



Lead recovery and the feasibility of foam glass production from funnel glass of dismantled cathode ray tube through pyrovacuum process

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ABSTRACT

Cathode ray tube (CRT) is the first and foremost problem that must be solved in electronic waste disposal, and the key of which lies in the detoxification and reutilization of lead-contained funnel glass. In this study, a novel and effective process for funnel glass of dismantled CRT treatment was developed. The key point of the process was to recover metallic lead from the funnel glass and to prepare foam glass synchronously. Experimental results showed that lead recovery rate increased first with the increase of temperature, carbon adding amount, and holding time, then reached a plateau value, but pressure was on the contrary. The optimum temperature, pressure, carbon adding amount and holding time for lead recovery were 1000 °C, 1000 Pa, 5% and 4 h, respectively, and the maximum lead recovery rate was 98.6%. In the pyrovacuum process, lead in the funnel glass was firstly detached and changed to PbO, then reduced and evaporated, and was recovered in the form of pure metal with a purity of 99.3%. The residue porous glass was environmentally acceptable for construction application.

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1. Introduction

The use of electrical and electronic equipment (EEE) has dramatically proliferated in recent decades, and proportionately, the quantity of wastes from EEE (WEEE), such as personal computers (PC), mobile telephones and entertainment electronics, is growing rapidly. It has been reported that the growth trend of WEEE represents a growth three times faster than that of the average municipal waste [1].

With regard to China, WEEE is generally sourced both from domestic generation and illegal imports. For domestic generation, TVs, refrigerators, washing machines and PCs are the main items. These equipments were widely used in the middle or the latter of the 1980s, and should have been replaced by new types after 2000. For example, there are more than 5 million TV sets, 4 million refrigerators, 6 million washing machines, 5 million personal computers and 10 million units of mobile telephones were discarded after 2001 [2]. On the other hand, China is the destination for a substantial proportion of WEEE from developed countries, e.g., representatives within the United States' recycling industry have indicated that around 80% of the WEEE they receive is exported to Asia, and 90% of which goes to China [3]. Accordingly, WEEE is becoming a significant waste stream, both in terms of quantity and toxicity,

causing a severe problem to the environment, people health and sustainable economic growth. Guiyu, located in southern China, is one of the most representative examples, where thousands of farmers, without protective equipments, are now engaged in primitive and highly polluting electronic waste recycling [4].

At present, the WEEE recycling industry is typically disorganized in China, and the situation of which has been well summarized by He et al. [5] and Liu et al. [6]. Valuable matters in WEEE, such as copper loop, electronic gun, printed circuit board etc., are generally separated and collected for monetary purpose, but the hazardous and less valuable materials are usually discarded. Thus the key point to serve this situation is to recycle and disposal such types of wastes. Among these materials, cathode ray tube (CRT) glass should be considered firstly. Waste CRT, containing high content of Pb in the funnel glass (20–30% PbO [7]), has been listed by the China EPA as hazardous waste. It has been reported that this type of waste accounts for approximately 47% by weight of commercial electronic devices and 30% by weight of data processing equipment [8].

In recent years, many scholars have paid great attention to the recycling of CRT glasses, and both closed-loop recycling (waste CRT to new CRT) and open-loop recycling (waste CRT to new products such as foam glass) were promoted. For the manufacture of new CRT, it could be profitable only in the case of an absolute separation of the lead-contained and uncontained glass, because the introduction of lead-contained glass in panel manufacturing is not acceptable for the solarization effect [1]. On the other hand, the

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

Oxide	wt%
SiO ₂	49.61
PbO	24.17
K ₂ O	7.79
Na ₂ O	5.32
Al ₂ O ₃	3.63
SrO	2.99
CaO	2.30
BaO	1.96
MgO	1.49
ZrO ₂	0.58
Fe ₂ O ₃	0.07
P ₂ O ₅	0.07

addition of panel glass to the funnel or neck glass is limited, since the mixture of Pb and Ba glasses has inferior mechanical properties [9]. Moreover, new products such as Liquid Crystal Display (LCD) and Plasma Display Panel (PDP) significantly cut down the production scale of CRT TVs in the very near future. Therefore, a dramatic reduction of closed-loop recycling is anticipated. Accordingly, most of recent studies on waste CRT mainly focused on open-loop recycling, e.g., it has been used as second raw material to manufacture lead glass [10], glass foam [11,12], glass matrix composites [13,14], glass-ceramics [15,16], and glaze [17].

