor

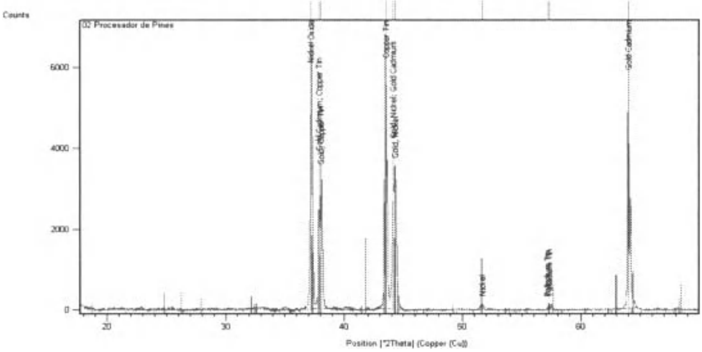


Figure 10. XRD for the electronic component pin processor. Phase Au_3Cd, $Pd_{.08}Sn_{0.92.}$ Cu_3Sn

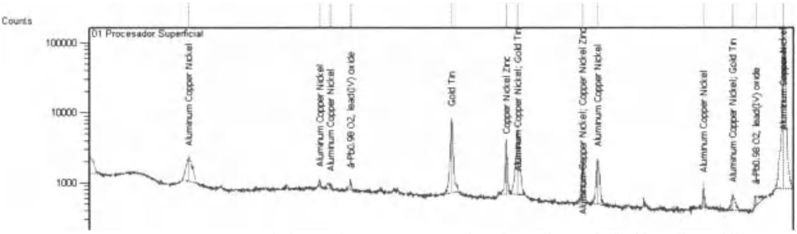


Figure 11. XRD for the integrated electronic component surface. $Au_{0.94}$ $Sn_{0\text{-}06,}$ Ag0, $Al_{20.88}Cu_{12.14}Ni_{3.04}$, ZnA_{l204}

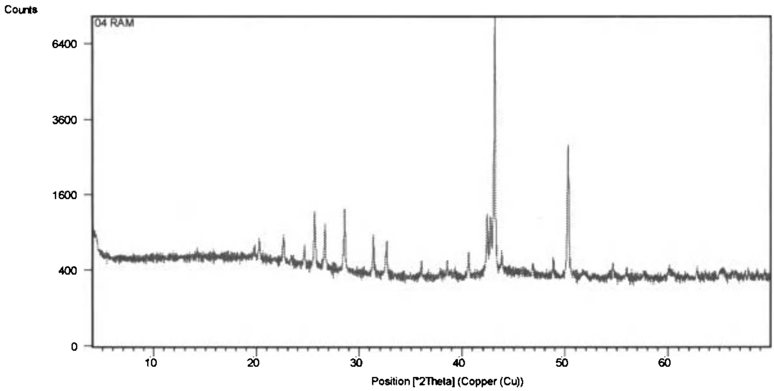


Figure 12. X-ray diffractogram (XRD) for the electronic component board RAM.
Al_2Au, Pt_30_4. $NiZn_{7.33}$

SUMMARY

Contrasting the results obtained by the two techniques of characterization, is that there can be electronic components and integrated processor pin surface coincide in the presence of gold, the two techniques have a presence of nickel in the integrated electronic component surface and the presence of platinum RAM card and the electronic component. Alloys for electronic components recorded by XRD technique were not observed in the SEM technique, but samples taken in both cases are replicas of each other, the SEM technique is timely and did not allow the electrons so retro alloys designed to clarify. It will be necessary to delve into the subject by chemical analysis by atomic absorption, in order to obtain a more detailed metal species by comparing the results of the three techniques.

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WEEE: OBSOLETE MOBILE PHONES CHARACTERIZATION AIMING AT RECYCLING

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Keywords: printed circuit board, mobile, recycling

Abstract

The development of mobile phone technology has increased the replacement of outdated equipments for more modern models, transforming disposal of such devices into a serious environmental problem. Recycling appears as an attractive alternative to minimize the environmental impact of disposing such large quantities. Recycling can be accomplished by treating the printed circuit boards of used mobile phones by using the same techniques used in ore treatments with hammer mill; magnetic separation, electrostatic separation and grain size range. Before performing the recycling process a PCB characterization was performed to identify the fraction with the higher metals concentration/content. This study demonstrated that the electrostatic separation was not the best metals concentration of PCB aiming the recycling, while the non-magnetic residue had presented a more significant metal concentration. Furthermore, after the magnetic separation was possible to separate the following metals: iron and nickel.

Introduction

Portable electronic devices have gained increasing acceptance over the last decades. Mobile phones sales in Brazil, for instance, have reached 104 million in 2007, and 128 million in 2008. It is estimated that, around the world, 100 million mobiles are thrown away every year, either because of loss of functionality or because newer models are launched in the market [1, 2, 3].

Printed circuit boards in mobile phones are made of many materials, with approximately 83% in weight being metals and fiber-glass, and the balance being plastics [3]. Several metals can be recovered from the electronics waste, such as copper, tin, iron, lead, nickel, titanium, aluminium as well as some precious metals such as gold, silver and palladium [4, 5, 6, 7, 8]. Concurrent with the increasing world demand for copper, there average metal content in ores has been decreasing. Economically interesting copper mines used to have 4% metal content, whereas presently, such content is around 1%, i.e., for every 1 ton of ore extracted, only 10 kg are copper [9, 10]. Approximately 33% of printed circuit boards (PCBs) composition is copper, that is, for every 1 ton of PCBs waste, 330 kg are copper [1]. Research in recycling PCB waste focuses on mechanical, electrometallurgy, pyrometallurgical and hydrometallurgical processes [3, 8]. Collecting and recycling obsoletes electro-electronic equipments is very important these days, in order to, not just preserve the non renewable natural resources but also to keep the environment and the population safe from the pollution caused by the toxic materials and heavy metals present in this kind of waste.

Materials and Methods

At first, printed circuit boards from obsolete mobile phone were manually separated from the other components such as batteries, liquid crystal display and the plastic body. Manual separation was followed by mechanical separation processes with hammer mill with grate around 3mm. The grinding material was submitted to magnetic separation, electrostatic separation and materials classification through grain size analysis method. The magnetic separation was separated in non magnetic and magnetic residue. Only the non magnetic residue was done the electrostatic separation. The electrostatic separation makes the separation among non conductor and conductor materials that produce the non conductor, conductor and mixed fractions. The mechanical process sequence can be seen in the Figure 1.

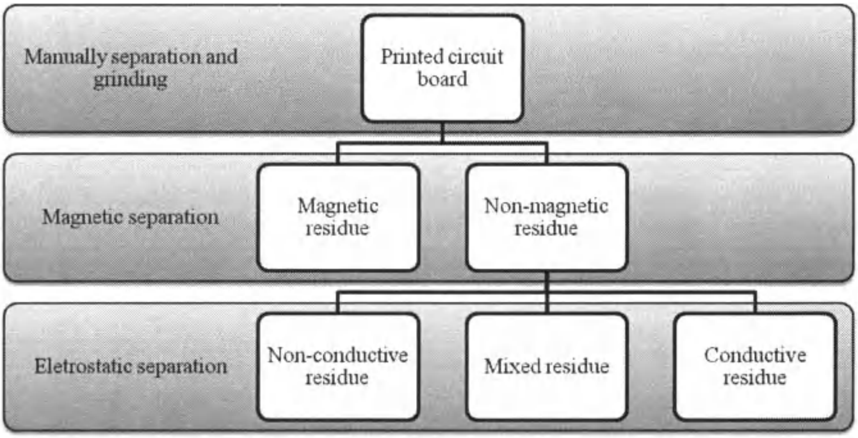

Figure 1 – The mechanical process sequence to recover metals from printed circuit boards.

