Lead recovery and high silica glass powder synthesis from waste CRT funnel glasses through carbon thermal reduction enhanced glass phase separation process

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HIGHLIGHTS

- CRT funnel glass was remelted with B₂O₃ in reducing atmosphere.
- A part of PbO was reduced into Pb and detached from the glass phase.
- The rest of PbO and other metal oxides were mainly concentrated in the B₂O₃ phase.
- PbO enriched in the interconnected B₂O₃ phase can be completely leached out by HNO₃.
- High silica glass powder (SiO₂ purity >95%) was obtained after the leaching process.

GRAPHICAL ABSTRACT

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ABSTRACT

In this study, a novel process for the removal of toxic lead from the CRT funnel glass and synchronous preparation of high silica glass powder was developed by a carbon-thermal reduction enhanced glass phase separation process. CRT funnel glass was remelted with B₂O₃ in reducing atmosphere. In the thermal process, a part of PbO contained in the funnel glass was reduced into metallic Pb and detached from the glass phase. The rest of PbO and other metal oxides (including Na₂O, K₂O, Al₂O₃, BaO and CaO) were mainly concentrated in the boric oxide phase. The metallic Pb phase and boric oxide phase were completely leached out by 5 mol/L HNO₃. The lead removal rate was 99.80% and high silica glass powder (SiO₂ purity >95 wt%) was obtained by setting the temperature, B₂O₃ added amount and holding time at 1000 °C, 20% and 30 mins, respectively. The prepared high silicate glass powders can be used as catalyst carrier, semipermeable membranes, adsorbents or be remelted into high silicate glass as an ideal substitute for quartz glass. Thus this study proposed an eco-friendly and economical process for recycling Pb-rich electronic glass waste.

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1. Introduction

Cathode ray tubes (CRT) have been widely used in television sets and computer monitors. However, CRTs would eventually be replaced by an advanced display technology resulting from a

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large amount of lead-containing CRT glass for disposal [1]. Radiation protection is the main function of the CRT funnel glass that contains considerable quantities (22%–25%) of toxic lead oxides [2,3]. The toxic lead oxides may be leached out when the broken lead-containing glass is mixed with acid water in waste landfills [4,5]. Lead has multiple deleterious health effects, especially on the human neurological and hematopoietic systems. Thus, the CRT funnel glass has been identified as a typical hazardous waste that should be recycled properly and safely.

A waste-containing CRT funnel glass can be directly prepared for use with building materials [6,7] and anti-radiation materials [8]. However, the migration of toxic lead oxides from the CRT funnel glass to the new products significantly limits the application of these methods. Meanwhile, recycling lead from a funnel glass is significant for environmental protection and lead resource cyclic utilization. Thus, a variety of advanced lead recovery methods have been developed, e.g., vacuum metallurgical methods [9,10], chloride volatility process [11], reduction melting methods [12–14], and enhanced leaching methods [15,16]. Lead oxides were tightly enveloped in silica tetrahedrons of a funnel glass [17]; however, these special characteristics often make lead recovery methods time consuming or high energy consumption leads to high treatment costs. To reduce the processing cost, many high value-added products, including foam glass [7,9], glass microspheres [18], and high silica glass powder [14], were synchronously produced during the detoxification process of the CRT funnel glass. Among these products, high silica glass is an ideal substitute for quartz glass, and has promising economic value because of its novel properties of thermal and chemical stability, high mechanical strength, and light transmission [19].