Although funnel glass recycling is the key point of CRT glass recycling, only limited previous reports discussed funnel glass reutilization [18,19]. Among these reports, dangerous heavy metal lead was generally transferred from the hazardous waste to new products but not removed or separated, hence the threat still remains. On some occasions, for example, glass foam prepared by powder technology from wasted CRT funnel glass [19], the threat could even be more aggregated because lead and other metals changed to crystal state from vitreous state which increased their leaching ability doubtlessly. As to our best knowledge, no other studies were reported on how to effectively separate lead from funnel glass except a report by ICER (2003) who concluded that this might be the last choice [20].

The objectives of this research were to: (1) examine lead recovery efficiency from funnel glass by pyrovacuum reduction and optimize the affecting factors; (2) synchronously transfer the residue into foam glass in the reduction process and evaluate the environmental safety of the product.

2. Materials and methods

2.1. Sample preparation

Funnel glasses of PC monitor was provided by Huaxing Environmental Protection Corporation. The glass was crushed into small pieces (around 3 cm) and coatings were fully removed by wet-scrubbing method [21]. Then the cleaned funnel glass particles were dry ball milled and sieved to smaller than 80 mesh, and the powder obtained was dried at 105 °C for 24 h. Chemical composition of the glass powder was examined by XRF and the results were presented in Table 1. Other materials used in the experiments were all analytical reagents unless otherwise mentioned.

2.2. Pyrovacuum reduction process

A brief scheme of the experimental system was shown in Fig. 1. In the pyrovacuum process, 5.00 g funnel glass powder were homogeneously mixed with 0–9% carbon powder (particle size <100 mesh, employed as reducing agent), and loaded in the sample boat, which was then placed in a quartz tube. The quartz tube was previ-

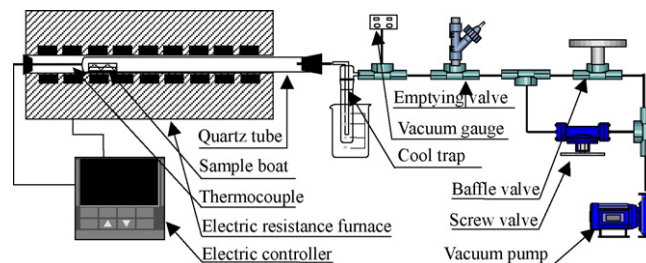


Fig. 1. Schematic diagram of the experimental system.

ously pumped to the setting pressure, then directly inserted to the tubular furnace (heated to the preset temperature) and held for 0.5–6 h. After pyrovacuum treatment, the quartz tube was taken out and cooled down to room temperature. Then the quartz tube was released to the ambient pressure, and the residue in the boat was taken out and weighed. The examined temperatures were 600, 700, 800, 900 and 1000 °C, vacuum pressures were 10, 100, 1000 and 10,000 Pa, carbon adding amounts were 0, 2, 5 and 9%, and holding times were 0.5, 1, 2, 4 and 6 h, respectively.

2.3. Residue analysis

After the treatment, the residues were digested (HNO₃–HClO₄–HF) [22] and analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, OPTIMA 2000, PerkinElmer, USA). Lead recovery rates were calculated according to the lead content before and after the pyrovacuum reduction treatment.

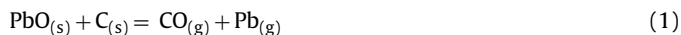
The recovered metal were characterized by X-ray diffraction (XRD) using the Ni-filtered Cu K α radiation on a Rigaku D/MAX2500 diffractometer. Lead leaching behavior of the residues was evaluated according to the Toxicity Characteristic Leaching Procedure (TCLP) of USEPA. The morphology of the foam residue was examined by scanning electron microscopy (SEM, S-3000N, Hitachi, Japan).