Around 100g printed circuit board was separated after grinding to do the materials classification through grain size analysis method. In the following the magnetic, non magnetic, non conductor, conductor and mixed residue can be characterized by analyses like loss on ignition and aqua regia leaching. In loss on ignition analyses at 800°C with argon inert atmosphere can be characterized the fixed residue (metals and ceramics) and volatile residue (polymers). The aqua regia leaching dissolved the printed circuit board after grinding (1g of printed circuit board sample to 20ml of aqua regia solution). The time contact between the fraction samples and aqua regia was about 24 hours; followed by simple filtration with quantitative filter paper. The insoluble portion indicates polymers and ceramic materials. The portion leached represents the soluble metals and was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). The analyzed metals were: iron, copper, nickel and aluminum.
The printed circuit boards' composition was calculated using the dates obtained in aqua regia leaching and loss on ignition by equations 1 e 2:

$$\text{Aqua regia leaching} = (\text{Metals}) + (\text{Polymers} + \text{Ceramics}) \quad (1)$$
$$\text{Loss on ignition} = (\text{Polymers}) + (\text{Metals} + \text{Ceramics}) \quad (2)$$

With these dates were possible determine the metals, polymers and ceramics percentual in the printed circuit board in each materials (magnetic, non-magnetic, conductive, mixed and non-conductive residue).

Results and discussion

The mechanical process was based in results from equations 1 and 2 to calculate the perceptual by each magnetic and electrostatic separation fraction (figure 2). In figure 2 was possible to see that only 50 wt. % from printed circuit board correspond to conductive residue, this is the concentrate which has more perceptual to copper, but only the aqua regia leaching with ICP-OES results will confirm this perceptual. The grain size analysis can be seen in figure 3.

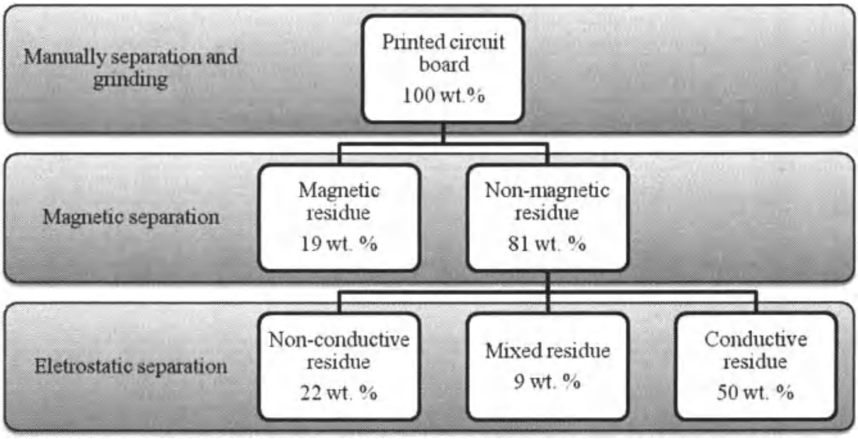

Figure 2 – Perceptual by each magnetic and electrostatic separation fraction.

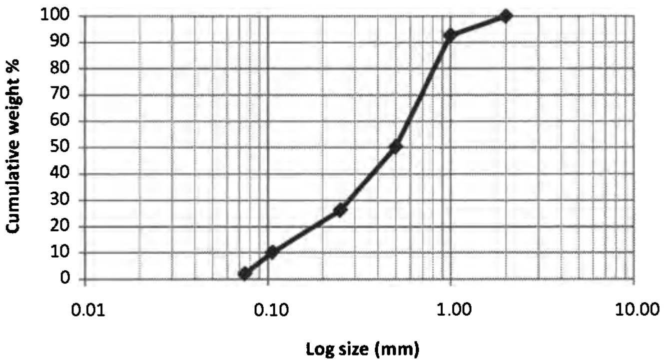

Figure 3 – Grain size analysis

The figure 3 shows the printed circuit board liberation after grinding. This liberation was efficient in this process because it is possible to note the equal distribution in each grade used. With the loss on ignition and aqua regia leaching results was possible calculating the perceptual from metals (ME), ceramics (CE) and polymers (PO) in printed circuit boards from mobile phone equipment after grinding in hammer mill (MM), like is possible to see in the figure 4.

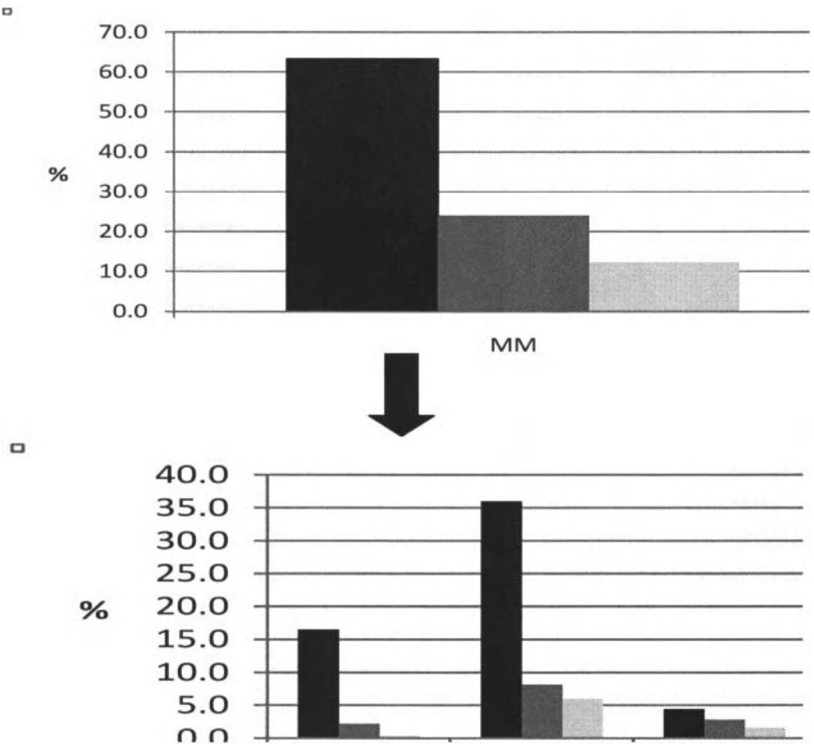

Figure 4 – Perceptual from metals, ceramics and polymers

With dates of figure 4 is possible to observe that around 63 wt. % of printed circuit board from mobile phone equipment was composed by metals. When it was available in each fraction after mechanical process was possible to observe that thesse metals were concentrating in magnetic (MMMA) and conductive (MMCD) fraction. But only the characterization using ICP-OES with the leached from aqua regia leaching is possible to determine which metals were concentrated in each fraction, like the results represented in figure 5.

