Waste Management 33 (2013) 1758–1763

Contents lists available at SciVerse ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Energy-efficient modification of reduction-melting for lead recovery from cathode ray tube funnel glass

Takashi Okada *, Susumu Yonezawa

Headquarters for Innovative Society-Academic Cooperation, University of Fukui, Bunkyo 3-9-1, Fukui 910-8507, Japan

ARTICLE INFO

Article history:
Received 25 October 2012
Accepted 24 April 2013
Available online 25 May 2013

Keywords:
Cathode ray tube
Funnel glass
Lead recovery
Reduction melting
Low energy consumption

ABSTRACT

Lead can be recovered from funnel glass of waste cathode ray tubes via reduction melting. While low-temperature melting is necessary for reduced energy consumption, previously proposed methods required high melting temperatures (1400 °C) for the reduction melting. In this study, the reduction melting of the funnel glass was performed at 900–1000 °C using a lab-scale reactor with varying concentrations of Na_2CO_3 at different melting temperatures and melting times. The optimum Na_2CO_3 dosage and melting temperature for efficient lead recovery was 0.5 g per 1 g of the funnel glass and 1000 °C respectively. By the reduction melting with the mentioned conditions, 92% of the lead in the funnel glass was recovered in 60 min. However, further lead recovery was difficult because the rate of the lead recovery decreased as with the recovery of increasing quantity of the lead from the glass. Thus, the lead remaining in the glass after the reduction melting was extracted with 1 M HCl, and the lead recovery improved to 98%.

1. Introduction

In Japan, the treatment of waste cathode ray tube (CRT) glass has attracted particular attention because flat-panel displays are rapidly replacing CRT monitors, and closed-loop recycling (waste CRT to new CRT) is becoming difficult. In 2007, the quantity of the waste CRT glass generated in Japan was approximately 60,000 tons (Japan Ministry of Economy, 2009); thus, the treatment of such large quantities of the waste CRT glass using techniques other than closed-loop recycling is necessary. Therefore, open-loop recycling (waste CRT to other products) of CRT glass has been studied to produce glass matrix composites, glass-ceramics, foam glass, porcelain stoneware tiles, dense glass, clay bricks, and roof tile bodies (Bernardo et al., 2003, 2007; Andreola et al., 2005; Méar et al., 2006a,b; Raimondo et al., 2007; Dondi et al., 2009). However, CRT contains funnel glass in which a considerable quantity of lead is present. The concentration of lead in the funnel glass was reported to be 19–24 wt% (Méar et al., 2006a,b); therefore, it is necessary to develop a process for lead recovery from the used funnel glass from the viewpoint of environmental protection.

For the lead recovery, Sasai et al. (2008) extracted lead from lead-glass using the reagent disodium ethylenediaminetetraacetate, but this process would not be effective because the optimal treatment time for the lead recovery was 20 h. Chen et al. (2009) volatilized lead from the CRT funnel glass at 600–1000 °C in a reactor, but the lead volatilization method requires a collection process for the lead vapor and the entire treatment process would be complicated. The authors recovered lead from the CRT funnel glass via a reduction-melting process in which the lead oxides in the glass were reduced to metallic lead with carbon at 1400 °C in a reactor, and the generated molten metallic lead was separated from the molten glass (Okada et al., 2012). The reduction-melting process would be simpler than the lead volatilization process because the metal separation in the former process is performed in a single reactor. However, the melting temperature in the reduction melting is 1400 °C and a large amount of energy is required. To reduce energy consumption, the reduction melting should be performed at a lower melting temperature. Chen et al. (2009) reported that the proposed heating temperature in the lead volatilization process was 1000 °C; thus, the temperature of the reduction melting is required to be decreased to this level. However, the reduction-melting process has not been performed at 1000 °C (Inano, 2009; Matsumoto et al., 2012; Okada et al., 2012), and it is necessary to clarify the appropriate conditions for achieving a high lead-recovery efficiency at this temperature.

In this study, the CRT funnel glass was subjected to the reduction melting at a temperature up to 1000 °C. The objective was the determination of the optimum melting conditions for highly efficient recovery of lead from the funnel glass. The funnel glass obtained from a domestic treatment facility for CRT monitors was melted in a reductive atmosphere in a lab-scale electric

* Corresponding author. Tel./fax: +81 776 27 9756.
E-mail address: t-okada@u-fukui.ac.jp (T. Okada).

0956-053X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.wasman.2013.04.009

Table 1
Chemical composition of the FG powder used in the melting experiments.

	Concentration	
	wt%	mol kg^{-1}
SiO_2	47	7.9
PbO	25	1.1
K_2O	8.5	0.90
Na_2O	5.6	0.91
$A1_2O_3$	3.6	0.36
CaO	3.4	0.60
SrO	2.3	0.23
MgO	1.9	0.46
BaO	1.8	0.12
Sb_2O_3	0.34	0.012
Fe_2O_3	0.21	0.013

furnace. The effects of the melting conditions on the efficiency of the lead recovery were evaluated and considered thermodynamically and kinetically.