3. Results and discussion

3.1. Effect of temperature on lead recovery rate

In the pyrovacuum process, lead oxide in the funnel glass is considered to be firstly reduced to metallic lead, then the lead evaporated into gaseous phase and was recovered after cooled down. Temperature is a key factor for both lead oxide reduction and metallic lead evaporation. Fig. 2 shows that lead recovery rate increased sharply with the increase of temperature below 800 °C, e.g., increased from 21.9% at 600 °C to 89.1% at 800 °C, then reached a plateau value at above 800 °C. When the temperature is 1000 °C, lead recovery rate reached 97.5%.

The stoichiometry of lead monoxide reduction by carbon powder in the funnel glass could be illustrated as follows [23,24]:



$$\Delta G_T = 289427 - 481.88T + 2RT \ln p(328 - 885 \text{ } ^\circ\text{C}) \quad (2)$$

where ΔG_T is the Gibbs free energy at a certain temperature, R is the universal gas constant, T is treatment temperature and p is the system pressure. The redox reaction between PbO and C takes place when $\Delta G_T < 0$. Under the pyrovacuum conditions in this study ($p = 10$ Pa), according to Eq. (2), PbO can be reduced to Pb by carbon when the temperature is higher than 380 °C ($\Delta G_T = 0$, $T = 380$ °C). Since the examined temperatures in the experiments

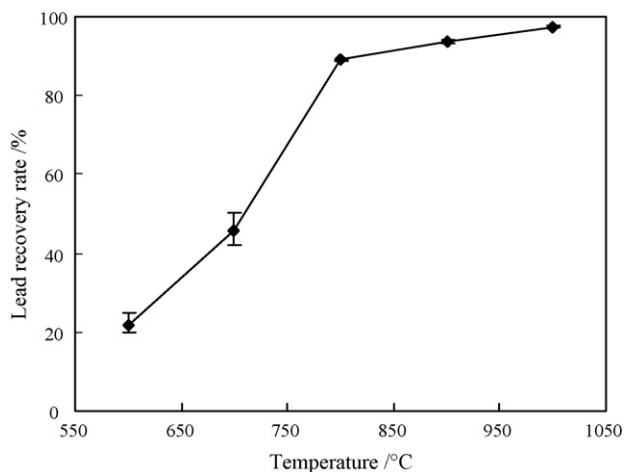


Fig. 2. Effect of temperature on lead recovery rate. Other conditions: pressure = 10 Pa; carbon adding amount = 9%; holding time = 4 h.

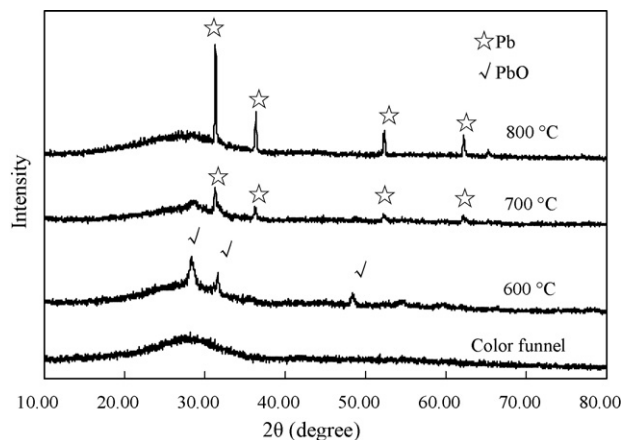


Fig. 3. XRD patterns of raw funnel glass powder and pyrovacuum residues. Other conditions for the residues: pressure = 10 Pa, carbon adding amount = 9%, holding time = 4 h.

were all higher than 380 °C, PbO in the glass sample was considered to be reduced to metallic Pb, but lower recovery rate for Pb was obtained within 380–800 °C, indicating that the reduced Pb could not be effectively recovered. Therefore, the key factor restricting Pb recovery rate at <800 °C was the evaporating velocity of the reduced Pb. This could be attributed to the fact that the saturated

