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Recovering lead from cathode ray tube funnel glass by mechano-chemical extraction in alkaline solution

Chenglong Zhang[1], Jingwei Wang[1], Jianfeng Bai[1], Jie Guan[1], Wenjie Wu[1] and Cuixiang Guo[2]

Abstract

This study evaluates the efficiency of lead (Pb) extraction from cathode ray tube (CRT) funnel glass in strongly alkaline solution using mechanical activation in a ball mill as the chemical breakage and defects formed in the inner structures will contribute to the easy dissolution of the activated Pb glass. The combination of mechanical activation and a chemical leaching process in a single operation (mechano-chemical leaching) is more effective than the mechanical activation and subsequent chemical leaching. More than 97% of Pb in the CRT funnel glass can be extracted with a stirring ball mill leaching process in 5 M sodium hydroxide at 70°C. The diameter of the stainless steel balls as the activation medium is 5 mm; the mass ratio of ball to raw materials is 25:1. Pb powder with a purity of 97% can be obtained by electrowinning from the leaching solution. The Pb-depleted solution can be recycled into the leaching step. After Pb is removed, the solid leaching residues can be used for preparation of foam glass. Thus, a novel hydrometallurgical process for recovering Pb from CRT funnel glass in alkaline solution is proposed.

Keywords

Cathode ray tube (CRT) funnel glass, alkaline leaching, mechano-chemical leaching, electrowinning, lead

Introduction

Lead (Pb) is an important nonferrous metal used in many applications in batteries, solders, dielectric materials, piezoelectric materials, and glass, for example. Pb glass is a variety of glass in which Pb replaces calcium (Ca) in a typical potash glass (Newton and Davison, 1989). Owing to its high x-ray absorption and high diffractive index Pb glass has become very popular, not only as a protection material against radiation, for example from cathode-ray tubes (CRTs), but also as a decorative glass. Owing to the potential health risks of Pb in the glass and other materials, research and development of Pb-free materials as substitutes are being promoted vigorously in all industrial fields.

With rapid development, conventional CRT monitors in televisions (TVs) and personal computers have been replaced by new products such as liquid crystal displays, light-emitting diodes and plasma display panels. Predictions indicate that huge numbers of CRTs will need to be disposed of in coming decades. It is estimated that in China, up to 30 November 2011, a total of around 95 million units of waste household appliances (including 27 million TV sets) were collected owing to the old-for-new home appliance replacement program that was implemented in 2009 (Ministry of Commerce of the People's Republic of China, 2011). Similar situations are also found in most other countries (Nnorom et al., 2011) and CRT waste is thus becoming a global environmental problem.

The main component of CRT glass can be divided into three parts: (i) panel (65%), a barium (Ba) strontium glass; (ii) funnel (30%), a Pb glass containing approximately 20 wt % lead (II) oxide (PbO); and (iii) neck (5%), a very Pb-Pb glass containing approximately 40 wt % PbO (Heart, 2008; Méar et al., 2006b; Xu et al., 2012).

Studies have been carried out by various researchers to address the discarded CRT waste problem, focusing particularly on methods for reuse or recycling leaded funnel glass as it contains a large amount of Pb (Lee and Hsi, 2002; Ling and Poon, 2011). Generally, there are two different routes for leaded CRT glass recycling: closed-loop and open-loop recycling (ICER, 2004; Siikamäki et al., 2002). In closed-loop recycling, discarded CRTs are used to produce new CRT glass. However, this route will partly close because the CRT glass supply will begin to exceed the demand of CRT manufacturing in approximately 2015 (Gregory et al., 2009). In open-loop recycling, the glass is used for other applications, such as flux in metal smelting, foam glass, ceramic glaze and clay bricks (Andreola et al., 2005; Chen et al., 2009; Méar et al., 2006a; Mostaghel and Samuelsson,

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Table 1. Chemical composition of the experimental cathode ray tube funnel glass.

Elements	Aluminium	Barium	Calcium	Bismuth	Iron	Sodium	Lead	Zinc	Magnesium
Wt %	1.44	0.68	3.10	0.05	0.59	5.90	25.1	0.16	1.09

2010). These methods are considered not profitable owing to the potential health risks from lead in the materials (Poon, 2008).

