Waste Management xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

Lead extraction and glass-ceramics synthesis from waste cathode ray tube funnel glass through cooperative smelting process with coal fly ash

Jianfang Lv, Hongying Yang, Zhenan Jin *, Minglei Zhao

School of Metallurgy, Northeastern University, Shenyang 110819, Liaoning, China

A R T I C L E   I N F O

Article history:
Received 27 October 2017
Revised 9 February 2018
Accepted 9 March 2018
Available online xxxx

Keywords:
CRT funnel glass
Coal fly ash
Carbon-thermal reduction
Lead recovery
Glass-ceramics synthesis

A B S T R A C T

In this study, a novel process was developed for extracting lead from the hazardous waste cathode ray tube (CRT) funnel glass and simultaneously producing glass-ceramics. CRT funnel glass was mixed with coal fly ash and subjected to carbon thermal reduction with the addition of CaO. The homogeneous glass melt and reduced metallic lead were quenched in water. Glass-ceramics were produced from the parent glass through an appropriate heat treatment. The optimum carbon loading amount (calculated as the molar ratio of C/PbO), CaO/SiO_2 ratio, smelting temperature and holding time for lead recovery were 1.0, 0.3–0.6, 1450 °C and 2 h, respectively. Under these conditions, more than 95% of lead can be extracted from the funnel glass and a low lead content of the resultant parent glass below 0.6 wt% was successfully achieved. CaO behaved as a network modifier to reduce the viscosity of the glass and also acted as a substitution to release lead oxide from the silicate network structure, resulting in a high lead separation efficiency. X-ray diffraction (XRD) analysis revealed that the main crystalline phase was gehlenite when 50–70 wt% funnel glass was added. Scanning electron microscopy (SEM) observation showed that well-crystallized crystals occurred in the specimens with 50–70 wt% funnel glass additions, whereas the specimens with 40 wt% and 80 wt% glass additions exhibited a relative low crystallization degree. Furthermore, property measurements, chemical resistance tests and leaching characteristics of heavy metals confirmed the possibility of engineering and construction applications of the superior glass-ceramic products. Overall results indicate that the process proposed in this paper is an effective and promising approach for reutilization of obsolete CRT funnel glass.

1. Introduction

Waste cathode-ray tubes (CRT) from televisions or computer monitors are generated at an increasing rate due to the technical innovation of replacing CRTs by advanced flat panel screens such as liquid crystal, plasma, or OLED (organic light emitting diode) displays (Singh et al., 2016b; Yu et al., 2016). According to a white paper on E-waste Recycling Industry in China (CHEARI, 2013), more than 32 million units of waste televisions and 37 million units of waste computers are produced only in 2013, and 43.11 million tons of CRT glasses are generated in 2013. The peak in CRT waste production was expected in the period 2015–2020 (Yoshida et al., 2016), but in most regions of Asia-Pacific, Eastern Europe, Middle East and Africa, CRT monitors are still in demand by low-income consumers due to the low cost of CRT set (Singh et al., 2016c). The CRT funnel glass contains high level of lead oxide (22–25 wt%) (Mear et al., 2006a; Nnorom et al., 2011) and accounts for about one third of a CRT's total weight (Gregory et al., 2009). Numerous studies have verified that the lead-containing CRT funnel glass is a hazardous waste (Musson et al., 2000; Spalvins et al., 2008), due to the high level of lead, which could be released and dissolved from lead glass, when mixed with acidic ground water in landfills. Currently, most of the discarded CRTs end up in landfills or incinerators, and only a small part is recycled. The CRT funnel glass may pose considerable threats to the environment and human beings if disposed improperly.

Waste CRT funnel glass can be used as secondary raw material to manufacture foam glass (Bernardo et al., 2007; Fernandes et al., 2013; Fernandes et al., 2014; Matamoros-Veloza et al., 2008; Mear et al., 2005; Mear et al., 2006b), glass ceramic (Andreola et al., 2005; Bernardo, 2007; Eftimie and Melinescu, 2015), cement mortar (Li et al., 2017; Ling and Poon, 2011, 2013; Liu et al., 2018), etc. However, these methods are quite problematic from the point of view of environmental security, because the toxic lead contained in funnel glass also transfers to the products but not removed or separated, which precludes the above-mentioned recycling methods. Therefore, lead extraction technologies have been developed

* Corresponding author.
E-mail address: jinzn@smm.neu.edu.cn (Z. Jin).

https://doi.org/10.1016/j.wasman.2018.03.019
0956-053X/© 2018 Elsevier Ltd. All rights reserved.

and employed for the recycling of funnel glass, which can be classified into leaching techniques, e.g., mechanical activation (Singh et al., 2016a; Yuan et al., 2012; Yuan et al., 2015), ultrasonically enhanced lead leaching (Saterlay et al., 2001), subcritical hydrothermal treatment (Miyoshi et al., 2004), chemical-electrochemical method (Pruksathorn and Damronglerd, 2005), zeolite synthesis through hydrothermal treatment (Yao et al., 2017), alkaline leaching with mechanochemical reduction (Zhang et al., 2016) and thermal treatments technique, e.g., carbon thermal reduction (Chen et al., 2009; Hu and Hui, 2018; Lv et al., 2016; Mingfei et al., 2016; Singh and Li, 2017; Xing et al., 2017; Xing and Zhang, 2011), thermal reduction with metallic iron (Lu et al., 2013) and with SiC or TiN (Yot and Mear, 2009), combined thermal treatment and leaching processes (Okada, 2016; Okada et al., 2015; Okada and Yonezawa, 2013, 2014), chloride volatilization (Grause et al., 2014a; Grause et al., 2016; Grause et al., 2014b), etc. Moreover, some novel approaches have also been developed for lead extraction from waste funnel glass in recent years. Xing et al. (Mingfei et al., 2016) proposed a novel process for detoxification and reutilization of waste funnel glass by carbon thermal reduction enhanced acid leaching process, where a high lead removal rate of 94.8% and glass microspheres with the sizes of 0.73 to 14.74 μm were obtained. They also developed a process for extracting lead and preparing high silica glass powder from funnel glass by remelting with B_2O_3 in reducing atmosphere (Xing et al., 2017). Furthermore, Hu et al. (Hu and Hui, 2017; Hu and Hui, 2018) demonstrated that lead could be extracted effectively from funnel glass by generating lead sulfide precipitate via a high temperature melting process, and metallic lead could be recovered by using sodium carbonate powder as a fusion agent, sodium sulfide as a catalytic agent and carbon powder as a reducing agent. These lead extracting technologies, though need further examination and optimization before the final practical application, seem to be more environmentally friendly and applicable for the treatment of obsolete CRT funnel glass when compared with the directly utilization without lead removal.

