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Recovery of Metals from Electronic Waste by Reduction Melting Method

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Abstract

This study investigates application of the reduction melting method to recover metals from electronic wastes. The study began with determination of the optimal conditions for metal recovery from cathode ray tube (CRT) glass by melting under various conditions. The recovery of metallic lead and lead oxide (PbO) remaining in the glass residues for each set of melting condition were compared. It was found that the optimal condition for metallic Pb recovery from the CRT glass was melting the glass at 1200^{o}C for 1 hour and then soaking at precipitation temperature of 500^{o}C for 1-2 hours. Under these conditions, recovery rates of metallic lead from CRT glass reached up to 85-89%. The optimal conditions identified in this preliminary study were then used to recover metals from a mixture of CRT glass and printed circuit boards (PCBs), as a proxy for electronic waste. Electron Probe Micro Analysis (EPMA) characterization indicated two categories of metal deposits; the first being metallic lead (Pb) and the second as a mixture of copper (Cu), tin (Sn), and antimony (Sb). The study also confirmed that incorporation of PCB did not affect lead recovery from CRT glass.

Keywords: E-waste recycling; reduction melting method; metal recovery from e-wastes

Introduction

In recent years, electronic waste (e-waste) has become a growing problem worldwide, and in Thailand up to 300,000-400,000 tons per year are produced (Figure 1), even excluding electronic waste stored at homes and offices. E-wastes such as televisions, computers, cell phones and batteries, contain significant quantities of important industrial metals such as iron (Fe), lead (Pb), copper (Cu), silver (Ag) and gold (Au).

Recovery of such metals from e-wastes is therefore important to conserve these finite mineral resources [1, 2].

The reduction melting method is a pyrometallurgical process used to recover metals from e-wastes; this study assessed optimal conditions for this process to recover metallic lead (Pb) from CRT glass, and a mixture of CRT glass mixed with printed circuit boards (PCB) at various conditions.

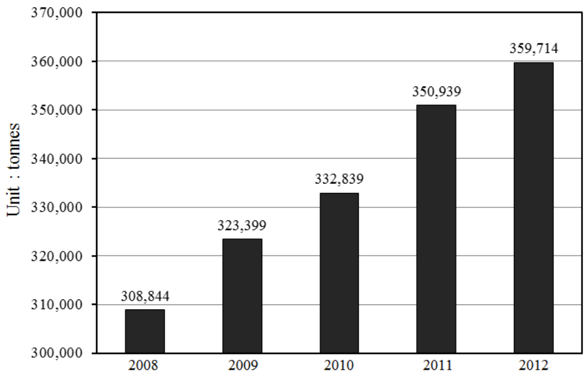

Figure 1 Amount of electronic wastes produced in Thailand (2008-2012)*

* Excluding E-wastes stored at homes and offices

Principle of Reduction Melting Method

A pyrometallurgical process known as the 'reduction melting method' or 'fusion reduction method' is commonly used to isolate metals from mixed e-wastes [3]. This is done by chemically reducing all metallic compounds to their metallic or reduced forms by heating with adequate fluxing and reducing agents. The method involves heating at an appropriate temperature to convert metallic waste or mixed metals to a form that can be refined.

Upon heating oxide compounds in waste with a reducing agent, such as carbon in the form of coke, coal, or charcoal, the oxide will react with carbon to yield CO and then the CO will reduce the metal oxides to their respective metallic forms [4]. Fluxing agents such as NaOH or Na_2CO_3 are also added to form a molten mass called 'slag' when heated. Being lighter than the metal, the slag floats and is skimmed or drawn off [5]. The reduction of PbO in CRT glass follows the standard Gibbs free energy of formation (ΔG^0) of oxides contained in the CRT glass as a function of temperature. It is called Ellingham's diagram. The magnitude of negative free energy of formation of an oxide is a measure of its stability. The line of Pb oxidation in the plot of ΔG^0 vs Temperature, which is mostly in the upper part, indicates that PbO is the oxide easily reduced thermodynamically. The PbO in glass was suggested to be reduced by CO generated from combustion of reducing agent [6].