As Pb atoms contained in Pb glass are fixed firmly in the glass network, Pb extraction is incomplete under ordinary temperature and pressure conditions. Pb in Pb glass is so strongly bonded that heating to temperatures higher than 1273 K, at which silicon dioxide (SiO_2) glass will melt, is usually required for extraction, evaporation and removal of lead from the SiO_2 glass network (Sasai et al., 2008). Some technologies, such as chemical reduction or ultrasonic and subcritical technology, have been developed recently for removing the Pb in order to detoxify waste funnel glass (Miyoshi et al., 2004; Saterlay et al., 2001; Yot and Méar, 2009).

The mechanical activation of minerals represents an important development in several solid processing technologies. In extractive metallurgy, activation by intensive grinding decreases the reaction temperature in pyrometallurgy, and increases leaching kinetics of several sulphide and oxide minerals in hydrometallurgy (Baláž, 1991; Godočíková et al., 2002; Welham, 2001). Application of the mechano-chemical technique to various waste disposals has been already reported (Birke et al., 2004; Guo et al., 2010). It is reported how to remove Pb atoms from Pb-glass powder by using the chelating reagent disodium ethylenediaminetetraacetic acid (EDTA) during the wet ball-milling process at room temperature (Sasai et al., 2008). Ninety-two and a half percent of Pb extracted from mechanically activated CRT funnel glass by diluted nitric acid leaching has been reported (Yuan et al., 2012). However, the process to recover Pb from the EDTA or the nitric acid leaching solutions of CRT funnel glass is complex because most of Pb, Ba, Ca, magnesium (Mg) and iron (Fe), etc. will also be dissolved. Alkaline leaching in caustic soda is a method used widely in the extraction of zinc and Pb from ores and wastes (Chenglong and Youcai, 2009; Cuixiang et al., 2007; Youcai and Stanforth, 2000), in which Ba, Ca, Mg, Fe, etc. will not dissolve in alkaline solution. Pb in the alkaline leach solution can be recovered further as metallic powder by electrowinning (Cuixiang and Youcai, 2008).

The objective of this study was to explore a novel process for recovering Pb from CRT funnel glass in alkaline solution through combining mechanical activation and chemical leaching processes into a single operation. The process is compared to the separate mechanical activation and subsequent chemical leaching processes, and the eventual and possible industrial application discussed.

Materials and methods

Materials

The CRT mixed funnel glass, provided by Shanghai Senlan Industrial Waste Management (Shanghai, China), was broken into small pieces (≤10 mm). The average composition of the glass is given in Table 1.

Mechanical activation and leaching

Two leaching methods were studied. The separate mechanical activation and subsequent chemical leaching processes was compared with the combined mechanical activation and chemical leaching process (mechano-chemical leaching).

Leaching of mechanically-activated glass powder. Mechanical activation tests of CRT funnel glass were carried out by using two mills, a planetary ball mill or a stirring ball mill. Stainless steel balls (1–5 mm) were used as the grinding body. The ground particle sizes were 20–200 µm.

Leaching experiments on the mechanically activated CRT funnel glass were carried out in a glass flask placed on a thermostatically controlled magnetic stirrer. The CRT funnel glass powder was immersed into 200 ml sodium hydroxide (NaOH) solution and leached at constant temperature. The solution volume was kept constant by adding water.

Mechano-chemical leaching of leaded glass. Mechano-chemical leaching was performed in a stirring ball mill under the following conditions: 5 mm stainless steel balls used as the activation medium, the mass ratio of ball to raw material was 25:1, the NaOH concentration was 5 M and the room temperature was 70°C. This temperature was chosen according to our previous work (Cuixiang et al., 2007), where the leaching rate of Pb in alkaline solution increased insignificantly when the leaching temperature was over 70°C. As the planetary ball mill is difficult to heat mechano-chemical leaching was performed in a planetary ball mill only at room temperature.

