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Research paper

Lead recovery from waste CRT funnel glass by high-temperature melting process

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HIGHLIGHTS

- Lead silicate in the waste CRT glass was reacted into lead sulfide by sodium sulfide.
- CRT funnel glass was sintered into glass slag in the high-temperature melting process.
- Lead sulfide was reduced into metallic lead.
- The generated metallic lead was collected at the bottom of the crucible.

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ABSTRACT

In this research, a novel and effective process for waste CRT funnel glass treatment was developed. The key to this process is removal of lead from the CRT funnel glass by high-temperature melting process. Sodium carbonate powder was used as a fusion agent, sodium sulfide serves as a catalytic agent and carbon powder acts as reducing agent. Experimental results showed that lead recovery rate increased with an increase in the amount of added sodium carbonate, sodium sulfide, carbonate, temperature and holding time initially, and then reached a stable value. The maximum lead recovery rate was approximately 94%, when the optimum adding amount of sodium carbonate, sodium sulfide, carbonate, temperature and holding time were 25%, 8%, 3.6%, 1200 °C and 120 min, respectively. In the high-temperature melting process, lead silicate in the funnel glass was firstly reduced, and then removed. The glass slag can be made into sodium and potassium silicate by hydrolysis process. This study proposed a practical and economical process for recovery of lead and utilization of waste glass slag.

1. Introduction

Waste CRT funnel glass are dismantling products of waste TV and computer display, which are the world's second major waste lead resources. At present, CRT technology for televisions and computers is obsolete, the market for new CRTs is dwindling and with almost no CRT manufacturers left to turn glass from end-of-life screens back into new televisions and monitors [1–3]. Recycling lead from waste CRT glass is an important issue for recycling metal and preventing lead pollution.

Lead removal from waste CRT glass has been studied in domestic and foreign country [4]. Although the waste CRT glass can be made into crafts and anti-radiation glass, the market demand is small [5,6]. The CRT glass can also be used to manufacture foam glass [7–10], building thermal insulation material [11,12], but the adding value of these products is small. In addition, waste funnel glass could be used as metal smelting flux [13] and compound glass ceramic [14], among others. However, heavy metallic lead in waste CRT glass still exists, these methods still have potential threat to the environment and human health.

The difficulty of treating waste CRT funnel glass is the complex structure of CRT glass. Lead atoms contained in lead glass are firmly fixed by encapsulation in the cavity of the glass network, which mainly consists of the —O—Si—O network and partly consists of the structural component of the glass network such as —O—Si—O—Pb—O— [15]. Lead oxide is tightly enveloped in silica tetrahedron, thereby limiting the leaching efficiency of lead [16,17]. In order to deal with waste CRT funnel glass safely, various approaches have been proposed for lead recovery from CRT funnel glass by researchers. These methods can be classified into pretreatment, solution leaching and thermal reduction [18] in high temperature. Some pretreatments include mechanical activation

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Table 1
Chemical composition of the waste funnel glass by X-ray fluorescence (XRF).

Oxide	wt/%
SiO_2	51.09
PbO	22.08
K_2O	6.15
Na_2O	6.67
Al_2O_3	3.63
CaO	3.86
MgO	2.70
BaO	1.24
Others	2.58
Total	100

method [19–22], subcritical water [23] and ultrasonically enhanced leaching [24]. However, these process have some defects, long process time, high energy consumption, additional thermal agents, the recovery rate of lead is not high. Leaching solution contains water, acid [25,26] and alkaline [27]. Some thermal reduction process were developed to lead recovery from waste CRT funnel glass, such as pyrovacuum reduction, chloride volatilization [28–30], hydrothermal sulphidisation [31,32], self-propagating method [33] et al. Nevertheless, these technologies still have some disadvantages, such as harsh reaction condition, the other components in the glass are not effectively utilized, lack of economic feasibility, and too complicated for industrial production.

In order to explore methods of dealing with the waste CRT glass and resources utilization, on the base of high-temperature reduction process [34–37], the author has carried out the research of preparation of water glass from scrap CRT glass by hydrometallurgical process, and experimental study of precipitating and recovering lead sulfide from waste CRT glass in the melting process [38], then putting forward directly reduction of metal lead and simultaneously method of generating water glass from waste CRT glass. This study aims to explore suiTable adding amount of flux, precipitant, and reducing agent and reaction conditions such as temperature and holding time in the melting reduction, providing technical support for utilization of the resource of waste CRT leaded glass.