2. Experimental

2.1. Materials

A powder of waste CRT funnel glass was obtained by crushing and grinding the funnel glass obtained from a Japanese CRT monitor treatment facility. The powder was sieved through a 1-mm screen. The obtained powder consisting of particles <1 mm in diameter is called "FG powder", and this FG powder was used for the melting experiments. The chemical composition of the FG powder was determined by X-ray Fluorescence (XRF) analysis on a Shimadzu LAB CENTER XRF-1800 system (Shimadzu, Kyoto, Japan). As shown in Table 1, the FG powder contained 25 wt% PbO. The lead concentration was higher than those in the funnel glass reported by Méar et al. (2006a,b). This may be because the FG powder used in this study was contaminated by a frit which contains a higher concentration of lead than the funnel glass and is used to joint the panel glass and the funnel glass in CRT. The concentration of lead in the frit was reported to be 73.5 wt% (Glass Manufacturers' Association of Japan, 1991).

2.2. Melting experiments

A schematic diagram of the melting experiment is shown in Fig. 1. The FG powder (10 g) was mixed with given amounts of reagent grade Na_2CO_3 (0–10 g). Each mixture was put in a 30-mL alumina crucible, which was placed into a 100-mL alumina crucible containing activated carbon (3 g, Wako Chemical Co. Ltd.). An alumina cover was then placed on the 100-mL crucible, and this reaction container was placed in the electric furnace. The temperature in the furnace was elevated to a given melting temperature (900–1000 °C) in 30 min, and the mixture was melted for a given time in the furnace at the specified melting temperature. Finally, the sample was allowed to cool naturally to room temperature.

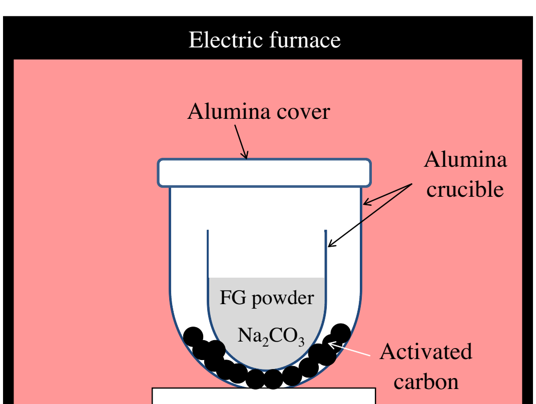

Fig. 1. Lab-scale reactor. The electric furnace, the reaction container, and the test sample are illustrated.

The products generated in the melting experiments were crushed, and the metallic lead was separated from the glass. The glass was ground in a mortar and evaluated using the XRF analysis and X-ray diffraction (XRD) analysis on a Bruker AXS D8 ADVANCE system (Bruker AXS, Kanagawa, Japan). A portion of the glass adhering to the surface of the separated metallic lead was removed by scraping it off the surface of the lead with a knife. The chemical composition of the metallic lead was determined by XRF on a Shimadzu Rayny EDX-800 system (Shimadzu, Kyoto, Japan).

In the melting experiment, the effect of the Na_2CO_3 dosage, melting temperature, and melting time on the lead recovery were investigated using the following equations:

$$\text{Lead recovery}(\%) = (1 - R^{\text{Lead}}/R_0^{\text{Lead}}) \times 100 \quad (1)$$

$$R^{\text{Lead}} = C^{\text{Lead}}/C^{\text{Silica}} \quad (2)$$

$$R_0^{\text{Lead}} = C_0^{\text{Lead}}/C_0^{\text{Silica}} \quad (3)$$

In the above equations, C_0^{Lead} is the lead concentration in the FG powder, C_0^{Silica} is the SiO_2 concentration in the FG powder, C^{Lead} is the lead concentration in the glass after the reduction melting, and C^{Silica} is the SiO_2 concentration in the glass after the reduction melting. The reason for using this unusual definition for the lead recovery in Eq. (1) is that the Lead/Silica ratio (R^{Lead} and R_0^{Lead}) in the glass is not affected by dilution due to the addition of Na_2CO_3 in the reduction-melting process.

3. Results and discussion

3.1. Factors affecting the efficiency of lead recovery

The thermodynamic and kinetic aspects of the reduction-melting process were investigated to determine whether it is possible to recover lead from the funnel glass at a temperature up to 1000 °C.

First, the reaction is thermodynamically discussed. In the authors' previous study (Okada et al., 2012), the Ellingham diagrams of the metal oxides in the funnel glass were discussed, and it was concluded that the PbO in the glass is theoretically reduced to metallic lead by CO generated via carbon combustion given as follows:

$$PbO + CO = Pb + CO_2 \quad (4)$$

Generally, in the melting process, the generated metallic lead particles move in the molten glass, collide with each other, and aggregate. The aggregate of the metallic lead settles at the bottom of the reactor because the density of metallic lead is greater than that of glass; The density of metallic lead is 11.34 g cm^{-3}, and that of glass is typically 2.56 g cm^{-3} (Bansal et al., 1986; Lide, 2003). Thus, the molten metallic lead phase is separated from the molten glass phase. To cause this phase separation, it is necessary to generate the liquid phase of both the metallic lead and glass, allowing the metallic lead particles move and collide with each other in the molten glass. Therefore, in this study, a thermodynamic equilibrium calculation was performed using the FactSage 5.4.1 program (GTT Technologies) (Bale et al., 2002) to investigate the possible presence of the liquid phases in the reduction melting of the funnel glass at a temperature up to 1000 °C. This program provides