Chemical analysis

After chemical or mechano-chemical leaching, the pulp was centrifuged, and the clear liquid phase was diluted for analysis of Pb in the extract by ICP-AES (inductively coupled plasma atomic emission spectroscopy). The leaching efficiencies of Pb were calculated according to the following equation:

$$\text{Lead extraction} = [(C_1 \times V_1) / (W_2 \times C_2)\ 100\%$$

where W_1 (g) is the mass of glass, V_1 (L) is the volume of leaching solution, C_1 (g L^{-1}) is the Pb concentration in the leaching solution, C_2 (%) is the percent of Pb concentration in the glass.

The raw glass samples and other solid phases were analysed after dissolution using standard methods and subsequent quantification by ICP-AES.

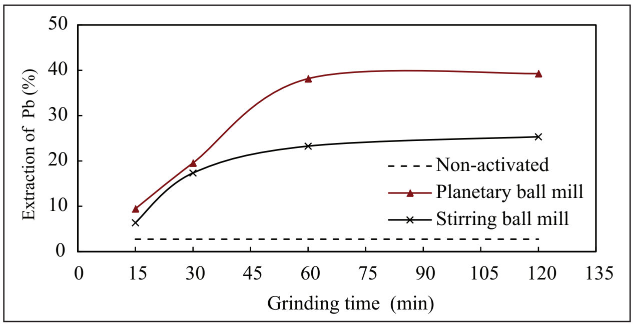

Figure 1. Effect of types of mills for mechanical activation on leaching rate of cathode ray tube funnel glass (sodium hydroxide concentration = 5 M, temperature = 70°C, leaching time = 2 h). Pb: lead.

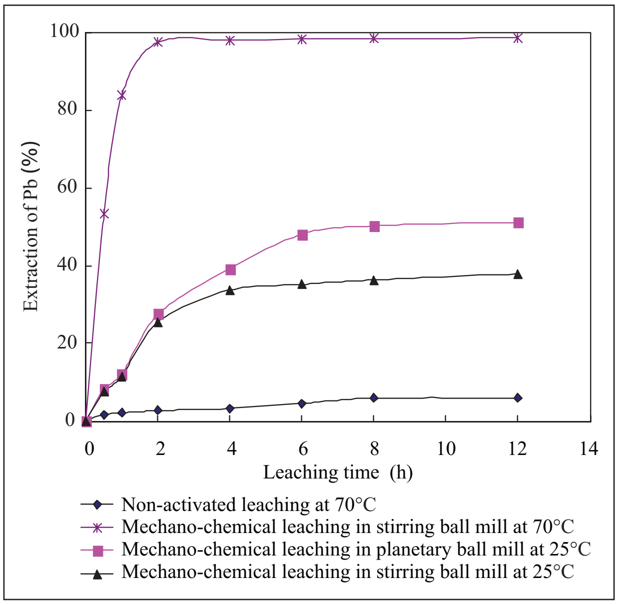

Figure 2. Effect of methods of mechanical–chemical leaching on leaching rate of cathode ray tube funnel glasses (sodium hydroxide concentration = 5 M, mass ratio of balls to raw glass material = 25:1). Pb: lead.

Results

Leaching of activated glass powder

The results of leaching of CRT funnel glasses previously mechanically activated by different mills are shown in Figure 1. By comparison with the non-activated sample, the leaching rate of the mechanically-activated glass increased considerably. The effect of activation in the planetary ball mill was better than that in the stirring ball mill.

The enhancement of the leaching due to mechanical activation is attributed to the increased specific surface area, enhanced surface reactivity and the changes in crystalline structure during the mechanical activation of minerals (Hu et al., 2004). For the nano-crystalline leaded glass, non-bridging oxygen hole centres (≡Si–O·) and peroxy radicals (≡Si–O–O·) are the most important structural point defects in silicate glass, which are generated during the process of mechanical activation (Weber, 1997; Yuan et al., 2012).