Phase separation is the main preparation method of high silica glass. The main technique in the phase separation process involves the following three steps [20,21]: First, the alkali borosilicate glass is melted. The glass is separated into two phases, namely, B_2O_3 -rich and SiO_2 -rich. The interconnected structure of the B_2O_3 -rich phase is rich in alkali and soluble in boric oxide, especially in hot acids; The SiO_2 -rich phase is high in silica and stable towards acids. After hot acid leaching, the unstable B_2O_3 -rich phase is leached out, leaving a porous structure with very high silica content. The prepared porous high silica glass powder could be used as semipermeable membrane, ultrafilter, catalyst carrier, and adsorbent [20]. Finally, the porous glass is remelted to more than 1200 °C, which shrinks slightly and becomes a non-porous high silica glass. Aside from some alkali metal ions, many heavy metal ions contained in a glass could also be removed by phase separation. Colored soda-lime-silica glass containing heavy metal Co or Cr as a colorant was re-melted with B_2O_3 to yield a soda-lime borosilicate glass [22]. All cations (Na, Ca, Cr, and Co) concentrated in the borate phase were successfully leached out with the dissolution of the borate phase. However, the traditional-phase separation process needed an annealing treatment between 500 °C and 580 °C for a long time to ensure complete phase separation.

Takashi Okada [14] successfully recovered lead from the funnel glass by combining reduction–melting and leaching processes. Funnel glass powder (10 g) was mixed with Na_2CO_3 (5 g), melted at 1000 °C for 1 h, and annealed at 700 °C for 2 h under a reductive atmosphere. In the thermal process, approximately 92% of the PbO in the funnel glass was reduced to metallic lead and detached from the glass phase [12]. The rest of the lead left in the reduction residue could be completely removed by 1 M HCl, and porous SiO_2 (purity >95 wt%) was obtained. Therefore, the reduction–melting process could help the traditional phase-separation process to shorten the processing time based on the new generated phase of metallic Pb. However, a large quantity of flux (Na_2CO_3) was added into the funnel glass to promote the lead recovery while the phase separation process was used to recover the flux (Na_2CO_3). Mean-

Table 1

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

Elements	wt%
SiO_2	50.62
PbO	21.50
Na_2O	10.64
K_2O	6.86
CaO	3.00
Al_2O_3	2.56
BaO	1.18
SrO	0.98
MgO	0.92
Fe_2O_3	0.27
Sb_2O_3	0.27
ZnO	0.12
NiO	0.02

while, Na_2CO_3 may react with SiO_2 , and the product of Na_2SiO_3 may cause silicon loss during the acid leaching treatment. In response to these problems, an improved method was proposed in which B_2O_3 was selected to recover lead from the funnel glass instead of Na_2CO_3 because of the following factors: (1) According to our current experiment results, the optimal B_2O_3 adding amount was approximately 20%, which was smaller than the adding amount of Na_2CO_3 . (2) B_2O_3 cannot be reacted with SiO_2 , which can effectively avoid silicon loss and obtain more high silica glass powder. Meanwhile, H_3BO_3 could be recovered from the acid leaching solution by freezing crystallization and decomposing B_2O_3 under high temperature.

Therefore, carbon-thermal reduction, which enhances the glass phase-separation process, was developed to detoxify the waste of a CRT funnel glass. The objectives of this study were to (1) discuss the transformation and migration mechanism of lead oxide in a funnel glass during carbon-thermal reduction that enhanced the phase separation process, (2) examine the effect of various experimental factors on lead removal efficiency and optimize the affecting factors, and (3) detect the chemical composition of an acid leaching residue.

2. Materials and methods

2.1. Sample preparation

The CRT funnel glass provided by Henan Hengchang Precious Metals Co. Ltd. (China) was first broken into small pieces (≤ 5 mm), and the coatings on the glass surface were removed by wet scrubbing and ultrasonic cleaning methods [23]. Thereafter, the CRT funnel glass was milled by a dry ball and sieved through a 200 mesh sieve ($\leq 74 \mu m$). The powder was dried at 105 °C after 24 h. The chemical composition of the glass powder was examined by X-ray fluorescence (XRF), and the results are presented in Table 1. Other materials used in the experiment were analytical reagents, unless otherwise stated.