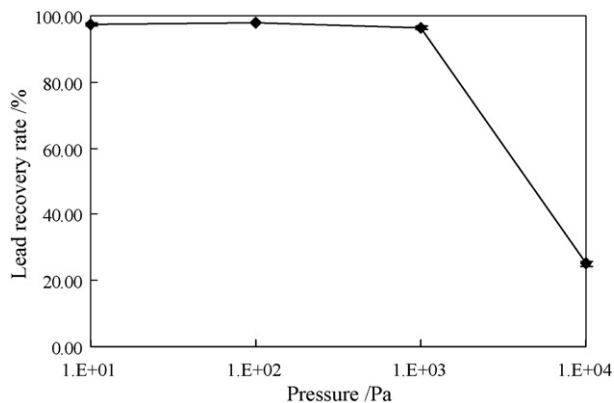


Fig. 4. Effect of pressure on lead recovery rate. Other conditions: temperature = 1000 °C, carbon adding amount = 9%, holding time = 4 h.

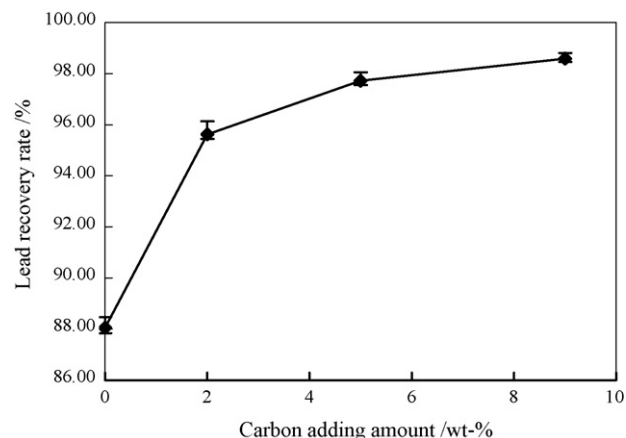


Fig. 5. Effect of carbon adding amount on lead recovery rate. Other conditions: temperature = 1000 °C, pressure = 1000 Pa, holding time = 4 h.

vapor pressure of metallic lead was significantly lower than the operation pressure 10 Pa, e.g., at 700 °C, the saturated vapor pressure of metallic lead is merely about 0.1 Pa. At above 800 °C, the reduced metallic Pb could immediately evaporate and be recovered since the boiling point of Pb was about 800 °C at 10 Pa [24], thus a plateau value was reached.

Fig. 3 presents the XRD patterns of the original funnel glass and the pyrovacuum residues obtained at different temperatures. No crystalline phase for the original glass sample was observed, but crystalline PbO appeared at 600 °C and the diffraction peaks of metallic Pb appeared while PbO disappeared at 700 °C or higher. It is well known that funnel glass is mainly produced from Pb₃O₄ (instead of PbO) to ensure oxidizing conditions, therefore a certain amount of oxygen is dissolved within the funnel glass. Accordingly, a possible mechanism for Pb recovery in the pyrovacuum process was proposed: at around 600 °C, the dissolved oxygen was attacked by carbon and released, the local structure of the lead oxide in the funnel glass changed leading it detaching from the funnel glass, thus crystalline PbO was formed. Along with the further increase of the temperature, PbO was completely reduced by carbon to Pb, and then Pb evaporated and was recovered.

3.2. Effect of pressure on lead recovery rate

Lead removal rate was almost the same (nearly 100%) when the pressure was lower than 1000 Pa, but it dropped down extremely at pressure higher than 1000 Pa, e.g., about 20% at 10,000 Pa (Fig. 4). Therefore, 1000 Pa is considered to be the optimum pressure.

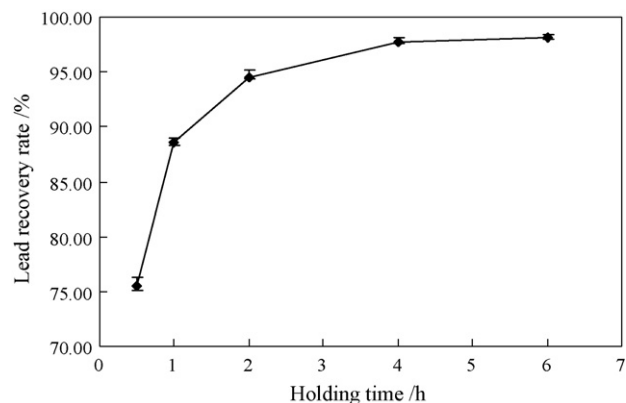


Fig. 6. Effect of holding time on lead recovery rate. Other conditions: temperature = 1000 °C, pressure = 1000 Pa, carbon adding amount = 5%.