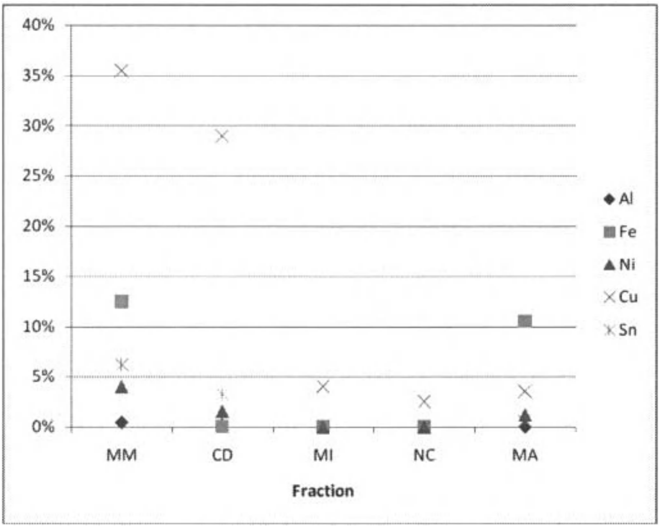

Figure 5 – Perceptual from metals in each fraction after mechanical process

In figure 5 it is possible to observe that copper is the element with the highest concentration in all fraction, but only in magnetic fraction the iron appears around 10 wt. % while copper appears around 4 wt. %. The conductive fraction has about 30 wt. % copper while the other metals were less than 5 wt. %. The summation mixed and non-conductive fraction the copper was around 6 wt. %, this is around 15 wt. % of copper in printed circuit board from mobile phone equipment. Considering that the copper perceptual in the mixed, conductive and non-conductive fractions were around 33 wt. %, which corresponds to around 93% of copper in printed circuit board from mobile phone, it was possible to conclude that the electrostatic separation process is not necessary for the copper recovery. But the magnetic fraction had around 85 wt. % of iron in printed circuit board from mobile phone, which showed that the magnetic separation is a necessary mechanical process to recover iron.

Conclusion

- The printed circuit boards from mobile phones obsoletes after grinding and magnetic separation had around 19 wt. % of magnetic residue and 81 wt. % of non-magnetic residue.
- After the electrostatic separation the non-magnetic residue was divided into 50 wt. % of conductive fraction; 9 wt. % of mixed fraction and 22 wt. % of non conductive fraction.
- The magnetic fraction had around 15 wt. % of metals, being that almost 10 wt. % was iron. The conductive fraction has around 30 wt. % of copper and less than 14 wt. % of ceramics and polymers.
- The non-conductive and mixed fraction had around 6 wt. % of copper, which means that 20 wt. % of copper was lose if this fractions were not used in the copper recover. These indicate that the electrostatic separation had not benefits in copper recover process. But the

magnetic separation was necessary to recover iron from printed circuit boards from mobile phones.

The final conclusion was that the grinding and magnetic separation was essential steps from mechanical process to recover metals, while the electrostatic separation was not necessary.

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Poster:
Recycling of Electronic Wastes

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A NOVEL PROCESS FOR FOAM GLASS PREPARATION FROM WASTE CRT PANEL GLASS

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Keywords: Sintering; Pressing; Glass; Glass ceramics; Relative density

Abstract

A novel approach for foam glass preparation, namely vacuum-aided powder sintering technique, was preliminarily investigated in the present communication. The key point of which was to prepare foam glass at a negative pressure. Compared to normal powder sintering process, the new approach could benefit the foaming process by shorting the holding time, reducing the amount of foaming agent and especially decreasing relative density of the product. Optimum conditions were 750 °C, 1000 Pa, 5 min and 1 wt.% foaming agent, respectively.

Introduction

Foam glass represents a highly valuable solution for thermal and acoustic insulation, since it possesses a generally higher mechanical, chemical and thermal stability than other foams[1]. The first industrial processing for foam glass production, the direct introduction of gases ("blowing") into the special molten glass, can be dated back to the end of 1930s[2]. At present, almost all foam glasses is prepared by powder sintering technique instead of blowing,[3] since it reduces the temperature by several hundred degrees. Moreover, as fine glass powders or similar powders can be used to substitute corresponding glasses by this technique, considerable attention has been focused on the production of foam glass by considering fully recycled glasses, coal fly ash, or other solid wastes as raw materials,[4] especially CRT glasses[3, 5], on the point of environmental protection.

In a previous report[6], when discussing the lead removal and recovery from CRT funnel glass by a pyrovacuum process, we found that foam glass could be prepared at a negative pressure. Therefore, in this communication, the similarities and differences between the powder sintering process for foam glass at normal and negative pressure was preliminarily discussed.

Materials and Methods

Panel glass, provided by Huaxing Environmental Protection Corporation, was crushed and dry ball milled to be smaller than 80 mesh. Then the obtained glass powders were dried at 105 °C for 24 h. Chemical composition of these powders was examined by X-ray fluorescence (XRF) and the results were presented in Table 1. $CaCO_3$ (99% purity, particle size <200 mesh) were added to the glass powders, and homogenized in the same ball mill. Then the homogenized mixtures were uniaxially pressed in a steel die of rectangular section (8 mm × 40 mm) at room temperature by a hydraulic press operating at 5 MPa, without any binder. At last, the obtained tiles were subjected to the vacuum-aided sintering treatment[6]. The investigated temperature increasing rate was in the range of 5~20 °C/min and foaming temperature was varied from 650

°C to 900 °C with an increment of 50 °C. The examined ambient pressures were 10, 100, 1000, 10,000 and 101,325 Pa, holding times were 5, 10, 20, 30 and 60 min, and $CaCO_3$ adding amounts were 1, 2, 3, 4 and 5 wt.%, respectively.

Table 1 Chemical composition of the panel glass determined by X-ray fluorescence (XRF)

Oxide	SiO_2	PbO	K_2O	Na_2O	Al_2O_3	SrO
wt.%	59.42	1.16	7.88	5.72	1.92	10.4
Oxide	CaO	BaO	MgO	ZrO_2	Fe_2O_3	P_2O_5
wt.%	0.32	9.67	0.01	2.32	0.01	0.01

The apparent density of the prepared foam glasses was figured out either by measuring the weight and dimensions of the produced materials or by Archimedes' method. The true density of the produced foam glasses was evaluated by means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA). At least five fragments were analyzed for each sample.

Results and Discussion

An optimum foaming temperature was preferred by considering the maximum foam stability and the internal cell structure. If the selected foaming temperature is too high, the glass viscosity is too low to maintain a uniform porous structure because small bubbles will disperse to big bubbles or release to the ambient atmosphere. According to preliminary experiments, products obtained at 850 and 900 °C were badly deformed and bubble distribution of these products was extremely heterogeneous. It was even impossible to give an approximate value of relative densities of these two products, therefore, it was impossible to present the relative densities of the products obtained at 850 and 900 °C in Fig. 1. On the contrary, if the temperature is too low, the glass viscosity is too high, bubble expansion is too difficult and little increase in volume occurs. Thus, it can be found from Fig. 1 that the increase in foaming temperature resulted in a significant decrease in the relative density. 750 °C was sufficient enough for the foaming process.

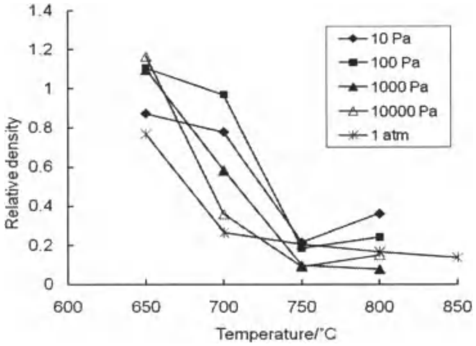

Fig. 1. Effect of foaming temperature on the relative density of foam glass, other conditions: ambient pressure = 1000 Pa, $CaCO_3$ adding amount = 3 wt.% and holding time = 30 min.