2.2. Carbon thermal reduction to enhance glass phase-separation process

In the thermal reduction process, 10.0 g of funnel glass powder was homogeneously mixed with 0%–30% B_2O_3 (particle size <200 mesh) by a planetary ball mill. Each mixture was placed in a 30 mL nickel crucible, which was placed in a rectangular corundum boat containing 20.0 g of carbon powder. Then, the corundum boat was placed in the tubular furnace (length, 1000 mm; inner diameter, 70 mm). The tubular furnace was sealed air-tight, and high-purity argon gas (99.999% purity) was blown into the tubular furnace to remove the air in the chamber. The mixed powder was then heated to 700–1300 °C and held for 30–240 min.

Table 2

Detailed experimental parameters of the thermal reduction process.

Temperature (°C)	B ₂ O ₃ adding amounts (%)	Holding time (min)
700	0	30
800	5	60
900	10	120
1000	15	240
1100	20	
1200	25	
1300	30	

In this study, the specific thermal treatment parameters, including temperature grades, time intervals, and B₂O₃ usage are shown in Table 2. When the heating process was finished, the process chamber was slowly cooled down to room temperature. The residue in a block form was then taken out of the nickel crucible and crushed into two different particle sizes (1–2 cm and ≤74 μm) according to the different experimental purposes. Finally, the crushed residue was stored in a desiccator for further analysis.

2.3. Acid leaching process

In the acid leaching treatment, 5.00 g of residue was placed in a 100 mL Teflon digestion bottle containing 20 mL of HNO₃ (5 mol/L), and agitated at 90 °C for 60 min. The solid residue was then separated from the leaching solution by centrifuge and washed by ion-exchange water twice. Finally, the separated solid residue was dried at 105 °C for 24 h.

2.4. Analysis

The funnel glass and residue were digested by HNO₃–HClO₄–HF, and the different elements contained in the funnel glass and residue were examined by an inductive coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 2000). All the experiments were repeated three times and only the mean values were reported. The measurement errors were around

±1%. The metal removal rates in this experiment were defined as follows:

$$\text{Lead removal rates}(\%) = (1 - R^{\text{Pb}}/R_0^{\text{Pb}}) \times 100, \quad (1)$$

$$R^{\text{Pb}} = C^{\text{Pb}}/C^{\text{silica}}, \quad (2)$$

$$R_0^{\text{Pb}} = C_0^{\text{Pb}}/C_0^{\text{silica}}. \quad (3)$$

In Eq. (3), C_0^{Pb} and C_0^{silica} are the lead and SiO₂ concentration of the CRT funnel glass. C^{Pb} and C^{silica} are the lead and SiO₂ concentration of the CRT funnel glass after acid leaching treatment. During the thermal and leaching treatments, the quantity of silicon oxide loss is negligible because of its thermal and chemical stabilities [22]. In addition, lead/silica ratio in the glass was not affected by dilution as a result of added B₂O₃ [12]. Therefore, the lead/silica ratio can effectively reflect the lead concentration changes used in this experiment. The mineral composition of the reduction residue was characterized by X-ray diffraction (XRD) using the Ni-filtered Cu–K radiation on a Rigaku D/MAX2500 diffractometer over an angle of 10° < 2θ < 80°. The morphology of the acid leached residue was examined by scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS).

3. Results and discussion

3.1. Characteristics of migration and transformation for PbO in carbon thermal reduction enhanced phase separation process

Fig. 1 shows photos of the reduction products obtained at different temperatures when the B₂O₃ adding amount and holding time were fixed at 20% and 30 min, respectively. When the temperature >800 °C, the mixed glass powder began to gradually change into a liquid state and a transparent surface with a vitreous luster was obtained. At 900 °C, the transparent surface was replaced by a nontransparent surface with silver-white metallic luster, as shown in Fig. 1(c). This phenomenon indicates that some metallic oxides contained in the funnel glass assembled on the surface of the residue. At 1000 °C, plenty of large spherical particles could

Fig. 1. Photographs of the reduction residue treated at different temperatures when B₂O₃ adding amount and holding time were fixed at 20% and 30 min. (a) 700 °C; (b) 800 °C; (c) 900 °C; (d) 1000 °C; (e) 1200 °C; (f) 1300 °C.