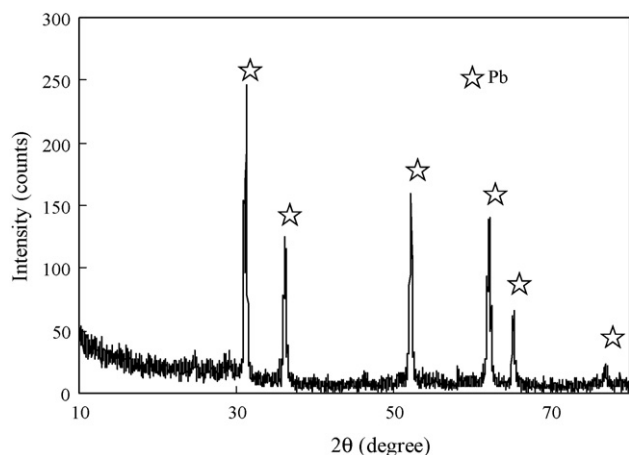


Fig. 7. XRD pattern of recovered metal.

System pressure, which affects lead evaporation velocity greatly, is another key point to the lead recovery rate. Generally, at a constant temperature and pressure (<1000 Pa), metal evaporation velocity increases sharply with the decrease of pressure, and then reaches its maximum as the pressure reducing to a certain value. This pressure is called critical pressure. According to a previous report [24], the critical pressure of lead at 1000 °C is 100 Pa, therefore 100 Pa is considered to be the turning point of Fig. 4, but the turning point found in Fig. 4 is 1000 Pa, where lead recovery rate is thought to be much lower than those of 100 Pa and 10 Pa. This indicates that lead evaporation velocity of 1000 Pa is still faster enough for lead completely evaporating from the funnel glass within 4 h, although it is far lower than those of 100 Pa and 10 Pa.

3.3. Effect of carbon and holding time on lead recovery rate

Fig. 5 indicates the effect of carbon adding amount on the lead recovery rate. Lead recovery rate increased with the increase of carbon adding amount, and then reached its maximum value at 5%. This percentage was considered to be the optimum carbon adding amount.

Fig. 6 illustrates that the highest lead recovery rate was obtained at a holding time of 4 h. Therefore, it is recommended that 4 h is the optimum holding time with temperature, pressure and carbon adding amount fixed at 1000 °C, 10 Pa and 5%, respectively.

Table 3

TCLP analytical results for the residues after the pyrovacuum process

Temperature (°C)	Pressure (Pa)	Carbon adding amount (%)	Holding time (h)	Recovery rate (%)	Pb (mg/L)
600	10	9	4	21.94	262.71
700	10	9	4	45.52	159.37
800	10	9	4	89.05	113.64
900	10	9	4	93.53	5.91
1000	10	9	4	97.47	1.29
1000	100	9	4	97.80	1.06
1000	1000	9	4	96.42	2.21
1000	10000	9	4	25.08	210.64
1000	1000	0	4	88.05	118.88
1000	1000	2	4	95.62	14.56
1000	1000	5	4	97.72	0.91
1000	1000	9	4	98.59	0.43
1000	1000	5	0.5	75.47	85.83
1000	1000	5	1	88.60	68.68
1000	1000	5	2	94.52	24.64
1000	1000	5	6	98.07	1.55