It was interested to find in Fig. 2, with increasing the ambient pressure, relative density first decreased and then increased. This suggested that suitable negative ambient pressure, compared to the atmospheric pressure, could benefit the foaming process, i.e., relative densities decreased from 0.16 to 0.09 when the ambient pressure decreased from 1 atm to 10000 Pa. This can be attributed to the bubble expansion. The bubbles will grow if the gas pressure inside the bubble exceeds the pressure value applied by external forces on the bubble, according to the following equation:

$$p_g = p_a + \frac{2\gamma}{r} \tag{1}$$

where p_g is the pressure inside the bubble, p_a is the ambient pressure, γ is the surface tension of the bubble and r is the radii of curvature of the bubble. According to Eq. 1, with the decrease of p_a, the force that blocked the growth of gas bubbles decreased, leading to the bubble expansion and increasing the gas part of the whole foam glass. Therefore, the relative density decreased with the decrease of ambient pressure. However, excessive decreasing the ambient pressure led to an inverse effect, as shown in Fig. 2, which can be attributed to the bubble diffusion. Further decreasing the ambient pressure, when p_g was higher than p_a, it may be much easier for the bubbles insider the glass to disperse to the ambient environment. Therefore, the gas volume could decrease with excessive decreasing the ambient pressure, causing an increase in the relative density.

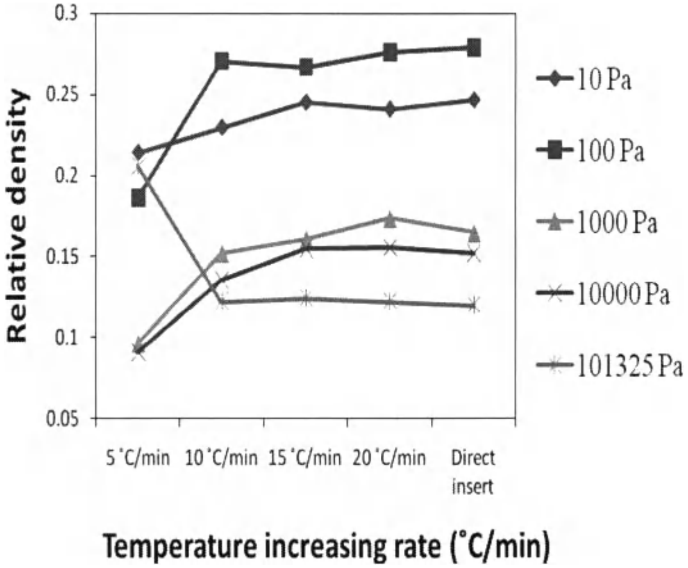

Fig. 2. Effect of ambient pressure on the relative density of foam glass, other conditions: foaming temperature = 750 °C, holding time = 30 min and $CaCO_3$ adding amount = 3 wt.%.

As the holding time extension, the relative densities showed a small variation around 0.1, suggesting that, at 1000 Pa, the effect of holding time on relative density was not obvious (Fig. 3). This was inconsistent with the common foaming process, since the increase of holding time generally caused a decrease in the relative density[7]. On the other hand, it also showed that, with the help of vacuum, foam glass with a lower relative density (about 0.1) could be prepared for a much shorter holding time, 5 min versus 15-30 min when compared to the normal powder sintering technique[2].

In Fig. 4, a slight increase in relative density was found along with the increase of $CaCO_3$ adding amount. During the gradual softening of the sintered glass under continuous heating, the $CaCO_3$ particles decompose to CaO with simultaneous release of gaseous CO_2. The decomposed CaO was incorporated into the glass, and the viscosity of which may increase with the increase of $CaCO_3$ adding amount, thus limiting its volume expansion[11]. It seems that 1 wt.% $CaCO_3$ was sufficient enough for the foaming process, a much lower amount of foaming agent than the normal powder sintering technique (3-7 wt.%)[7].

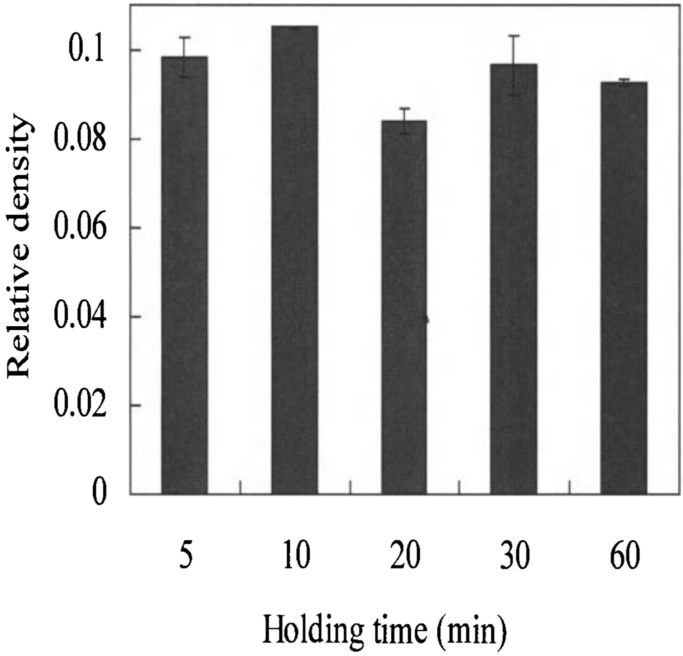

Fig. 3. Effect of holding time on the relative density of foam glass, other conditions: foaming temperature = 750 °C, ambient pressure = 1000 Pa and $CaCO_3$ adding amount = 3 wt.%.

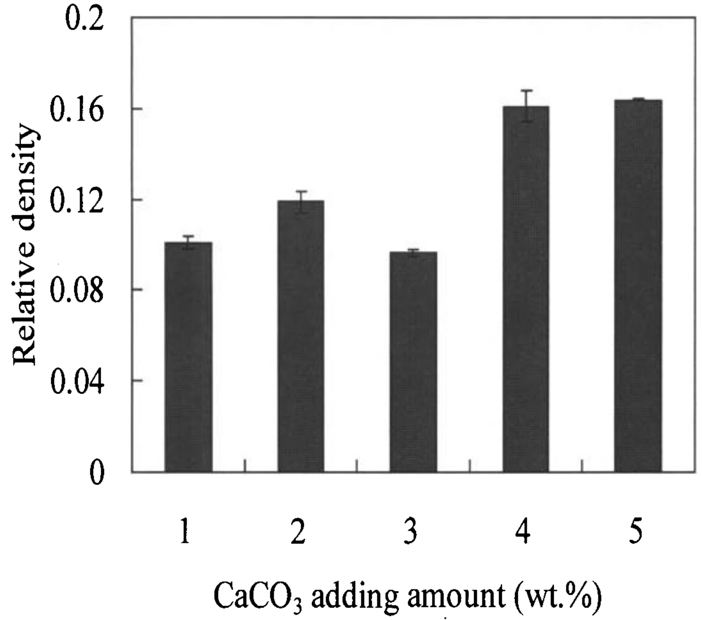

Fig. 4. Effect of $CaCO_3$ adding amount on the relative density of foam glass, other conditions: foaming temperature = 750 °C, ambient pressure = 1000 Pa and holding time = 5 min.