Fig. 2. XRD patterns of raw funnel glass and the formed metallic particles (temperature, B_2O_3 adding amount and reaction time were 1000 °C, 20% and 30 min).

Fig. 3. Picture of the metallic lead assembled on the bottom of the nickel crucible (temperature, B_2O_3 adding amount and reaction time were 1300 °C, 20% and 30 min).

be seen with the naked eye on the surface of the residue. Fig. 2 shows that the raw funnel glass was non-crystalline and no characteristic peaks could be found. After thermal reduction treatment at 1000 °C, no other crystal phase except metallic lead could be observed in the XRD spectrum. Thus, the spherical particles were made up mostly of metallic Pb. Then, the number of spherical metallic particles continued to decrease with an increase in temperature. At 1300 °C, most of the spherical metallic particles that were originally located on the surface of the reduction residue disappeared, and many large solid metallic Pb droplets could be found at the bottom of the nickel crucible, as shown in Fig. 3. The migration process of the metallic Pb during the thermal treatment could be illustrated as follows: PbO contained in the upper surface of the molten glass phase could be reduced to metallic Pb by CO existing in the gas phase. At 1000 °C, the viscosity of the glass phase was still high that most of the metallic Pb was located on the upper surface of the molten glass phase, as shown in Fig. 1(d). The viscosity of the glass phase was quickly decreased with an increase in temperature that led to further PbO reduction into Pb at high temperature. The liquid

Table 3

EDS results of the reduction residue obtained under the reductive atmosphere with the temperature, B_2O_3 adding amount and reaction time were fixed at 1000 °C, 20% and 30 min, respectively (wt%).

Elements	Si	O	Pb	Na	K	other
Point A	0	0	100	0	0	0
Point B	0	0	100	0	0	0
Point C	57.81	21.55	0	10.84	9.80	0
Raw funnel glass	28.90	26.78	19.78	12.01	10.53	2.98

Pb particles began to collide with one another, and larger molten Pb droplets were formed. At 1300 °C, the viscosity of the glass phase was low enough that the molten Pb droplets sank from the upper surface of the molten glass phase to its bottom under the action of gravity.

The morphology and chemical composition of the spherical metallic particles on the reduction residue surface in Fig. 1(d) was examined by SEM and EDS. The metallic luster surface consisted of a layer of tiny spherical metal particles. The size of the spherical metallic particles ranged from 1.50 μm to 53.18 μm , and most of these particles were smaller than 10 μm . The EDS results show that the main element of the selected spherical metal particles (points A and B) was pure metallic Pb. Most of the residue surface was covered by a large number of tiny spherical Pb particles as shown in Fig. 4(a). The formation of the spherical Pb particles indicated the excellent separability between the metallic Pb phase and the glass phase. In some small areas, a smooth surface uncovered the Pb particles shown in Fig. 4(c). Thus, the chemical composition of the glass phase could be detected by EDS (Table 3). The main element of point C in Fig. 4(d) was Si, which had a weight percentage of approximately 57.81 wt%, whereas the remaining elements and their weight percentages were O (21.55 wt%), Na (10.84 wt%), and K (9.80 wt%). As shown by the EDS results, the raw funnel glass contained approximately 19.78 wt% of Pb. However, the Pb content of the residue decreased to 0% after the carbon thermal reduction process. The EDS comparison results between the raw funnel glass and point C indicated that most of the PbO contained in the surface of molten funnel glass was reduced to metallic Pb and detached from the glass phase.