Methodology

The experiment was divided into 2 parts. First, a preliminary study was conducted to establish the optimal conditions for recovery of metallic lead from CRT glass. These optimal conditions were then applied to recover metals in a mixture of CRT glass and PCB. The mixture was used as a proxy for e-waste because these items are widely found as components of e-waste. The CRT glass used in this study was collected from general television wastes and ground using a disc mill (Kawazaki-SIEB T-100). The CRT powder was then subjected to elemental analysis using X-ray fluorescence (XRF; Bruker S4 Pioneer) as shown in Table 1. Each sample was prepared by mixing 30 grams of the CRT powder with 12 grams alkali carbonate fluxing agent [7] and 4 grams wood charcoal reducing agent (composition shown in Table 2) in an alumina crucible, After heating in an electrical furnace (Naber Therm) at 1,200 °C for 1 hour, the samples were then allowed to cool to room temperature either through natural cooling or by soaking at various precipitation temperatures and times before cooling to room temperature. Metallic lead recovery for each set of conditions is shown in Table 3 and Figure 2. Since lead oxide (PbO) is a major metallic component in the CRT glass, recovery of Pb from the CRT waste is the only metal of concern in this preliminary study. The amount of PbO remaining in each residue was analyzed by XRF to establish the optimum precipitation conditions for recovery of Pb from the CRT waste.

Table 1 Chemical composition of CRT glass by XRF analysis

Oxide	Wt%
PbO	27.30
SiO_2	46.50
K_2O	8.53
Na_2O	6.02
CaO	4.38
Al_2O_3	4.31
MgO	1.57
SrO	0.51
BaO	0.28
Sb_2O_3	0.28
ZrO_2	0.11
Others	0.21

Table 2 Chemical composition of wood charcoal

Oxide	Wt%
CaO	11.00
SiO_2	5.58
K_2O	2.73
Fe_2O_3	1.44
SO_3	0.64
Al_2O_3	0.54
Cl	0.41
P_2O_5	0.38
SrO	0.33
MgO	0.31
BaO	0.25
TiO_2	0.19
MnO	0.14

The PCB sample, prepared with a size of 0.5×0.5 cm^2 - a similar size to that obtained by hammer crushers in commercial recycling plants-was mixed with CRT powder in ratios as shown in Table 4. Fluxing agent and wood charcoal were added to the mixture in an alumina crucible and heated at melting temperature of 1200°C for 1 hour, before reducing the heat to a precipitation temperature of 500°C for a further 2 hours. Having established the optimal reaction conditions, these were then applied to recover metals from a mixture of CRT glass PCB waste in various rations to investigate the effect of added PCB on metal recovery, as well as on the value of the PCB combustion gas as a reducing agent in the reduction melting process [8].

Table 3 Experimental study conditions at melting temperature of 1200°C and soaking time 1 h

Condition	Precipitation Temperature (°C)	Soaking time (h)
1	none	none
2	500	1
3	500	2
4	600	1
5	600	2
6	700	1
7	700	2

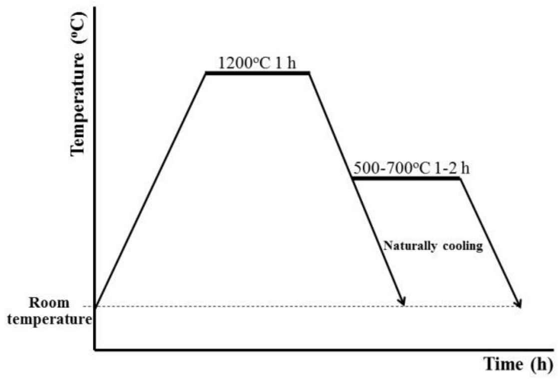

Figure 2 Steps of melting and precipitation

Table 4 Mixing ratios of CRT glass and PCB.

Sample No.	CRT (g)	PCB (g)
1	30	10
2		15
3		20
4		30

Results and discussion

Table 5 shows XRF data of the composition of the CRT glass after reduction melting compared with its original composition. The percentage of PbO remaining in the CRT residues, obtained by XRF analysis, and those of metallic Pb recovery (obtained by weighing the separated metallic Pb part after soaking at each precipitation condition) are shown in Figure 3. The results indicate a remarkable reduction of PbO levels from 27.3% in the original CRT glass to only about 2.5-3.5% in the CRT residues following treatment, and vice versa for the percentage of metallic Pb recovery. This result confirms that metallic Pb can be successfully separated from CRT glass by the reduction melting method, consistent with the findings of Inano [6,7]. However, this study consumed lower amounts of alkali carbonate fluxing agent and carbon reducing agent. In addition, the present study used wood charcoal as a reducing agent instead of the more expensive activated carbon used in the Inano study.

The study found that the optimal process conditions for recovery of metallic lead are melting the CRT glass at 1200 °C for 1 hour and then soaking at the precipitation temperature of 500 °C for 1-2 hours. These conditions resulted in the lowest amount of PbO remaining in the glass residue and the highest level of metallic Pb recovery. Meanwhile, the remarkably high amount of PbO remaining in the CRT waste was observed when soaking at a precipitation temperature of 600 °C for 1 hour. This may be because this temperature is close to the glass transition temperature of lead oxide (PbO) where it is difficult for the metallic Pb to separate from its glass. This is confirmed by the decreasing amount of PbO remaining in the CRT glass soaking at precipitation temperatures above 600 °C.

