A typical e-waste—cathode ray tube glass: alkaline leaching in the sulfur-containing medium

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Abstract

With more and more cathode ray tube (CRT)-based sets reaching their end-of-life or being replaced, how to deal with the CRT glass has become a global concern due to its high lead level. There is a pressing and ongoing need to develop new recycling methods for CRT glass. In this work, the alkaline leaching of CRT funnel glass in the sulfur-containing medium (S and NaS) was probed. The effects of alkaline concentration, S/Pb molar ratio, temperature and leaching time were investigated. The results showed that the recovery rate of both Si and Pb increased with increasing alkaline concentration; however, it decreased again when the concentration was higher than the critical value 6 M. The recovery rate of Pb in both media decreased with increasing S/Pb molar ratio. As a comparison, the recovery rate of Si did not change significantly. The extraction of Si and Pb, especially Si, tightly depended on the temperature. They also increased with extending of time, however, they tended to decrease when the reaction time exceeded 8 h. The optimal condition was determined as: alkaline concentration 6 M, S/Pb molar ratio 1.0:1, temperature 180 °C and leaching time 8 h.

1. Introduction

Cathode ray tube (CRT) has been widely used in televisions and computer displays for more than 100 years[1,2]. However, with the innovation of display device technology, the CRT has been gradually replaced by the liquid crystal display, plasma display panel and digital light procession. With more and more CRT-based sets reaching their end-of-life or being discarded, a large amount of CRT glass will be generated and thus how to deal with it...
becomes a significant environmental problem. A typical CRT consists of three primary components—the glass envelope, the electron gun assembly, and the phosphor viewing surface. Among them, the glass envelope consists of an optically flat face plate, a funnel section, and a neck section. The funnel is made of lead silicate glass and contains approximately 20 wt.% PbO [3-5]. The high level of lead in the CRT funnel glass becomes an environmental concern, because the toxicity characteristic leaching procedure (TCLP) analysis has confirmed its hazardous characteristics [6-10]. There is a pressing and ongoing need to develop new recycling methods for CRT glass.

The closed-loop recycling and best practicable option is using it to manufacture new CRT screens. However, with the increasing replacement of CRTs with flat-panel displays, the demand for CRT displays has shrunk drastically [11]. In China, the CRT manufacturers have ceased production of CRT sets since the end of 2012. In order to develop alternative recycling methods, some researches have been conducted using it as raw material to prepare concrete and cement [12,13], foam glass [14,15], ceramic glaze [16], and clay brick [17,18]. However, for these solutions, the lead remains in the regenerated products, which might migrate into the environment and threaten human health. Thus, it is necessary to recover lead from the CRT glass to produce a lead-free product or more ideally for glass recycling purposes. Recently, some technologies have been developed, such as the self-propagating process [19,20], the reduction process by reaction with silicon carbide and titanium nitride [21], power ultrasound, subcritical water, and mechanical activation facilitating the lead removal [22-24]. One of the cleanest ways of removing undesirable elements from solid materials is via some kind of leaching protocol [25-27]. However, to the best of our knowledge, there are no reports on the alkaline leaching of CRT glass. In this work, we attempted to study the alkaline leaching behavior of CRT funnel glass in the sulfur-containing medium (S and NaS) to develop a potential green route for CRT recycling. The effects of various factors, including the alkaline concentration, S/Pb molar ratio, temperature, and leaching time on the recovery rate of Si and Pb were investigated.

2. Materials and Methods

2.1 Material

CRT funnel glass was collected from Henan Ancai Hi-Tech Co., Ltd. The glass block was first crushed into small pieces and then ground in a horizontal planetary ball mill (Pulverisette 7, Fritsch). Its chemical composition consists of the following oxides (in wt.%): SiO2 51.02, PbO 21.15, Na2O 9.75, K2O 6.30, Al2O3 3.60, CaO 3.45, MgO 3.38, and other compounds 1.35.

2.2 Alkaline leaching

In this series of leaching test, variable amounts of NaOH were added into distilled water to prepare alkaline solutions with different concentrations (4, 6, 8, 10, 12, 15 and 20 M). Then, the CRT funnel glass was added with a liquid/solid ratio of 4:1. The sulfur (S and NaS) was also added according to the S/Pb molar ratio (1.0:1, 1.2:1, 1.5:1, 2.0:1, and 3.0:1) under continuous stirring. The mixture was put into a Teflon-lined stainless steel autoclave and thereafter the leaching was conducted. The temperatures and leaching time were set at desired temperatures (120, 140, 160, 180 and 200 °C) for a scheduled time (8 h, unless otherwise stated). Once the time was reached, reactors were removed from the oven and quenched in cold water. The mixture was then filtered and the concentration of Si and Pb in the filtrate was tested.