However, the EDS results were semi-quantitative and could reflect only the surface chemical composition of the residue. Therefore, ICP-OES was used to examine the actual lead content of the inner part of the residue. Fig. 5 shows the lead removal rates of the carbon thermal reduction process obtained at different temperatures when the B_2O_3 adding amount and holding time were fixed at 20% and 30 min, respectively (without acid leaching treatment). The lead removal rate was lower than 20% when the temperature was <1000 °C. Then, the lead removal rate increased quickly and reached its maximum of 85.45% at 1300 °C. The ICP-OES results show that a certain PbO portion could not be reacted with CO and was left in the inner part of the residue during the thermal treatment. To completely remove the PbO left in the inner part of the reduction residue, the reduction residue was broken into large pieces (particle size >1 cm) by a stainless steel hammer, and then acid leaching treatment was applied to remove the PbO left in the reduction residue.

Fig. 6 shows the pictures and corresponding SEM images of the acid leaching residues obtained with different additional amounts of B_2O_3 when the temperature and holding time were fixed at 1000 °C and 30 min, respectively. In addition, some larger bubbles can be found in the broken residue. The foaming phenomenon is mainly attributed to the volatilization of Pb and B_2O_3 when the viscosity of the glass phase was higher at low temperature. After the acid leaching treatment, the surface of the residue was still smooth and characterized by vitreous luster when the added amount of B_2O_3 was 0%. The vitreous luster surface indicated that a funnel

Fig. 4. SEM images of the residue's surface obtained under the reductive atmosphere with the temperature, B_2O_3 adding amount and reaction time were fixed at 1000°C , 20% and 30 min, respectively. (b) and (d) are the corresponding partial enlarged SEM images of (a) and (d).

glass could tolerate the corrosion of a strong acid. Only a few small spherical holes were observed on the surface, as shown in Fig. 6(e). These small spherical holes were mainly attributed to the removal of spherical Pb particles that were originally located on the residue surface, while a part of the particle was embedded into the residue. After the acid leaching treatment, the spherical Pb particles were removed, leaving many circular holes on the surface of the glass. When the additional amount of B_2O_3 was increased to 10%, many white stripes appeared on the surface of the residue, as shown in Fig. 6(b). Although the residue was leached in the hot HNO_3 solution for 60 min, the corrosion layer on the surface of the residue was still very thin. The corresponding SEM pictures in Fig. 6(f) show that many cracks were formed on the surface. The formation of these cracks were mainly attributed to the dissolution of B_2O_3 , which was easily dissolved in hot water or hot acid. The length of the cracks range from $35.69\ \mu\text{m}$ to $72.78\ \mu\text{m}$, and the width of the cracks range from $1.71\ \mu\text{m}$ to $8.19\ \mu\text{m}$. When the added amount of B_2O_3 was increased to 20%, the surface of the residue completely changed to white. The depth of the corrosion layer was about 1–2 mm, which was much thicker than that in Fig. 6(b). More large cracks could be seen on the surface of the residue in Fig. 6(g). When 30% of B_2O_3 was mixed with a funnel glass, the reduction residue was completely corroded and splintered into small white fragments. The cracks became denser and smaller. The length of the cracks ranged from $1.47\ \mu\text{m}$ to $5.03\ \mu\text{m}$, and the width of the cracks ranged from $0.23\ \mu\text{m}$ to $0.92\ \mu\text{m}$.

Table 4 shows the EDS results of the acid leaching residue. The content of Pb, Na, K, and Al decreased quickly when the added amount of B_2O_3 was increased, but Si and O exhibited a contrary behavior. When no B_2O_3 was added, the Pb content of the acid

leaching residue was about 17.86% (point A). When the added amount was increased to 10%, Pb was completely removed, while the contents of Na and Al were 1.31% and 1.38%, respectively. When 20% of B_2O_3 was added, almost all of the Pb, Na, K, and Al were leached out, leaving only Si (52.59%) and O (47.41%). Therefore, B_2O_3 has a significant impact on the lead removal rate and the function of B_2O_3 can be illustrated by the following factors: (1) B_2O_3 could be used as a pore-forming agent so that the pore surface area of the cracks increases quickly with an increased in the

Fig. 5. The effect of temperature on the lead removal rate in the carbon thermal reduction process (B_2O_3 adding amount = 20% and reaction time = 30 min).