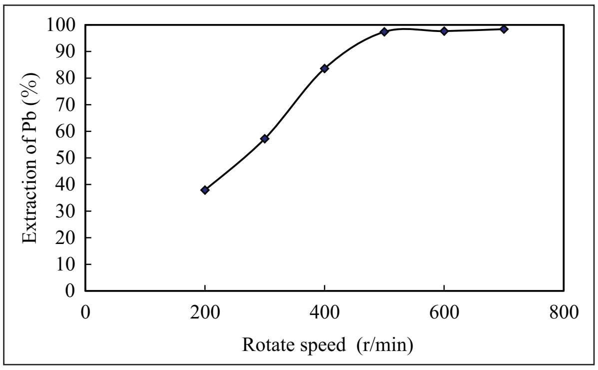

Figure 3. Effect of rotational speed on lead extraction (sodium hydroxide concentration = 5 M, temperature = 70°C, mass ratio of ball to raw materials = 25:1, leaching time = 2 h). Pb: lead.

Leaching of CRT glass in the mechano-chemical modes

Comparative studies were done with mechano-chemical leaching in two different mill types and chemical leaching of raw CRT funnel glass samples (Figure 2). The results confirm the favourable influence of mechano-chemical leaching on the recovery of Pb and that the mechano-chemical leaching efficiencies increased with increasing leaching temperature. The efficiency of Pb extraction by mechano-chemical leaching in a stirring ball mill at 70°C reached 97.4%—much higher than the 2.8% Pb extraction by chemical leaching of non-activated samples and the 27.5% Pb extraction by chemical leaching of previously activated samples for 120 min at room temperature by the planetary ball mill.

During mechanical activation, the structure of a mineral or material is usually disordered, and the generation of defects or other metastable forms can be registered. These effects are not stable and have different relaxation times (Baláž and Achimovičová, 2006). If the process of mechanical activation is preceding leaching a number of highly excited states in the solids may form and decay before leaching. Ljachov (1993) described the concept of slowly changing states after interrupting mechanical activation, which showed that all the short-lived states are not present for subsequent chemical leaching. However, if the mechanical activation and chemical leaching are integrated into a common step (mechano-chemical leaching), all the excitation states can be utilized. Thus, the mechano-chemical leaching enhances the recovery of lead from CRT funnel glass.

Effect of rotational speed

The effect of rotational speed on Pb extraction is shown in Figure 3. Pb extraction increased as the rotational speed increased, and the extraction efficiency of Pb leaching as high as 97.4% was obtained at >500 r/min of rotational speed. It indicated that higher rotational speed of milling produced higher breakage of chemical bonds in the Pb glass.

Table 2. Typical composition of the leaching solution of the glasses.

Elements	Lead	Aluminium	Barium	Calcium	Bismuth	Iron	Zinc	Magnesium
g/l	17.2	0.37	0.048	0.017	0.012	0.007	0.025	0.011

Table 3. Typical electrowinning conditions for production of lead (Pb) from the alkaline leaching solution of cathode ray tube funnel glasses.

Pb (g/l)	Voltage (V)	Current density (A/m^2)	Specific energy consumption (kWh/kg Pb)	Electrical current efficiency (%)	Pb metal purity (%)
17–20	1.7–1.9	400–500	0.6–0.7	97.5%	>97.2

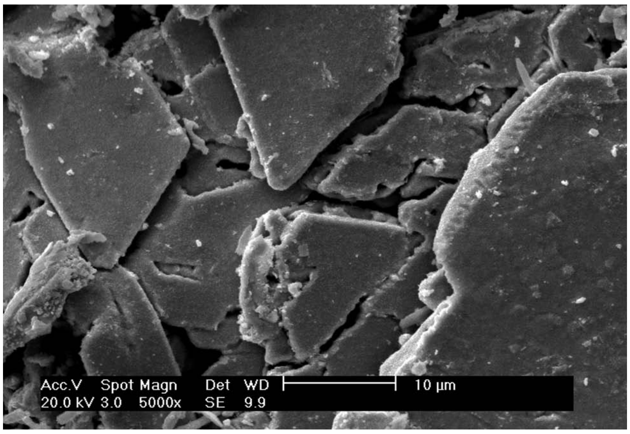

Figure 4. Scanning electron photo micrographs of cathode lead electrowon at 500 A/m^2.