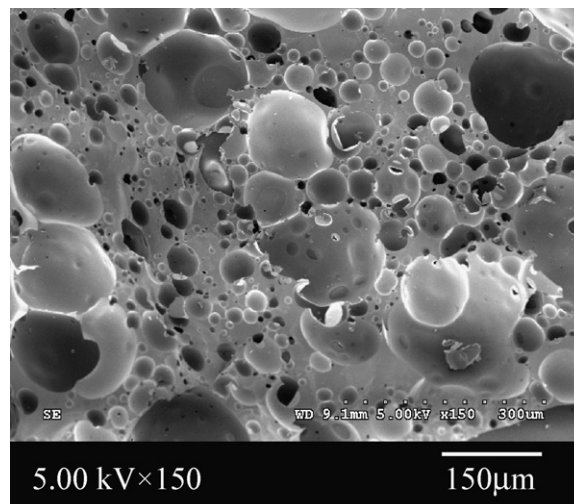


Fig. 8. SEM micrograph of the foam glass prepared from funnel glass by pyrovacuum reduction with the temperature, pressure, reducing agent and reaction time fixed at 700 °C, 10 Pa, 5% and 0.5 h, respectively.

Table 2

Chemical composition of the recovered metallic lead by ICP-OES

Element	wt%
Pb	99.32
Na	0.26
Si	0.17
K	0.07
Al	0.01
Fe	0.01
Ca	0.03
Mg	0.01

3.4. Properties of the recovered lead

Metallic lead, which was evaporated from the funnel glass and condensed on the inner wall of the quartz tube, was recovered and examined by XRD and ICP-OES.

Fig. 7 illustrates that no other crystal phase except metallic lead could be observed in the XRD spectrum of the recovered metal. To further understand the chemical composition of the recovered metal, the product was digested and analyzed by ICP-OES and the results are shown in Table 2. It can be seen that lead occupied 99.3% in the recovered product. The other elements, occupied less than 0.7%, were mainly Na (0.26%), Si (0.17%) and K (0.07%), respectively.

3.5. Properties of the foam residues

Some of the residues after the treatment were in porous form. To our best knowledge, this is the first to use pyrovacuum process for foam glass preparation, and furthermore, these foams are harmless because lead-contained in the funnel glass could be completely separated and recovered. One example is shown in Fig. 8.

All the parameters discussed in this paper may have reverse impact on lead recovery rate and the characteristics of foam glass. For example, lead recovery rate increased with increasing carbon amount and time, and these parameters led to an extension of pores “coalescence” [24], which might weak its physical properties. Thus, it is important to adjust these parameters to obtain a sufficient lead recovery rate and a foam glass with high quality. Details will be studied in our future work.

Table 3 presents the lead concentrations of the TCLP leachates for all residues after the treatment by the pyrovacuum reduction. Generally, the lowest lead concentrations were obtained when the temperature, reducing agent, reaction time were at their maximum values and the pressure was at its lower value, i.e., lead concentration was 1.29 mg/L with the temperature, reducing agent, reaction time and pressure fixed at 1000 °C, 9%, 4 h and 10 Pa, respectively. Second, lower concentrations of lead were obtained from the residues with a higher lead recovery rate, and vice versa. It may be concluded that lead concentration is inversely proportional to its lead recovery rate. Third, the concentrations that exceed the regulatory limit of 5.0 mg/L for TCLP lead [25,26] all have a lead recovery rate lower than 96%, as seen in Table 3. Thus, for safe treatment of funnel glass, it is necessary to obtain a relative higher lead recovery rate, such as higher than 96%, to meet the TCLP lead threshold.

4. Conclusions

The dramatic effect of pyrovacuum reduction on the detoxification and reutilization of lead-contained funnel glass was well demonstrated in this study. Lead, with a purity of 99.3%, was successfully separated and recovered from the funnel glass in the process, which attributed to the vitreous lead oxides changing to metallic lead by carbon and the lower boiling point of metallic lead at vacuum condition. The maximum lead removal rate reached 98.6% when the temperature, pressure, carbon adding amount and holding time were 1000 °C, 1000 Pa, 9% and 4 h, respectively. Meanwhile, foam glass was synchronously developed in the pyrovacuum process. TCLP test indicated that lead leached from the foam glass was below the regulated value at optimum conditions. Therefore, it is believed that the pyrovacuum process developed in this study is an applicable option for CRT funnel glass detoxification and reutilization.

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