Table 4

EDS results of the acid leaching residue treated with different B_2O_3 adding amounts when temperature and holding time were fixed at 1000°C and 30 min(wt%).

Elements	Si	O	Pb	Na	K	Al
Point A	27.96	26.34	17.86	14.92	10.53	2.39
Point B	48.96	48.37	0	1.31	0	1.38
Point C	52.59	47.41	0	0	0	0
Point D	63.25	36.75	0	0	0	0

added amount of B_2O_3 . The higher the pore surface area, the higher the Pb removal rate. (2) B_2O_3 could be used as a fluxing agent that reduces the viscosity of the glass phase, especially under high temperature. The lower viscosity of the glass phase can speed up the migration velocity of lead oxide from the inner part to the surface of the residue. Thus, a larger amount of PbO could be reduced to metallic Pb by CO in the gas phase and detached from the glass phase. (3) B_2O_3 could be used as a concentrating and phase separation agent to grab many types of metal oxide from the silica network. The unreduced PbO and many other metal oxides were mainly concentrated in the B_2O_3 -rich phase, which could be completely leached out by an acid leaching treatment.

Therefore, the characteristics of a migration and transformation rule for PbO in the carbon reduction process could be described in Fig. 7. Before the thermal treatment, PbO and other metal oxides were evenly dispersed in the funnel glass. When the temperature was $>800^\circ\text{C}$, the funnel glass changed gradually into a liquid state. PbO near the surface of the solid glass was continuously reduced to Pb and detached from the glass phase. Thus, the PbO content in the residue surface was lower than that in the inner portion such that the concentration gradient of PbO caused the flow of PbO from the inner glass phase of the surface. The viscosity of the glass phase was quickly decreased with the increase of temperature lead to PbO that could quickly move the surface of the glass phase. When more Pb assembled on the residue surface, the liquid Pb particles began colliding with each other, and metallic Pb phase was formed on the residue surface. Meanwhile, most of the unreduced PbO and other metal oxides migrated from the silicon oxide phase to the boric oxide phase during the thermal treatment. After the acid leaching treatment, the metallic Pb phase located on the surface of the residue and PbO contained in the interconnected boric oxide phase

were completely leached out, thereby leaving a porous structure with very high silica content.

3.2. Effects of various parameters on lead removal rate

After the carbon-thermal reduction process, the metallic Pb phase was assembled on the residue surface, and unreduced PbO was mainly concentrated in the interconnected B_2O_3 phase. Both two-phase systems could be easily leached out by acid leaching. However, the acid corrosion velocity was quite slow and the depth of the corrosion layer was less than 2 mm when the added amount of B_2O_3 was $<20\%$. To improve the lead removal efficiency of acid leaching, the large reduction product was broken into powders with particle size of $<74\ \mu\text{m}$.

Fig. 8(a) shows the lead removal rates of the acid leaching process obtained at different temperatures when the added amount of B_2O_3 and holding time were fixed at 20% and 30 mins, respectively. Lead removal rate was only approximately 34.88% at 700°C , which rapidly increased to 99.80% at 1000°C . The growth of lead removal rate was then slowed down and reached its maximum of 99.98% at 1300°C . In addition, a part of PbO had already been removed from the glass phase before the acid leaching process. Therefore, lead removal rates could be divided into two parts. The first part of PbO could be removed by the thermal process, and the other parts of PbO could be removed by an acid leaching process. As shown in Fig. 5, at 1000°C , the lead removal rate caused by the thermal process was only 17.60%, and about 82.20% of PbO was removed by the acid leaching process. When the temperature was raised to 1300°C , the lead removal rate caused by the thermal process was predominant at 85.45%. Therefore, carbon thermal reduction shows a great strengthening effect on the phase separation process at high temperature. The effect of the temperature on the lead removal rate can be illustrated as follows: PbO was distributed evenly in the funnel glass before the thermal treatment. Unlike PbO, Pb cannot be distributed in the glass phase. At the beginning of the thermal reduction treatment, PbO near the surface of the residue was reduced to Pb and located on the surface of the residue. Thus, the PbO content of the residue surface was lower than that in the inner portion and PbO concentration gradient was formed. The concentration gradient of PbO caused the flow of PbO from the inner glass phase of the surface. The migration velocity of PbO was