2.3 Characterization and test

The chemical composition of CRT funnel glass was measured by X-ray fluorescence spectrometry (XRF, ARL ADVANT’ X IntelliPowerTM 4200, Thermo Fisher, U.S.A). Concentrations of lead and silicon were measured by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Optima 2100 DV, Perkin Elmer, USA).
3. Results and discussion

3.1 Effect of alkaline concentration

A series of experiments were undertaken to investigate the effect of alkaline concentration on the recovery rate of Si and Pb. From Fig. 1, it can be seen that the recovery rate for both Si and Pb increased with increasing alkaline concentration when the concentration was lower than 6 M; however, it decreased again when the concentration was higher than the critical value. With the concentration increasing from 4 to 6 M, the recovery rate of Si and Pb in the NaS medium increased from 74.8 to 88.3% and 12.7 to 41.3%, respectively. As a comparison, the recovery rate of Si and Pb in the S medium increased from 60.0 to 66.7% and 39.3 to 41.8%, respectively. This may be attributed to the greater alkaline concentration the faster reaction, which thus incurred the forming of silica gel. The gel would cover on the glass surface and inhibit its reaction with alkali [28]. The results indicated that the optimal alkaline concentration was 6 M and it was selected for further studies.

![Fig. 1. Recovery rate of Si and Pb with a function of alkaline concentration (leaching conditions: temperature 180 °C, leaching time 8 h, L/S ratio 4:1, and S/Pb molar ratio 1.0:1)](image)

3.2 Effect of S/Pb molar ratio

The effect of S/Pb molar ratio on the recovery rate of Si and Pb is displayed in Fig. 2. It can be observed that the recovery rate of Pb in both media decreased with S/Pb ratio increasing. As a comparison, the recovery rate of Si did not change significantly, although a decreasing trend was observed when the S/Pb ratio was larger than 2.0:1. This
was due to that the Pb leached from the CRT glass was precipitated by sulfur and thus the dissolved Pb decreased. Comparing the recovery rate of Si and Pb in both media, it can also be found that adding NaS could facilitate the reaction. The results indicated that the preferred S/Pb ratio was 1.0:1 and it was selected for further studies.

![Graph showing recovery rate of Si and Pb with function of S/Pb molar ratio](image)

**Fig. 2.** Recovery rate of Si and Pb with a function of S/Pb molar ratio (leaching conditions: alkaline concentration 6 M, leaching time 8 h, temperature 180 °C, and L/S ratio 4:1)

### 3.3 Effect of temperature

The extraction of Si and Pb, especially Si, tightly depended on the temperature (see in Fig. 3). When temperature increasing from 100 to 180°C, the recovery rate of Pb increased from 34.3 to 68.3% and 52.6 to 88.2°C, respectively, in the S and NaS medium. This also confirmed the better leaching efficiency in the NaS medium. As a comparison, the recovery rate of Si increased from 4.2 to 38.3% and 0.4 to 41.3%, respectively. However, further increasing the temperature would result in a decrease of the recovery rate. In addition, taken into account of the equipment and leaching cost, the temperature should not be higher than 180 °C, which was also selected for further studies.
3.4 Effect of leaching time

The effect of leaching time on Si and Pb extraction was also investigated and the results were illustrated in Fig. 4. It can be observed that the extraction efficiency for both Si and Pb increased with the extending of time. However, it tended to decrease when the reaction time exceeded 8 h. This was because that the alkaline concentration was large at the initial of reaction and the active sites of funnel glass could efficiently contact with alkali. With the proceeding of reaction, the internal diffusion rate reduced and the alkaline concentration decreased, thus the recovery rate decreased. The optimal leaching time was determined as 8 h for lower energy consumption and higher efficiency.
Fig. 4—Recovery rate of Si and Pb with a function of reaction time (leaching conditions: alkaline concentration 6 M, temperature 180 °C, S/Pb molar ratio 1.0:1, and L/S ratio 4:1)

4. Conclusions

The alkaline leaching behavior of CRT funnel glass in the sulfur-containing medium was investigated to develop a potential greener route for CRT recycling. The recovery rate for both Si and Pb increased with increasing alkaline concentration when the concentration was lower than 6 M; however, it decreased again when the concentration was higher than the critical value. The recovery rate of Pb in both media decreased with S/Pb increasing. As a comparison, the recovery rate of Si did not change significantly, although a decreasing trend was observed when the S/Pb molar ratio was larger than 2.0:1. The extraction of Si and Pb, especially Si, from the CRT glass tightly depended on the temperature. The extraction efficiency for both Si and Pb increased with the extending of time. However, it tended to decrease when the reaction time exceeded 8 h. The optimal condition was determined as: alkaline concentration 6 M, S/Pb molar ratio was 1.0:1, temperature 180 °C and leaching time 8 h.

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References


