Removal of lead from cathode ray tube funnel glass by combined thermal treatment and leaching processes

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ABSTRACT

The reduction melting process is useful to recover toxic lead from cathode ray tube funnel glass; however, this process generates SiO_2-containing residues that are disposed in landfill sites. To reduce the volume of landfill waste, it is desirable to recycle the SiO_2-containing residues. In this study, SiO_2 powder was recovered from the residue generated by reduction melting. The funnel glass was treated by a process combining reduction melting at 1000 °C and annealing at 700 °C to recover a large quantity of lead from the glass. The oxide phase generated by the thermal treatment was subjected to water leaching and acid leaching with 1 M hydrochloric acid to wash out unwanted non-SiO_2 elements for SiO_2 purification. In the water washing, the oxide phase was microparticulated, and porous structures formed on the oxide surfaces. This increased the surface area of the oxide phase, and the unwanted elements were effectively washed out during the subsequent acid leaching. By controlling the acid leaching time and the amount of added acid, porous and amorphous SiO_2 (purity >95 wt%) was recovered. In the obtained SiO_2-concentrated product, unrecovered lead remained at concentrations of 0.25–0.79 wt%. When the Na_2CO_3 dosage in the thermal treatment was increased, the lead removal by acid leaching was enhanced, and the lead concentration in the obtained product decreased to 0.016 wt%.

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1. Introduction

Cathode ray tubes (CRTs) containing panel and funnel glasses have been widely used in computer monitors and television sets, and the generation of CRT waste is expected to increase in Asia (Gregory et al., 2009). Waste CRT glass generated in Japan has been recycled for the production of new CRT glass; however, this closed-loop recycling is becoming difficult because flat-panel displays are rapidly replacing CRTs. As alternatives to closed-loop recycling, previous studies have proposed new recycling techniques to convert the waste CRT glass into other products, such as glass matrix composites, glass–ceramics, foam glass, porcelain stoneware tiles, dense glass, clay bricks, and roof tile bodies (Bernardo et al., 2003 and Bernardo et al., 2007; Andreola et al., 2005; Méar et al., 2006a,b; Raimondo et al., 2007; Dondi et al., 2009). These open-loop recycling techniques can be applied to panel glass, which contains no hazardous heavy metals (Méar et al., 2006a,b), and the products obtained from the glass can be used safely in environment. In contrast, funnel glass contains considerable quantities of toxic lead oxides (Méar et al., 2006a,b), and

the glass should not be directly converted into products for use in the environment. For environmental protection, it is necessary to develop a process for lead recovery from used funnel glass.

Thermal treatments and leaching techniques have been proposed as lead recovery methods (Chen et al., 2009; Sasai et al., 2008; Wang and Zhu, 2012; Matsumoto et al., 2012; Okada et al., 2012; Okada and Yonezawa, 2013 and Okada and Yonezawa, 2014). This study focuses on the reduction melting process in which the lead oxides in the funnel glass are reduced to metallic lead under a reductive atmosphere generated by carbon combustion, and the generated molten metallic lead is separated from the molten oxide phase. Using reduction melting, over 90% of lead oxides in funnel glass can be recovered. As explained below, we have modified this process for higher treatment efficiency. An additional melting stage in an oxidative atmosphere was combined with the reduction melting to immobilize unrecovered lead remaining in the glass after reduction melting (Okada et al., 2012). In addition, a combination of reduction melting and the recycling of Na_2CO_3, which was used as a flux in the reduction melting, was employed (Okada and Yonezawa, 2014) to reduce the cost of the flux. The treatments using these processes generate waste oxide phases containing mainly SiO_2 as a residue. From the perspective of reducing the volume of landfill wastes at limited

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landfill sites in Japan, recycling these residues would be better than direct disposal.

Unfortunately, the residues from the funnel glass treatments contain a variety of elements because the funnel glass itself is multicomponent glass (Méar et al., 2006a,b), and it is difficult to use these residues as raw materials for manufacturing. In the above-mentioned oxidation melting, SiO_2, Al_2O_3, MgO, and $NaNO_3$ are added to the glass to promote the immobilization of lead, complicating the chemical composition of the residue. In recycling, it is better to recover pure materials from the residue; thus, we study the recovery of SiO_2 which is the main component of the residue. If SiO_2 powder is recovered from the residue, the recovered SiO_2 can be recycled for glass manufacturing. In our previous study, the glassy residue generated by reduction melting was washed using 1 M hydrochloric acid (HCl) to remove elements other than SiO_2 (Okada and Yonezawa, 2013). As a result, the SiO_2 in the residue was concentrated from 47 wt% to 81 wt%; however, the concentration was still lower than that in silica powder (Song et al., 2014). To obtain more SiO_2 concentrated materials, it is necessary to develop a highly efficient SiO_2 purification process. As noted in this study, SiO_2 purification was promoted by the combination of the multistage thermal and leaching treatments that we developed previously. This SiO_2 purification process has not been studied for funnel glass.