Fig. 6. Photographs and the corresponding SEM images of the acid leaching residues obtained with different B_2O_3 adding amounts (temperature = 1000°C , holding time = 30 min). (a) 0%; (b) 10%; (c) 20%; (d) 30%; (e)–(h) was the corresponding SEM images of (a)–(d).

Fig. 7. Schematic diagram of the migration and transformation rule for PbO during the carbon thermal enhanced glass phase separation process.

mainly influenced by the viscosity of the glass phase, which quickly decreased with the increase in temperature. The higher the temperature, the faster the migration velocity of PbO. Accordingly, the reduction rate of PbO increased rapidly with the increase in temperature. Meanwhile, PbO could quickly migrate from the silicon oxide phase to the boron-rich phase when the viscosity of the glass phase was lower at high temperature. Once PbO was concentrated in the boron-rich phase, it could be efficiently removed by an acid leaching treatment. Therefore, temperature plays an important role in the lead removal rate.

Fig. 8(b) shows lead removal rates with different added amounts of B_2O_3 when the temperatures and holding time were respectively fixed at 1000°C and 30 mins. Lead removal rates were only about 30.03% when no B_2O_3 was mixed with a funnel glass. Thereafter, lead removal rates rapidly increased from 61.80% to 99.27% when the added amount was increased from 5% to 15%. The growth of the lead evaporation rate then slowed down, while the lead removal rates increased from 99.80% to 99.96% when the added amount was increased from 20% to 30%. The effect of the B_2O_3 added amount on the lead removal rate could be illustrated as follows: (1) After thermal reduction treatment, the unreduced PbO and many other metal oxides were mainly concentrated in the borate phase. The structure of the borate-rich phase was largely dependent on the added amount of B_2O_3 . When this amount was $<15\%$, the borate-rich phase was isolated, thereby greatly limiting the dissolution rate of the boric oxide phase. When the B_2O_3 added amount was $>15\%$, the interconnected structure of the boric oxide phase was formed so that most of the unreduced PbO that concentrated in the borate phase was completely leached out with the dissolution of the borate phase. (2) B_2O_3 could also reduce the viscosity of the glass phase, especially in a high-temperature environment. The lower viscosity can speed up the migration velocity of PbO from the inner part to the surface of the residue. As shown in Fig. 5, approximately 85.45% of PbO was reduced to metallic Pb and separated from the glass phase during the thermal treatment when the B_2O_3 added amount, temperature, and reaction time were fixed at 20%, 1300°C , and 30 mins. The content of PbO left in the residue was no more than 15%, which can be easily removed by the following acid leaching treatment. Thus, carbon thermal reduction was a useful method to enhance the glass phase separation.

Fig. 8(c) shows the effect of the holding time on lead removal rates when the temperatures and B_2O_3 added amount were respectively fixed at 1000°C and 30 min. The lead removal rate was already at 99.80% when the holding time was only 30 min and reached its maximum of 99.98% at 240 min. We can conclude that PbO could be quickly concentrated in the borate-rich phase under high temperature and efficiently leached out by hot acid. Therefore,

Table 5

Chemical composition of the acid leaching residue by ICP-OES.