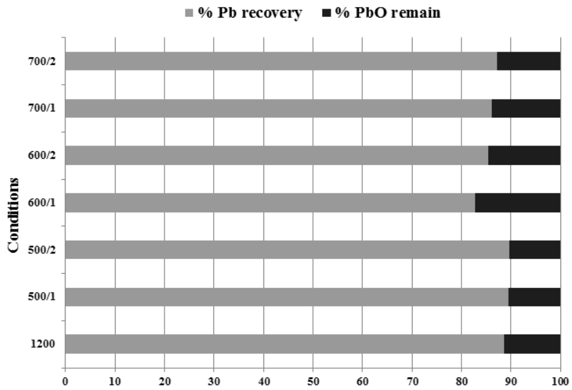

Figure 3 Percentage of metallic Pb recovery and PbO remaining under each set of conditions

Table 5 Chemical composition of CRT glass residue after melting at various reducing conditions compared with the original CRT glass (XRF analysis)

Oxide	Original CRT Glass	Condition: Temperature (°C) / Soaking duration (h)						
		w/o Treatment	500/1	500/2	600/1	600/2	700/1	700/2
SiO_2	46.50	48.00	47.90	48.00	46.60	47.10	47.40	47.40
PbO	***27.30***	***2.72***	***2.51***	***2.49***	***4.25***	***3.51***	***3.42***	***3.14***
K_2O	8.53	8.18	8.10	8.30	8.34	8.31	8.15	8.21
Na_2O	6.02	27.50	27.70	27.20	26.90	27.20	27.30	27.50
CaO	4.38	4.88	4.87	5.05	4.90	4.95	4.87	4.92
Al_2O_3	4.31	5.65	5.78	5.76	5.91	5.78	5.76	5.82
MgO	1.57	1.59	1.61	1.60	1.55	1.56	1.56	1.58
SrO	0.51	0.46	0.47	0.49	0.49	0.48	0.48	0.47
BaO	0.28	0.50	0.49	0.51	0.48	0.49	0.48	0.49
ZrO_2	0.11	0.12	0.13	0.13	0.13	0.13	0.12	0.13
Sb_2O_3	0.28	-	-	-	-	-	-	-
Fe_2O_3	-	0.20	0.24	0.24	0.20	0.20	0.20	0.20

Note: - All samples were melted at 1200 °C for 1 h prior to cooling to room temperature.
- w/o Treatment means natural cooling to room temperature.
- 500/1 means keeping a constant temperature of 500 °C for 1 h prior to cooling to room temperature.

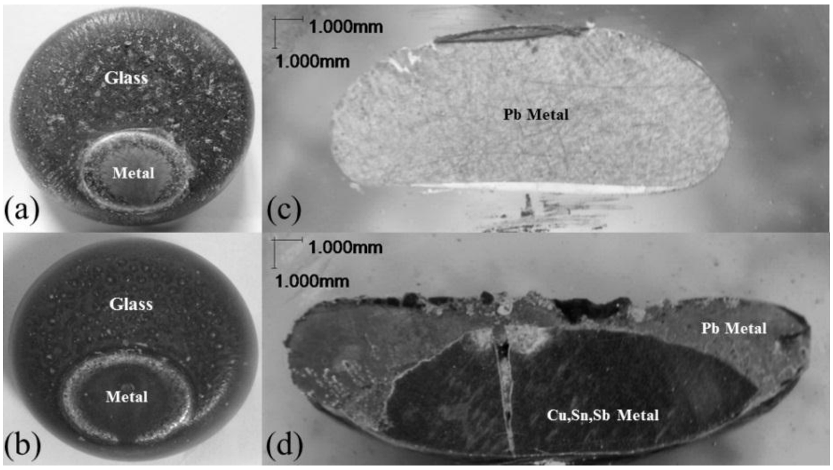

Figure 4 Separation of metallic Pb from (a) CRT glass and (b) CRT/PCB mixture. Cross-section view of metallic Pb separated from (c) CRT glass and (d) CRT/PCB mixture.