In this study, SiO_2 was recovered from the residue generated by the reduction melting of CRT funnel glass. Our objective was to identify the appropriate treatment conditions for highly efficient SiO_2 purification. The funnel glass obtained from a domestic treatment facility for CRT monitors was melted at 1000 °C and annealed at 700 °C under a reductive atmosphere. The generated oxide phase was washed sequentially using water followed by 1 M HCl to recover and purify SiO_2 in the oxide phase. The appropriate treatment conditions to reduce the lead remaining in the recovered SiO_2-concentrated material were also studied.

2. Materials and methods

2.1. Materials

In our previous study, a powdered sample of waste CRT funnel glass comprising particles less than 1 mm in diameter (referred to as "FG powder") was used (Okada et al., 2012; Okada and Yonezawa, 2013 and 2014). In this study, the same FG powder was employed in the experiments. The chemical composition of the FG powder (Table 1) was determined by wavelength-dispersive X-ray fluorescence (XRF) analysis on a Shimadzu LAB CENTER XRF-1800 system (Shimadzu, Kyoto, Japan). Detailed information on the FG powder can be found in our previous study (Okada et al., 2012).

2.2. Thermal treatment

Fig. 1 shows a schematic diagram of the experimental setup. A mixture of FG powder (10 g), activated carbon (0.5 g, Wako Chemical Co.), and a given amount of reagent-grade Na_2CO_3 (5–10 g) was placed in a 30-mL alumina crucible. The crucible was placed in a 100-mL alumina crucible containing 3 g of activated carbon and covered with an alumina cover. This reaction container was placed in an electric furnace, and the temperature of the furnace was elevated to 1000 °C over a period of 30 min. The temperature of the furnace was detected by thermo-couples placed in the furnace. The mixture in the crucible was melted for 1 h at this temperature (referred to as the "reduction–melting stage"). Subsequently, the furnace was allowed to cool naturally to 700 °C. The mixture was then heated at this temperature for 2 h to separate water-soluble sodium oxide phases (Okada and Yonezawa, 2014) that can be extracted in water for SiO_2 purification. This treatment is referred to as the "annealing stage." In the annealing process, sodium oxides phase was separated (Okada and Yonezawa, 2014), and the phase separation is basically due to incompatibilities between network-former and network-modifier cations and coulombic repulsions between network-modifier cations (Hudon and Baker, 2002). Finally, the mixture was allowed to cool naturally to room temperature. The products generated by the heat treatment were crushed, and the metallic lead generated in the reduction–melting stage was removed from the oxide phase. The obtained oxide phase is referred to as the "heat treatment product."

For comparison, in some experiments, only reduction melting was performed at 1000 °C for 2 h without annealing, and the oxide phase was obtained in the same manner as above. This material is referred to as the "reduction melting product."

2.3. Leaching experiments

The heat treatment product was ground in a mortar and sieved to obtain a powder sample with particle sizes ranging from 32 to 125 μm. In some experiments, the particle size range of the powder was varied (125–212 μm, 212–500 μm, and 500–1000 μm). In the water leaching, 2.5 g of the powder was placed into a 100-mL glass flask containing 100 mL of ion-exchange water, and the flask was covered with watch glass. The mixture was agitated for 1 h at around 75 °C using a magnetic stirrer at steering rate of
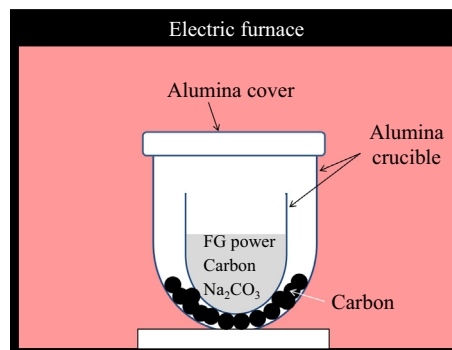
Table 1
Chemical compositions of the FG powder and the products generated by the experiments.

	Concentration (wt%)			
	FG powder	Reduction melting product	Water leaching product	Acid leaching product
SiO_2	47.4	45.6	48.2	91.7
PbO	24.9	1.5	4.6	0.25
Na_2O	5.6	30.3	12.8	0.76
BaO	1.8	1.6	2.3	0.23
Sb_2O_3	0.34	0.38	0.45	0.28
SrO	2.3	1.8	2.6	0.06
Fe_2O_3	0.21	0.39	0.78	0.32
CaO	3.4	4.6	6.3	0.25
K_2O	8.5	8.1	12.3	1.0
Al_2O_3	3.6	3.9	7.2	5.0
MgO	1.9	1.8	2.4	0.13

Na_2CO_3 dosage to the FG powder in the reduction melting: 0.5 kg kg-FG powder^{-1}.
Particle size of the heat treatment product used for the leaching tests: 32–125 μm.
Mass ratio of 1 M HCl to the heat treatment product in the acid leaching: 8 L kg^{-1}.
Acid leaching time: 60 min.

Fig. 1. Schematic diagram of the lab-scale reactor.