2. Materials and methods

2.1. Materials

All agents include waste CRT leaded glass, sodium sulfide (Na_2S), sodium carbonate (Na_2CO_3), carbon (C) powder. Waste CRT leaded glass was got from a 34 inch scrap color TV picture tube glass funnel, and Chemical composition of the funnel glass was measured by X-ray Fluorescence(EDX3000; Shimadzu, Tokyo, Japan) as shown in Table 1. The waste CRT leaded glass was broken, crushed, grinded, passed through 100-mesh sieve. The powder was dried at 106 °C for 24 h. Sodium carbonate was analysis agent. Wiping agglomeration, particle passed 100-mesh sieve. Carbon after crushing passed through 80-mesh molecular sieve. Pure Na_2S was crushed and passed through 80-mesh sieve. Other materials used in the experiments were all analytical reagents unless otherwise mentioned.

2.2. Experimental process

The specific process route is shown in Fig. 1 and can be divided into two stages: the recovery of metallic lead and the extraction of silicate solution.

2.2.1. Generating lead process

In the generation of metallic lead, 100 g of waste funnel glass power was homogeneously mixed with 0–30 wt% sodium carbonate power (particle size <100 mesh, used as a flux) and 0–10 wt% sodium sulfide (particle size <80 mesh, used as a precipitating agent) and 0–6.0 wt% carbon powder(particle size <80 mesh, used as a reducing agent). Each mixture was placed in a 300 ml cylindrical crucible, which was then placed in a box-type resistance furnace (XS-6-13; Jingwei Electric Furnace, Yixing, China). The temperature was linearly increased from room temperature to 950–1250 °C over 60–90 min and held for 60–180 min.

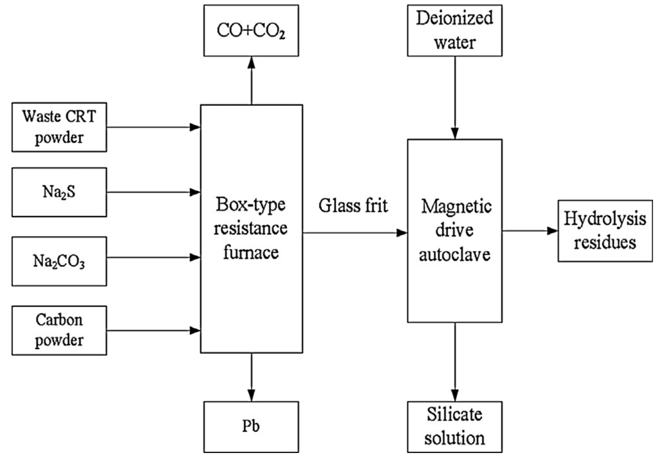

Fig. 1. Process route of the technology.

The maximum melting temperature in this experiment was 950, 1000, 1050, 1100, 1150, 1200, and 1250 °C; the amount of added sodium carbonate power was 0, 5, 10, 15, 20, 25, and 30 wt%; the amount of added sodium sulfide power was 0, 2, 4, 6, 8, and 10 wt%; the amount of added carbon powder was 0, 1.2, 2.4, 3.6, 4.8, and 6.0 wt%; and the holding time was 60, 120, and 180 min. The hearth of the box-type resistance furnace was gradually cooled to room temperature. There is clear boundary between glass frit and metallic lead, so it is easy to extract lead from glass frit. The metallic lead obtained at the bottom of the crucible was taken out and weighed for further analysis.

2.2.2. Hydrolysis process

The glass frit was crushed, ground and sieved through a 100-mesh sieve. In the hydrolysis process, 100 g of glass frit powder mixed with 200 ml of distilled water was placed into a magnetic drive autoclave (GS1L, Zhengwei Machinery, Shanghai, China) and agitated at 200 °C(at the pressure of the system) for 4 h. The hydrolysis residue was then separated from the silicate solution by filtration and then washed twice with ion exchanged water. The silicate solution is concentrated and purified for further analysis. The removal gray residue was dried and weighed for further analysis.

2.3. Analysis

The composition of the raw waste CRT glass and silicate crystals were examined by automatic XRF spectrometry (EDX3000; Shimadzu, Tokyo, Japan). The hydrolysis residue were digested (HNO_3-$HClO_4$-HF) and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES; Vista MPX; Varian, CA, USA). The analytical accuracy of XRF was 0.05%; the range of analysis was ^{5}B to ^{90}U; and the voltage was 5–50 keV. The lead recovery rate was calculated according to the lead content before and after the high-temperature melting process. All experiments were repeated thrice, and only the mean values were reported.

The structure and composition of the raw CRT funnel glass, the recovered metal, and hydrolysis residue were characterized by X-ray diffraction (D/max-2500PC; Rigaku, Tokyo, Japan). The morphology and structural characteristics of hydrolysis residue were examined by scanning electron microscopy(S-4800; Hitachi,