Conclusions

In this research, foam glass with a lower relative density, around 0.1, was successfully prepared by vacuum-aided powder sintering technique. Experiment results indicated that, when the ambient pressure was 1000 Pa, relative density significantly decreased with the increase of foaming temperature. With the aid of vacuum, the holding time was shorted from 15-30 min to 5 min and the amount of foaming agent was reduced from 3-7 wt.% to 1 wt.%. Especially, the relative density was decreased efficiently with a suitable negative environmental pressure. The optimum foaming temperature, ambient pressure, holding time and $CaCO_3$ adding amount were 750 °C, 1000 Pa, 5 min and 1 wt.%, respectively.

Acknowledgements

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ENVIRONMENTAL LEACHING CHARACTERISTICS AND BIOAVAILABILITIES OF WASTE CATHODE RAY TUBE GLASS

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Keywords: E-waste; CRT glasses; Hazardous element; Sequential extraction; Leaching toxicity

Abstract

In China, hazardous e-waste—cathode ray tube (CRT) glass is usually left around, and it is likely to contact with water resources directly. To identify the real leaching characteristics and bioavailabilities of heavy metals Pb and Ba contained in CRT glass in the nature environment, experiments were carried out by simulating the nature environment. The results indicated that Pb and Ba contained in CRT glass were stable in most conditions, which only showed obvious leaching toxicities in strong acidic/alkali conditions. EDTA and DTPA extractable Pb and Ba amounts were extremely high, e.g., EDTA extractable Pb of color funnel glass was up to 1960.07 μg/kg, indicating that the potential bioavailability of waste CRT glass is very high.

Introduction

In recent years, cathode ray tube (CRT) contained monitors or TV sets has been substituted by novel and better electronic and electric equipments such as LCD and PDP, leaving huge amounts of end-of-life CRTs. 50~85% of the total weight of a computer monitor or a TV set is glass[1,2], which was classified to three categories: black & white glass (BW), color panel glass (CP) and color funnel glass (CF), according to their chemical compositions[3] (Méar *et al.*, 2006). In order to provide shielding from X-rays generated during the picture projection process, lead, barium and strontium oxides were used in the glass. In general, a color CRT contains 1.6-3.2 kg of lead[4]. Concerning the high toxicity of lead, these waste glasses have posed a potential risk to the environment and human health and researches on these glasses have been attracting wide and tense attention currently.

At present, environmental impact assessment of waste CRT glass mainly focused on its lead leachability by toxic characterization leaching procedure (TCLP)[5]. Jang *et al.*[4] also reported the lead leachability by California's waste extraction test and the synthetic precipitation leaching procedure with landfill leachates. It is well known that glass vitrification is one of the final disposal methods for hazardous waste immobilization, especially for nuclear waste. Hence, these waste CRT glasses were thought to be very stable and hazardous elements, such as Pb, should be encapsulated and hardly to leach out. However, the two studies reported that these CRT glasses showed an extremely high lead leaching toxicity and reasons were not well presented. In addition, these CRT glasses also contain other hazardous elements, such as barium, which is also one of the eight heavy elements on the regulatory list by both US EPA and the Ministry of Environmental Protection (MEP) of China, and only limited information is available for these hazardous elements. Besides, In China, the e-waste recycle is badly disorganized presently and few of the discarded matters have been properly treated[6,7]. In the case of directly discharge, heavy metals contained in CRT glasses can dissolve and cause water pollution. Therefore, it is necessary to investigate the leachabilities and bioavailabilities in the nature environment.

The present study aimed to give basic information about the leaching properties and bioavailabilities of Pb and Ba containing in CRT glasses in the nature environment, and to provide possible explanations for the high leaching toxicity.

Materials and methods

Materials

As concluded by Méar *et al.*[3], the chemical compositions of different bands of BW, CP and CF are similar, though they were produced by different producers at a different time. Therefore, in this study, three typical BW, CP and CF were collected from Huaxing Environmental Protection Corporation. The CRT glasses were crushed, dry ball milled and sieved to be smaller than 80 meshes. The powder obtained was dried at 105 °C for 24 h. Pb and Ba concentrations in the samples were analyzed by an inductively coupled plasma-optical emission specrometry (ICP-OES, Perkin-Elmer) after digested with HNO_3, $HClO_4$ and HF[8] and the results were given in Table 1.

Table 1 Pb and Ba concentrations in black & white, color panel and funnel glass

	Pb (wt.%)	Ba (wt.%)		Pb (wt.%)	Ba (wt.%)		Pb (wt.%)	Ba (wt.%)
BW	4.03	8.66	CP	1.08	8.66	CF	22.44	1.75

Leaching properties of Pb and Ba in the CRT glasses

In the case of directly discharge, CRT glasses may directly contact with water having different liquid to solid (L/S) ratio and pH in a certain time before properly disposal. In order to check this situation, a series experiments were carried out in the batch reactors containing various amounts of CRT glass in 50 ml solutions for 30 min to 48 h. The batch reactors were shaken at 180 rpm at 25 °C. De-ionized water was used as extraction solution. When pH effect was investigated, a series acidic (HNO_3, pH ranging from 1-6) or alkali (NaOH, pH ranging from 8-13) solutions were adopted. After leaching, the leachates were separated from solid residues by centrifugation for 5 min. The supernatants were then removed and stored in a polyethylene tube at 4 °C for analysis.

Bioavailability of Pb and Ba

Diethylenetriamine pentaacetic acid (DTPA) extract test was suggested by Lindsay and Norvell[9]. According to the method, 10 g sample was mixed with 20 ml 0.005 mol/L DTPA and 0.01 mol/L $CaCl_2$. pH of the suspension was adjusted to 7.3 in a 50 ml plastic centrifuge tube, and shaken for 2 h. Ethylene diamine tetraacetic acid (EDTA) extract test was conducted by Wear and Evans[10] method: 2.0 g ash sample was mixed with 20 ml 0.05 mol/L EDTA and its pH was adjusted with ammonia solution to 7.0 in a 50ml plastic centrifuge tube, and the suspension was shaken for 1 h. For all extraction procedures, after shaking, the suspensions were centrifuged at 3000 rpm for 20 min and the supernatant was filtered through a 0.45 μm cellulose acetate membrane filter prior to determination.

All the experiments were repeated for three times and mean values were given in the tables or figures.

Results and Discussion

CF is generally concerned because of lead and CP is concerned because of barium. According to Table 1, all the three kinds of CRT glasses contain both Pb and Ba. Though the contents of Ba in CF and Pb in CP are not in high level (17.5 and 10.8 mg/g, respectively). They are equally as those contained in fly ashes, e.g., Pb and Ba concentrations in a city waste incineration ash BCR 176 were 10.87 mg/g and 4.5 mg/g[11], respectively. Therefore, when the properties and environmental impact of CRT glasses were investigated, both Pb and Ba should be considered.

Leaching properties of Pb and Ba

Effect of L/S ratio and contact time. It can be seen from Table 2 that both Pb and Ba leaching concentrations were very low, ranging from 0.01 to 1.15 for Pb and 0.06 to 5.48 mg/L for Ba. All these concentrations were below the limits for hazardous wastes regulated by US EPA and China MEP, which is 5 mg/L for Pb and 100 mg/L for Ba.