Coal fly ash, an industrial by-product, is generated during the coal combustion in thermal power plants. The current annual production of coal fly ash is estimated to be more than 500 million tons (Ahmaruzzaman, 2010), a number that continues to increase to account for the growth in power demand. The increasing production of coal fly ash waste has compounded environmental and economic problems worldwide. A considerable amount of research pertaining to the utilization of coal fly ash has been undertaken in the past decade. One of the most promising approaches is converting coal fly ash into high performance glass-ceramic materials (Wang et al., 2014). Coal fly ash contains appreciable amounts of SiO_2, Al_2O_3, CaO and Fe_2O_3, which can be a good candidate for the glass-ceramic production as a low cost raw material source. A common route for producing glass-ceramics from coal fly ash is sintering method, which involves glass preparation at high temperatures and re-heating of the parent glass to two stages heat treatment for internal nucleation and crystal growth (Kim and Kim, 2004; Rawlings et al., 2006). In our previous work (Lv et al., 2016), we have proposed an effective process for recycling lead from waste funnel glass by smelting funnel glass with high lead slag through carbon thermal reduction. Resembling the glass preparation process of glass-ceramics production, the reduction of lead silicate was also performed at high temperatures and required the presence of basic oxides, such as CaO, FeO, and MgO, etc., to replace the PbO from silicate network. Therefore, the glass-ceramics production posed a favorable condition for lead extraction from funnel glass and, in turn, the basic oxides in funnel glass like Na_2O and K_2O were introduced into the glass-ceramics material to improve the product properties.

Accordingly, in the present paper, a novel approach for lead extraction and simultaneously glass-ceramics synthesis from waste funnel glass and coal fly ash was developed. The starting material was made of funnel glass and coal fly ash, with carbon acting as a reducing agent and CaO as an ingredient additive. The influences of the funnel glass addition, the amount of carbon addition, the calcium-silicate ratio, the smelting temperature and the treatment time on lead extraction efficiency were investigated to establish the optimal reducing conditions. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed to investigate the changes in characterization and morphological properties of the obtained glass-ceramics. Furthermore, physicochemical and mechanical properties were measured to confirm the feasibility of using the nucleated glass-ceramics products as construction materials or decoration materials.

2. Experimental procedure

2.1. Starting material

The CRT funnel glass used in this study was provided by an appliance dismantling enterprise in Liaoning province, China. Coal fly ash and anthracite were obtained from a thermal power plant and a metallurgical plant in China, respectively. The chemical compositions of coal fly ash and funnel glass, determined by using X-ray fluorescence (XRF) spectroscopy, are given in Table 1. It is clear that the main constitutes of coal fly ash samples are SiO_2, CaO and Al_2O_3. The chemical composition of coal fly ash is typical of the most common parent glass with ternary systems (Erol et al., 2007). For funnel glass, the main components are SiO_2, PbO, K_2O and Na_2O. XRD pattern of coal fly ash and funnel glass are shown in Fig. 1. As expected, the spectra of funnel glass showed a total amorphous state. Coal fly ash exhibited as a bad-crystallized material and only peaks attributable to SiO_2 were detected in the spectra. Analytical-grade CaO was introduced as an ingredient additive to increase the alkalinity of raw materials. Anthracite was used as a reducing agent, and the carbon loading amount was defined as the molar ratio of C/PbO.

Prior to use the samples were crushed, ball-milled into powder and dried at 105 °C for 24 h. Different amounts of funnel glass, coal fly ash, anthracite and CaO were homogenized by a blender mixer and then placed in an alumina crucible. The weight fractions of the samples are presented in Table 2. The calculation methods for the adding amount of CaO and carbon are also included in the table.

2.2. Experimental procedure

The process route of the technology is shown in Fig. 2. After being homogenized, the samples were transferred into an electric resistance furnace with six U-shape $MoSi_2$ heating elements. The furnace was heated to the target temperatures (1400–1475 °C)

Table 1
Chemical compositions of coal fly ash and funnel glass used for experiments.

Components	Concentration (wt%)	
	Coal fly ash	Funnel Glass
SiO_2	56.9	53.4
PbO	–	20.3
CaO	10.0	4.5
K_2O	2.2	9.9
Fe_2O_3	3.8	0.3
Al_2O_3	21.5	3.7
MgO	1.4	1.7
Na_2O	1.2	4.4
TiO_2	1.2	–

Please cite this article in press as: Lv, J., et al. Lead extraction and glass-ceramics synthesis from waste cathode ray tube funnel glass through cooperative smelting process with coal fly ash. Waste Management (2018), https://doi.org/10.1016/j.wasman.2018.03.019