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Lead extraction from cathode ray tube funnel glass melted under different oxidizing conditions

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HIGHLIGHTS

- After reduction melting of funnel glass, metallic lead is suspended in the glass.
- The metallic lead particles are readily extracted by hydrochloric acid.
- On oxidative melting, the corrosion resistance of the glass in the acid is enhanced.
- This can be attributed to an increase in the covalently bonded network in the glass.

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ABSTRACT

Lead was extracted into hydrochloric acid from cathode ray tube funnel glass melted under reducing atmosphere, oxidizing atmosphere, or a sequential combination of both to mechanistically investigate effects of the melting atmosphere on lead extraction. Melting funnel glass in a reductive atmosphere led to the generation of metallic lead particles that were readily soluble in the acid, increasing the quantity of lead extracted into the acid. Meanwhile, the glass product obtained after melting funnel glass in an oxidative atmosphere exhibited higher corrosion resistance in the acid, and the quantity of lead extracted from the treated glass decreased. However, Na_2CO_3 addition to the glass during melting hindered the enhancement of corrosion resistance and the immobilization of lead in the acid. X-ray photoelectron spectroscopic analysis of the treated glass samples showed that the positions of the peak or the profiles of the spectra attributed to Pb 4f, Si 2p, and O 1s signals were modified by oxidative melting, an indication that oxidative melting results in structural changes in the SiO_2 framework of the glass.

1. Introduction

Panel and funnel glass from waste cathode ray tubes (CRTs) are recycled for use in a new CRT in a process referred to as closed-loop recycling. With flat panel displays replacing CRTs, the need for this closed-loop recycling is weakening. With an increase in the amount of CRT glass cullet from 2010 to 2020 in Asia [1], other treatments of waste CRT glass have attracted particular attention.

Open-loop recycling, wherein glass in CRT is recycled for use in the production of other products, has been proposed [2–7]. The products obtained by the proposed open-loop recycling techniques can be used as construction materials. However, the presence of significant amounts of lead [8] and other process-related considerations explained below presents challenges to the recycling of funnel glass. If the recycled funnel glass is used as a construction material in a residential/workspace environment, a part of the material containing lead can scatter and can result in the oral intake of the dispersed lead by humans. In the body, lead dissolved by the acid in the stomach can transfer to blood and negatively impact human health, in particular, the nervous system in children [9]. Therefore, developing a process for the recovery of lead from the used funnel glass is necessary for environmental protection. A previous study reported that lead in funnel glass can be extracted into an acid solution [10].

Processes based on pyrovaccum [11], leaching [12–13], self-propagation [14], chlorination [15], and reduction melting [16–18] have been proposed for the recovery of lead. The reduction-melting process has been used in this study; in this process, the lead oxides in funnel glass are reduced to metallic lead with carbon, and the generated molten metallic lead is separated from the molten glass.

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Table 1
Chemical composition of FG powder and glass products obtained by the melting experiments.

Oxide	Concentration (wt%)							
	FG powder	Rd-glass	Ox-glass	Rd-glass^{Na}	Rd–Ox-glass^{Na}	Rd–Rd-glass^{Na}	Rd–Ox-glass$^{Na+Na_2CO_3}$	Rd–Ox-glass$^{Na+NaNO_3}$
SiO_2	45.9	51.8	47.2	44.5	44.9	44.8	43.7	44.4
PbO	25.2	15.2	23.3	2.0	2.0	1.7	2.2	1.9
Na_2O	5.8	7.0	5.9	31.2	31.1	31.2	32.5	33.0
K_2O	8.9	10.6	8.8	7.7	7.6	7.8	7.4	7.1
CaO	4.0	4.9	4.2	4.5	4.3	4.4	4.2	4.1
MgO	1.5	1.8	1.8	1.5	1.5	1.5	1.5	1.6
Al_2O_3	3.3	4.1	4.5	4.6	4.3	4.3	4.3	4.2
SrO	1.9	1.5	1.4	1.4	1.5	1.5	1.4	1.4
BaO	2.0	2.0	1.4	1.5	1.6	1.6	1.6	1.5
Others	1.5	1.1	1.6	1.1	1.2	1.2	1.2	1.0

While >90% of lead in funnel glass is recovered using the reduction-melting process, a large fraction of the remnant lead is extracted using 1 M hydrochloric acid (HCl) and the quantity of the extracted lead exceeds the tolerance level established by Japanese standards [19]. Acid leaching of the reduction-melting-processed funnel glass does not reduce the levels of lead to <1 wt%, a level that does not completely mitigate its environmental impact [17]. Lead in funnel glass obtained after reduction melting was immobilized on remelting the glass in an oxidative atmosphere [19]. Therefore, the application of a hybrid process involving both reduction and oxidation melting to recycle funnel glass resulted in acceptable levels of lead. However, a systematic study to delineate the relationship between the melting atmosphere and lead extraction has not been performed. Such a mechanistic study can significantly help in establishing appropriate conditions for the efficient removal and immobilization of lead using the above hybrid process.