Table 2 Effect of liquid/solid ratio on the dissolution of Pb and Ba in the CRT glasses (contact time: 120 min; temperature: 25 °C)

L/S	CP		CF		BW	
	Pb (mg/L)	Ba (mg/L)	Pb (mg/L)	Ba (mg/L)	Pb (mg/L)	Ba (mg/L)
100/1	0.01	0.82	0.20	0.04	0.01	1.59
100/2	0.02	1.50	0.12	0.05	0.02	2.47
100/3	0.11	2.62	0.17	0.12	0.02	3.16
100/4	0.01	2.11	0.47	0.25	0.05	3.48
100/5	0.02	2.29	0.06	0.32	0.07	3.98
100/6	0.02	1.49	1.15	0.24	0.09	3.82
100/7	0.03	1.93	0.54	0.36	0.76	5.60
100/8	0.05	2.14	1.12	0.48	0.30	3.82
100/9	0.05	2.48	0.31	0.35	0.05	4.01
100/10	0.10	2.28	0.06	0.25	0.11	5.48

Table 3 shows the effect of contact time on Pb and Ba leachability. It was found that Pb and Ba leaching concentrations increased as the extension of contact time, e.g., Pb and Ba leaching concentrations of CP increased from 0.15 and 2.09 mg/L to 0.7 and 6.10 mg/L when the contact time increased from 30 min to 48 h. From Table 3, it also can be found that none of these leaching concentrations exceeded the regulation limits. Therefore, the toxicities of Pb and Ba contained in the CRT glasses may be limited.

Effect of pH. Effect of pH on Pb and Ba leaching from BW, CP and CF was investigated in the pH range of 1~13, and the results were given in Table 4. As can be seen, Pb and Ba leaching concentrations first significantly decreased as the pH increasing from 1 to 2 or 3, then it almost become constant as further increasing pH to 12. At last, for pH 13, Pb leaching concentration increased again, while Ba leaching concentration didn't change.

When pH was 1, the results suggested that the leachability of Pb was much higher than Ba. For Ba, its leaching concentration of BW and CP exceeded the regulation limit 100 mg/L, while that of CF was merely 6.78 mg/L. This concentration is far below the regulation limit, which may be attributed to its lower content in CF (Table 1). For Pb, the leaching concentrations of BW, CP and CF were far higher than the regulation limit. And Pb leaching concentration of CF was even up to 303.04 mg/L, which is more than 150 times of the regulation limit, showing a great threat to the environment. When the pH was 13, only the leaching concentration of Pb of CF, which was 6.55 mg/L, exceeded the maximum allowance concentration. Consequently, Pb and Ba contained in the CRT glasses were easier to leach out in a strong acidic environment than in a strong alkali environment, and the CRT glasses should definitely not be released to a strong acidic or alkali environment.

Pb and Ba leaching concentrations didn't significantly affected by pH in the range of 3~12. And in these conditions, Pb and Ba leaching concentrations were very low, which were no more than 1 mg/L for Pb and 20 mg/L for Ba. For example, for CF, when the pH value of the extraction solution was 3, Pb leaching concentration was only 0.66 mg/L; for BW, the highest Ba leaching concentration was 16.40 mg/L when pH was between 3~12. These results implied that Pb and Ba were stable in the CRT glass in a wide range of pH.

Table 3 Effect of contact time on the dissolution of Pb and Ba in the CRT glasses (liquid/solid: 20; temperature: 25 °C)

Time	CP		CF		BW	
	Pb (mg/L)	Ba (mg/L)	Pb (mg/L)	Ba (mg/L)	Pb (mg/L)	Ba (mg/L)
30 min	0.15	2.09	0.57	0.15	0.07	0.07
1 h	0.17	2.25	0.40	0.05	0.04	1.09
2 h	0.23	2.52	0.48	0.32	0.06	2.55
4 h	0.22	2.94	0.87	0.35	0.17	2.90
8 h	0.65	3.24	0.24	0.22	0.22	3.24
16 h	0.64	3.35	2.84	0.34	0.28	3.79
24 h	0.58	4.35	1.49	0.36	0.37	4.80
48 h	0.70	6.10	2.48	0.48	1.01	10.04

Table 4 Effect of pH on the dissolution of Pb and Ba in the CRT glasses (liquid/solid: 20; temperature: 25 °C; contact time: 18 h)

pH	1	2	3	4	5	6	7	8	9	10	11	12	13
BW													
Pb (ppm)	50.27	0.17	0.29	0.56	0.39	0.46	0.32	0.80	0.45	0.44	0.37	0.58	0.78
Ba (ppm)	105.27	51.86	7.58	13.24	12.17	13.18	13.41	12.22	12.36	12.52	16.40	4.09	5.47
CP													
Pb (ppm)	62.64	0.17	0.10	0.10	0.14	0.23	0.23	0.07	0.07	0.03	0.05	0.10	1.36
Ba (ppm)	145.16	38.83	2.19	2.64	2.63	2.44	2.95	2.43	2.21	2.25	2.69	2.62	2.35
CF													
Pb (ppm)	303.04	66.69	0.66	0.40	0.43	0.63	0.28	0.27	0.19	0.22	0.19	0.32	6.65
Ba (ppm)	6.78	3.08	0.23	0.24	0.14	0.16	0.14	0.16	0.16	0.13	0.30	0.06	0.12

Bioavailability of Pb and Ba in CRT glasses

The DTPA extractant has been widely used to assess the bioavailability of many trace metals, and concentrations of DTPA-extractable trace metals have been reported to correlate well with plant uptake for a wide range of metals[12-14]. Therefore, in this study, DTPA and EDTA were used to evaluate the bioavailability of Pb and Ba, and the results were given in Table 5.

Generally, EDTA-extractable Pb and Ba were much higher than those of DTPA. This could be mainly ascribed that the extraction capacity of EDTA is larger than that of DTPA, as reported by previous studies[15]. In addition, both DTPA- and EDTA-extractable Pb and Ba were no more than 0.01% of the total contents of Pb and Ba contained in CRT glasses. This is an extremely lower fraction. However, it also could not be concluded that the bioavailability of Pb and Ba in CRT glasses is very low, because the absolute DTPA- and EDTA-extractable concentrations were very high. For example, the extractable Pb concentration by EDTA of CF was up to 1960.07 μg/kg. The lower extractable fraction value was caused by the higher Pb and Ba content contained in CRT glass. For example, Pb accounts for 22.41 wt.% of CF. Therefore, the bioavailability of Pb and Ba in CRT glasses is possible potentially high and CRT glass is a great threat to the environment, which is consistence with that of sequential extraction as mentioned before.

Table 5 DTPA- and EDTA-extractable Pb and Ba in the black & white, color panel and funnel glasses (μg/kg)

	Available fraction		Unavailable fraction	
	Pb (μg/kg)	Ba (μg/kg)	Pb (g/kg)	Ba (g/kg)
BW				
DTPA	75.60	12.47	40.29	40.29
EDTA	530.12	1287.95	40.29	40.29
CP				
DTPA	258.60	12.97	10.77	86.59
EDTA	817.93	1507.58	10.77	86.59
CF				
DTPA	829.64	1.92	224.36	17.55
EDTA	1960.07	46.95	224.36	17.55

Conclusions

(1) Leaching experiments showed that Pb and Ba contained in CRT glasses were stable in most situations, but they were easy to leach out in a strong acidic or alkali environment.