Elements	wt%
SiO_2	95.19
Na_2O	2.97
B_2O_3	0.98
Al_2O_3	0.49
BaO	0.12
PbO	0.08
Fe_2O_3	0.06
NiO	0.02
CaO	0.01
K_2O	0.01

the effect of holding time on the lead removal rate was not obvious. However, the metallic Pb and B_2O_3 were volatile under the condition of high temperature. If the processing time was extremely long, more metallic lead might evaporate into the gas phase and cause harm to human health. Based on the consideration of lead removal rate and energy consumption, 30 min was recommended as the optimum holding time with temperature and B_2O_3 added amount fixed at 1200°C and 20%, respectively.

3.3. Properties of acid leaching residue

The reduction residue was black, but it turns white after exposure to hot acid of HNO_3 for 60 min, as shown in Fig. 9(a). Fig. 9(b) shows that the acid leaching residue mainly had an irregular shape and the particle size ranged from 1.11 to $48.12\ \mu\text{m}$ with an average of $9.43\ \mu\text{m}$. To further understand the chemical composition of the acid leaching residue, the residue (1000°C , 20% B_2O_3 , and 30 min) was analyzed by ICP-OES; the results are shown in Table 5. Under optimum experimental conditions, 20% of B_2O_3 was added into the funnel glass. After the acid leaching treatment, most of the B_2O_3 was leached out and the B_2O_3 content of the leaching residue was 0.87%. Only 0.08% of PbO was left in the residue, which was much lower than that of the raw funnel glass. The main composition of the acid leaching residue was SiO_2 , which accounted for 95.19%, while the other elements were Na_2O (2.97%), B_2O_3 (0.98%), Al_2O_3 (0.79%), BaO (0.12%), and F_2O_3 (0.06%). The chemical composition of the acid leaching residue indicated that PbO, Na_2O , K_2O , Al_2O_3 , and CaO were mainly concentrated in the boric oxide phase during the thermal reduction process. However, about 30% of Na_2O residue was left in the silica-rich phase probably because of insufficient annealing treatment. In this experiment, the process chamber was slowly cooled down to room temperature so that the annealing time between 500°C and 580°C was

Fig. 8. Effects of various parameters on lead removal rate of acid leaching treatment (a). Effect of temperature on lead removal rate (B_2O_3 adding amount = 20% and holding time = 30 min). (b). Effect of B_2O_3 adding amount on lead removal rate (temperature = 1000 °C and holding time = 30 min). (c). Effect of holding time on lead removal rate (temperature = 1000 °C and B_2O_3 adding amount = 20%).

no more than 30 min, which could be ignored when compared with the traditional phase separation process. Therefore, sufficient annealing treatment may increase the enrichment degree of Na_2O in the boric oxide phase to further increase the purity of the silica.

Fig. 9. Photograph (a) and the corresponding SEM image (b) of the acid leaching residue with the temperature, B_2O_3 adding amount and reaction time were fixed at 1000 °C, 20% and 30 min, respectively.

4. Conclusions

In this study, high silica glass powder was prepared from the CRT funnel glass, together with the lead recovery by the carbon-thermal reduction that enhanced the glass phase-separation process. B_2O_3 could be used as a pore-forming, fluxing, and phase separation agent to improve the lead removal rate. During the thermal reduction process, three different phases were obtained, namely, metallic Pb, boric oxide, and silicon oxide. A part of the PbO contained in the funnel glass was reduced to metallic Pb by CO and detached from the glass phase. The unreduced PbO that accompanied many other metal oxides (including Na_2O , K_2O , Al_2O_3 , BaO , and CaO) were mainly concentrated in the boric oxide phase. After the acid leaching process, the metallic Pb phase on the surface of the residue and PbO contained in the boric oxide phase were completely leached out. Experimental results showed that the lead recovery rate increased with an increase in temperature, B_2O_3 added amount, and holding time. The optimum temperature, carbon powder added amount, and holding time for the process were 1000 °C, 20%, and 30 min, respectively, and the lead removal rate was 99.80%. The SiO_2 content of the acid leaching residue was 95.19%. Therefore, the findings of this study may be an applicable option for the CRT funnel glass detoxification and reutilization.

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