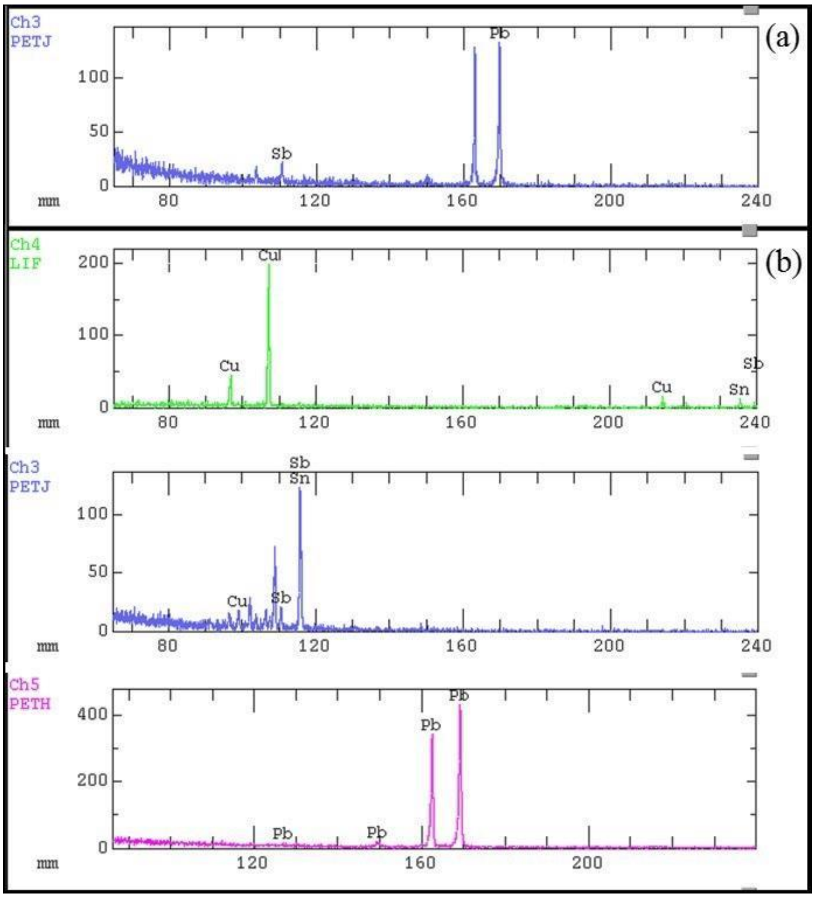

Figure 5 EPMA micrograph of samples: (a) metallic Pb from CRT glass and (b) Metals from CRT/PCB mixture.

Figure 5 presents EPMA micrographs of each sample of separated metals, indicating that Pb is a main component of the CRT glass. Meanwhile composition of metals from the CRT and PCB mixture can be divided in 2 parts; the first part composed by 97%Pb and 3%Sb. The second part was made up of 71.29 % Cu, 25.22% Sn and 3.49% Sb.

The study of metals recovery from CRT glass mixed with various amount of PCB indicates that addition of PCB exhibits no effect on Pb recovery from the CRT glass. This is confirmed by nearly constant PbO remaining in the glass of all mixture. Meanwhile, percentage of other oxides like CuO, SnO and ZnO increases with amount of the PCB addition, as shown in Figure 6.

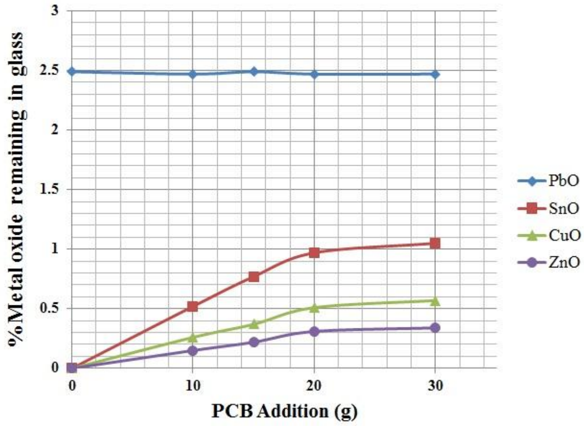

Figure 6 Metal oxides remaining in glass residues after reduction melting of CRT/PCB mixture

Conclusions

This preliminary study confirms that metallic lead (Pb) can be successfully recovered from CRT glass by the reduction melting method. Its optimal process conditions were found to be melting the waste at 1200°C for 1 hour and then soaking at precipitation temperature of 500°C for 1-2 hours. This condition was also successfully applied for recovery of metals from mixture of CRT and PCB waste. Therefore, the reduction melting method under appropriate conditions is suggested as a successful method for metals recovery from electronic wastes. In addition to recover the metallic lead, the glass residue after lead removal from the CRT glass is clean and clear enough to be utilized in glass industry. Meanwhile, the glass residue after lead removal from the CRT/PCB mixture still contains too many impurities. However, higher value materials like metallic copper (Cu), tin (Sn), and antinomy (Sb) can be successfully recovered by reduction melting of the CRT/ PCB mixture. In order to confirm that reduction melting of the CRT/PCB mixture is an option to recovery metallic copper (Cu), tin (Sn), and antinomy (Sb) from the PCB waste, various melting conditions as well as various ratios of CRT and PCB, even PCB without CRT addition, are suggested to be further studied.

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