In this study, the CRT funnel glass is melted in an atmosphere that changes from reductive to oxidative. Herein, the effects of the melting atmosphere on the subsequent extraction of the remaining lead is investigated via acid treatment; moreover, the structure of the treated glass is evaluated after melting the waste funnel glass with a reductant or oxidant using a lab-scale melting furnace.

2. Materials and methods

2.1. Materials

In this study, for the melting experiments, funnel glass (FG) powder with a particle size <1 mm was used. The chemical composition of the powder is shown in Table 1. The powder was collected from a domestic treatment facility of CRT monitors in Japan. In this facility, the funnel and panel glass of CRTs are separated; however, the separated funnel glass retains a fraction of the panel and solder glass (used to join the panel and funnel glass) [8]. The chemical compositions of the panel and solder glass are different from that of funnel glass. Furthermore, the inner surface of the separated funnel glass is coated with carbon or iron oxides. This funnel glass is crushed to generate the FG powder; therefore, this heterogeneous FG powder comprises particles of the panel glass, solder glass, and the coating materials.

2.2. Reduction or oxidation melting

In reduction melting, the FG powder (20 g) was mixed with activated carbon (3 g, Wako Chemical Co., Ltd., Osaka, Japan). In some experiments, reagent grade Na_2CO_3 (10 g) was added to the mixture. This mixture (with or without Na_2CO_3) was collected in a 30-mL alumina crucible (Al_2O_3 = 95%) and placed in an electric furnace. The temperature in the furnace was first elevated to 1200 °C with a heating rate of 5 °C min^{-1} and then maintained at 1200 °C for 1 h in an air atmosphere. During heating, lead oxides in the melted FG powder are reduced by the added carbon or CO (resulting from the combustion of carbon in air). Subsequently, the mixture was allowed to cool to room temperature. The resulting reduction-melting product consisted of glass and the agglomerate of the metallic lead. The product was crushed to separate the metallic lead from the glass. The glass obtained by reduction melting when Na_2CO_3 was not added to the FG powder is called "Rd-glass", whereas that obtained when Na_2CO_3 was added is called "Rd-glass^{Na}".

In oxidation melting, the FG power (20 g) was melted under atmospheric conditions in an air atmosphere in the same manner as mentioned above. No activated carbon or Na_2CO_3 was used. The glass obtained by oxidation melting is called "Ox-glass".

2.3. Hybrid process (reduction and oxidation melting)

The Rd-glass^{Na} was ground in a mortar and sieved to obtain a powder (particle size <1 mm). This powder was placed in the alumina crucible and melted in the electric furnace under atmospheric conditions reported in the previous section. This hybrid process is called "hybrid process", and the glass obtained by the process is called "Rd–Ox-glass^{Na}". In some experiments, powdered Rd-glass^{Na} (16 g) was melted in the presence of Na_2CO_3 (0.6 g) and $NaNO_3$ (1 g) under atmospheric conditions described above, and the obtained glass materials are called "Rd–Ox-glass$^{Na+Na_2CO_3}$" and "Rd–Ox-glass$^{Na+NaNO_3}$", respectively.

2.4. Two-stage reduction melting

To investigate the effect of remelting atmosphere on lead extraction, a two-stage reduction melting was performed. Powdered Rd-glass^{Na} (16 g, particle size <1 mm) was melted with activated carbon (1 g) under atmospheric conditions described above. The resulting glass is called "Rd–Rd-glass^{Na}".

2.5. Study of glass generated by the melting experiments

The chemical composition of the treated glass was determined by X-ray fluorescence analysis using a Rigaku ZSX Primus II system (Rigaku Co., Ltd., Tokyo, Japan). Based on the chemical compositions, the residual lead in the treated glass is defined as follows:

$$\text{Residual lead in glass}\,(\%) = \frac{R^{\text{Lead}}}{R_0^{\text{Lead}}} \times 100, \quad (1)$$

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

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