(2) Though EDTA- and DTPA-extractable species were extremely low (no more than 0.01 wt.%), the higher extractable concentration, i.e., EDTA-extractable Pb of CF was 1960.07 μg/kg, suggested a high bioavailability. Consequently, it is believed that Pb and Ba of CRT glass present a great environmental risk.

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LEACHING TOXICITY OF PB AND BA CONTAINING IN CATHODE RAY TUBE GLASSES BY SEP-TCLP

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Keywords: E-waste; CRT glasses; Sequential extraction; Leaching toxicity

Abstract

In the present study, different types of cathode ray tube (CRT) glasses were examined by sequential extraction combined with TCLP to provide possible explanations for how Pb and Ba leach out from the waste CRT glasses and to give possible reasons for why they leach out. Sequential extraction results showed that Pb and Ba in the CRT glasses dominantly presented as the residual fraction. The exchangeable fractions of Pb and Ba were extremely low, less than 0.01 % of the total content, but they were higher than those required by the regulation limits, 5 and 100 mg/L for Pb and Ba, respectively. TCLP tests of the original CRT glasses and CRT glasses residues after each step of sequential extraction demonstrated that the extremely high leaching toxicity of CRT glasses mainly caused by its exchangeable and carbonate fractions of Pb and Ba.

Introduction

In recent years, the amount of cathode ray tube (CRT) contained monitors or TV sets in the market were sharply reduced, since they were substituted by novel and better electronic and electric equipments such as LCD and PDP, leaving huge amount of end-of-life CRTs. 50~85% of the total weight of this kind of computer monitor or a TV set is glass[1,2], which was classified to three categories according to their chemical compositions: black & white glass (BW), color panel glass (CP) and color funnel glass (CF)[3]. In order to provide shielding from X-rays generated during the picture projection process, lead, barium and strontium oxides were used in the glass. In general, a color CRT contains 1.6-3.2 kg of lead[4]. Therefore, these glasses have attracted wide and tense attention due to the potential risk to the environment and human health.

At present, environmental impact assessment of waste CRT glass mainly focused on its lead leachability by toxic characterization leaching procedure (TCLP)[5] or other leaching procedure with landfill leachates[4]. And little information is available on evaluating leaching toxicities of other hazardous metals contained in waste CRT glasses such as barium, which, like lead, is also one of the eight heavy elements on the regulatory list by both US EPA and the Ministry of Environmental Protection (MEP) of China. Furthermore, explanations for how Pb and Ba leached out from waste CRT glasses and reasons for why they could leach out are still unclear.

The current study aimed to provide possible explanations for how Pb and Ba leach out from the waste CRT glasses and to give possible reasons for why they leach out by sequential extraction combined with TCLP.

Materials and Methods

Materials

As concluded by Méar *et al.*[3], the chemical compositions of BW, CP and CF are similar, though they were produced by different producers at a different time. Therefore, in this study, three typical BW, CP and CF were collected from Huaxing Environmental Protection Corporation. The CRT glasses were crushed, dry ball milled and sieved to be smaller than 80 meshes. The powder obtained was dried at 105 °C for 24 h. Pb and Ba concentrations in the samples were analyzed by an inductively coupled plasma-optical emission specrometry (ICP-OES, Perkin-Elmer) after digested with HNO_3, $HClO_4$ and HF[6] and the results were given in Table 1.

Table 1 Pb and Ba concentrations in black & white, color panel and funnel glass

	Pb (wt.%)	Ba(wt.%)		Pb (wt.%)	Ba(wt.%)		Pb (wt.%)	Ba(wt.%)
BW	4.03	8.66	CP	1.08	8.66	CF	22.44	1.75

Sequential extraction procedure

The five-step sequential extraction procedure was performed by using the method suggested by Tesseir *et al.*[7], which is described in Table 2. The metals were fractionated into five fractions: exchangeable (F1), bound to carbonate (F2), bound to Fe-Mn oxides (F3), bound to organic matters (F4) and residual fraction (F5). After each extraction, the separation was achieved by centrifuging at 3000 rpm for 20 min and the supernatant was filtered through 0.45 μm membranes. Pb and Ba in the extraction solutions were determined by ICP-OES.

Table 2 Sequential extraction procedure for heavy metals in CRT glasses

Fractions	Reagent/5 g sample	Experiment conditionss
Exchangeable	100 ml 1 M NaOAc (pH=8.2)	1 h at 25 °C
Carbonate	100 ml 1 M NaOAc (pH=5.0)	5 h at 25 °C
Fe-Mn Oxides	100 ml 0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) CH_3COOH	5 h at 96±3 °C
Organic matters	15 ml 0.02 M HNO_3 + 25 mL 30% H_2O_2 (pH=2.0)	2 h at 85±2 °C
	15 mL 30% H_2O_2 (pH=2.0)	3 h at 85±2 °C
	25 ml 3.2 M CH_3COONH_4 in 20% (v/v) HNO_3	30 min at 85±2 °C
Residual	ASTM D 6357-11a	

TCLP test

The standard method of TCLP[8] was used to examine the leachability of Pb and Ba in the CRT glasses after each extraction. To determine the appropriate extraction fluid for the TCLP test, a preliminary test was performed to measure the pH of the treated CRT glass samples (5 g sample, 96.5 ml of reagent water). If the pH was <5.0, use extraction fluid #1. If the pH was > 5.0, use extraction fluid #2.

Extraction fluid #1: Add 5.7 ml glacial acetic acid to 500 ml of reagent water with 64.3 ml of 1 N NaOH, and dilute to a volume of 1 L. The pH of this fluid will be 4.93.

Extraction fluid #2: Dilute 5.7 ml glacial acetic acid with reagent water to a volume of 1 L. The pH of this fluid will be 2.88.

About 1 g of each sample and 20 ml extraction fluid was added to a series of bottles. The bottles were shaken at 30 rpm for 18±2 h. At the end of the exaction, the leachate was filtered through a glass fiber filter of 0.45 μm pore size and preserved using 2 ml of nitric acid before being analyzed by ICP-OES.

All the experiments were repeated for three times and mean values were given in the tables or figures.

Results and discussion

Fractional distribution of Pb and Ba in CRT glasses

Figure 1 illustrated the distribution patterns of Pb and Ba in the CRT glasses. Pb and Ba distribution patterns in the three kinds of CRT glasses were quite similar. In general, for the three kinds of CRT glasses, residual fraction was predominant for Pb and Ba, accounting for 88.22-95.83%, and Fe-Mn oxide associated fraction was the second abundant fraction, in the range of 2.34-8.54%. In contrast, carbonate fraction and organic matter (0.48-2.12% and 0.04-2.36%, respectively) were relatively low, while the exchangeable fraction (0-0.84%) was the lowest. Residual fraction is considered to be stable thus difficult to leach out into the environment, while exchangeable and carbonate fractions represent the potential availability and leaching abilities of metals[9]. Though the exchangeable and carbonate fractions of Pb and Ba were very low, it cannot be deduced from this that Pb and Ba in CRT glasses are safe by landfill, because the exchangeable and carbonate fractions of Pb and Ba were higher than their regulation limit. Tack CF as an example, the exchangeable fraction of Pb was only taken about 0.03%. If this part of Pb was fully leached out into the solution in TCLP test, then its leaching concentration would be 6.73 mg/L, which is higher than its regulation limit 5 mg/L. Further, if the carbonate fraction was also leached out, then the leaching concentration could be 3030.88 mg/L, extremely higher than the regulation limit. In order to check this, TCLP tests were conducted.