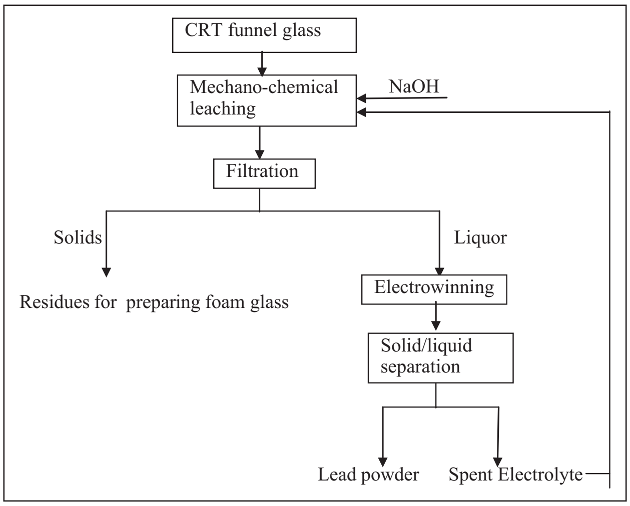

Figure 5. Schematic flow sheet for recovery of lead from lead glasses by alkaline mechanical-chemical leaching and electrowinning. CRT: cathode ray tube; NaOH: sodium hydroxide.

Eletrowinning of Pb powder

Much work has been done on the electrolysis of Pb powder from alkaline solution of PbO (Cuixiang, 2008; Wong and Abrantes, 2005). In this study, the electrolysis process was tested on the leach solution of CRT funnel glasses. The typical composition of leachate of CRT funnel glasses is shown in Table 2. The electrodeposition was conducted under a galvanostatic condition for 2 h at ambient temperature. Experimental results are shown in Table 3. The deposited lead (Pb>97.2 %) was in spongy form and gray with a slight bright metallic lustre. The morphologic structure of the deposited Pb is given in Figure 4.

Discussion

The main species of Pb in strongly alkaline solution is PbO_2^{-2}. The dissolution of Pb in CRT funnel glass in alkaline solution can be represented as:

$$PbO(s) + 2OH\text{-}(aq.) = PbO_2^{-2} + H_2O$$

Based on the experimental results obtained a flow sheet was suggested for an alkaline recovery process for Pb in CRT funnel glass, as shown in Figure 5. Pb in the leachate can be recovered as metallic Pb powder by electrowinning, and the NaOH solution can be recycled to the leaching operation after most of the Pb is electrowon. A high-purity Pb powder with a metallic Pb concentration of >97% can be obtained.

NaOH losses in the whole process may be around 50–60 g per kg of Pb judged titration results. The loss may exceed this figure in practical application as the consumption of NaOH depends on the type and composition of the leaded glass.

The main operational cost of the process may be from the energy consumed by mechano-chemical leaching and electrowinning. Around 4.0–4.5 kWh of electricity is needed for mechano-chemical leaching to recover 1 kg of metallic Pb from the CRT funnel glasses, and the energy needed for electrowinning is around 0.6–0.7 kWh kg^{-1} Pb on average. The operational costs will be around €1000 to recover 1 ton of metallic Pb from the CRT funnel glasses. Thus, the profit can reach around €750 per ton of metallic Pb according to the official prices of Pb powder on 2012, excluding initial investment costs.

After the Pb in the waste CRT funnel glasses is removed through alkaline leaching, the solid residues with fine granularity may be used to prepare foam glass in an economically and environmentally friendly way. Further experiments are ongoing to find the best conditions for the production of foam glass.

Comparing the developed process with other current methodologies, the mechano-chemical alkaline leaching and electrowinning methodology for recovering Pb from CRT funnel glasses is a simple process, with a high recovery of Pb metal powder with high purity from waste CRT funnel glass.

Conclusion

Pb in waste CRT funnel glasses can be leached effectively and transferred into NaOH solution by a combined mechano-chemical process. Pb powder with high purity can be obtained by electrowinning the leaching solution. The Pb-depleted solution can be recycled into the leaching step. After Pb is leached away, the leached solids can be characterized as a non-hazardous waste and be used to prepare foam glass. An environmentally friendly and efficient method is proposed to deal with the impending troublesome issue of Pb recovery from increasing amounts of waste CRT funnel glasses and other leaded glasses.

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