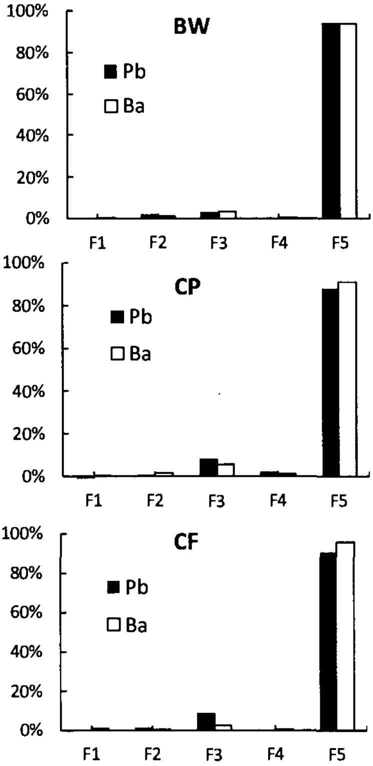
TCLP test

To better understand the relationship between the leaching characteristics and chemical fraction distributions of Pb and Ba contained the waste CRT glasses, residues for the three kinds of CRT glasses after each step of sequential extraction were analyzed by TCLP, successively named as FII, FIII, FIV and FV. The results were shown in Fig. 2, where TCLP leaching results of step five were not given, since no substances were left after step five.

From Fig. 2, it can be seen that Pb and Ba TCLP leaching concentrations of the original BW, CP and CF were the highest, and it decreased as the proceeding of sequential extraction. TCLP leaching concentrations of Pb and Ba were in the order: original CRT glasses > FII > FIII > FIV > FV.

Pb and Ba TCLP leaching concentrations of the original BW, CP and CF were 83.61mg/L (Pb, BW), 178.06 mg/L (Ba, BW), 56.46 mg/L (Pb, CP), 235.83 mg/L (Ba, CP), 361.72 mg/L (Pb, CF) and 7.94 mg/L (Ba, CF), respectively. Pb TCLP leaching concentrations of the three kinds of waste CRT glasses were about 11.29 – 72.34 folds to its regulation limit 5 mg/L. And it were 1.78 and 2.36 folds for Ba for BW and CP. Ba leaching concentration of CF was far below the regulation limit 100 mg/L, while those of BW and CP exceeded the regulation limit, which were 1.78 and 2.36 times to the regulation limit. According to the folds, it can be deduced that Pb and Ba contained in the waste CRT glasses showed a strong leaching toxicity, especially Pb. And that's why it is listed as a kind of hazardous waste.

For BW and CP, when the exchangeable and carbonate fraction of Ba was extracted out, Ba TCLP leaching concentrations of BW and CP were below 100 mg/L. When the exchangeable, carbonate and Fe-Mn oxides fraction of Pb had extracted out, Pb TCLP leaching concentrations of BW and CP were also lower than its regulation limit 5 mg/L. For CF, leaching concentration of Ba was very low, which was only 7.94 mg/L, less than 1/10 of its regulation limit. On the contrary, Pb showed an extremely higher leaching toxicity, which was 361.72 mg/L. Even the TCLP leaching concentration of its residue fraction exceeded the regulation limit, which was 10.90 mg/L, more than twice of the regulation limit, showing a strong leaching toxicity.



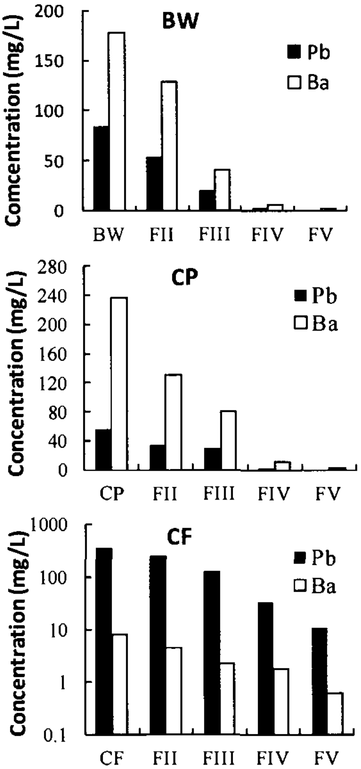


Fig. 1. Fraction distribution of Pb and Ba in the CRT glasses.

Fig. 2. TCLP results of the original CRT glasses and corresponding glasses after each step of SEP.

Connection between chemical fraction and leaching toxicity of Pb and Ba

To further investigate the relationship between the leaching characteristics and chemical fraction distributions of Pb and Ba, Pb and Ba TCLP leaching concentrations of the original waste CRT glasses minus those of the residues after the first step of sequential extraction, obtaining Pb and Ba TCLP leaching concentrations for their exchangeable fraction. According to this, Pb and Ba TCLP leaching concentrations for each fraction can also be obtained, and the results were given in Table 3.

From Table 3, it can be seen that Pb and Ba leaching toxicities were mainly attributed to F1 (Pb 25.77~37.40%, Ba 27.57~44.26%), F2 (Pb 10.42~38.80%, Ba 21.95~49.99%) and F3 (Pb 20.33~47.72%, Ba 5.36~28.90%). F4 and F5 showed a little contribution, which can be neglected. In other words, in the TCLP examinations, exchangeable fraction and fractions bound to carbonate and Fe-Mn oxides are likely to leach to the leachate, while the fraction bound to organic matters and the residue fraction are hard to leach out.

From Fig. 2, it can be figured out that F1, F2 and F3 of Pb and Ba contained in waste BW, CP and CF were 2.15 (BW, Pb), 4.85 (BW, Ba), 1.02 (CP, Pb), 6.90 (CP, Ba), 22.19 (CF, Pb) and 0.65 (CF, Ba) mg/g, respectively. Although the sums of F1, F2 and F3 of Pb and Ba contained in BW, CP and CF are no more than 10% of their total contents, they are several or even hundred times beyond its limits. Therefore, leaching toxicity of the three waste CRT glasses are very strong, showing a serious potential dangerous to the environment, since the regulation limits for Pb and Ba leaching toxicities are 5 and 100 mg/L.

Table 3 TCLP leaching concentrations of Pb and Ba contained in waste CRT glasses and TCLP leaching concentrations for each fraction of Pb and Ba (mg/L)

	Pb	Ba		Pb	Ba		Pb	Ba
CP	56.46	235.83	CF	361.72	7.94	BW	83.61	178.06
F1	21.12	104.39	F1	93.22	3.51	F1	30.01	49.08
F2	5.89	51.77	F2	138.05	2.21	F2	32.44	89.01
F3	26.94	68.16	F3	96.45	0.43	F3	17.00	33.33
F4	0.98	7.59	F4	23.09	1.16	F4	2.43	4.41
F5	1.54	3.92	F5	10.90	0.63	F5	1.73	2.22

Conclusions

Pb and Ba distribution in the CRT glasses followed the sequence of residual (88.22-95.83%) > Fe-Mn oxide associated fraction > carbonate fraction and organic matter > exchangeable fraction. The high Pb and Ba TCLP leaching concentrations of the CRT glasses were mainly attributed to its exchangeable and carbonate fraction, while Fe-Mn oxide, organic matter and even the residual fraction showed some contributions. Consequently, it is believed that Pb and Ba of CRT glass present a great environmental risk.

Acknowledgments

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