Journal of Hazardous Materials 215–216 (2012) 90–97

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Preparation of lead oxide nanoparticles from cathode-ray tube funnel glass by self-propagating method

Yu Wang [a,b], Jianxin Zhu [a,*]

[a] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 9 October 2011
Received in revised form 8 December 2011
Accepted 14 February 2012
Available online 22 February 2012

Keywords:
Self-propagating high-temperature synthesis
Cathode-ray tube
Funnel glass
Extraction
Lead oxide
TCLP

ABSTRACT

This paper presents a novel process of extracting lead oxide nanoparticles from cathode-ray tube (CRT) funnel glass using self-propagating high-temperature synthesis (SHS) method. The impacts of added amount of funnel glass on the extraction ratio of lead, the lead extraction velocity and the micromorphology, as well as particle size of extracted nanoparticles were investigated. We found that self-propagating reaction in the presence of Mg and Fe_2O_3 could separate lead preferentially and superfine lead oxide nanoparticles were obtained from a collecting chamber. The separation ratio was related closely to the amount of funnel glass added in the original mixture. At funnel glass addition of no more than 40 wt.%, over 90 wt.% of lead was recovered from funnel glass. High extraction yield reveals that the network structure of funnel glass was fractured due to the dramatic energy generated during the SHS melting process. The PbO nanoparticles collected show good dispersion and morphology with a mean grain size of 40–50 nm.

1. Introduction

Waste cathode-ray tubes (CRT) from televisions or computer monitors are growing at an escalating rate because of the widespread use of LCD screens and replacement of electronic products in these years [1–3]. A recent study has estimated that the amount of CRT glass generated in Asia will increase with a factor of two and climb up from 800 to 1500 metric tons by 2020 [4]. As one of the biggest manufacturers and consumers of electronic appliances, China will face its sharp rise of obsolete personal computers and televisions between 2008 and 2012 [5]. The estimated amount of discarded PCs and TVs will reach 93.36 and 74.31 million units in 2012, respectively [6,7]. In addition, the "trade-in policy of home appliances" and illegal importation also enlarge the size of waste CRT stream in China. The proper recycling or disposing of waste CRTs is a very important issue in response to its growing volume.

The treatment of funnel glass is one of the major challenges in the recycling of waste CRT glass due to its high lead concentration. The funnel glass is designed and produced with 20–30 wt.% of lead to stabilize the glass and absorb X-ray radiation emitted by the electron gun in televisions or computer monitors [8]. However, the lead existed in the waste CRTs possess a high risk to the human health, which has irreversible effects on the central and peripheral nervous systems, blood system, kidneys, as well as the endocrine system [9]. Currently, the vast majority of non-recycled CRTs end up in landfills or incinerators, which may make secondary pollution to the environment. It is well known that even the "state of the art" landfill is not completely sealed and a certain amount of chemical and heavy metal leakage may occur. The heavy metal lead may also emit into the environment with the flue gas and incineration fly ash. More and more countries prohibit the landfill and incineration of waste CRTs [10,11].

However, it is hard to separate lead from waste CRTs, because lead exits in the funnel glass as a network intermediate. PbO_3 polyhedron is the dominant structural unit in the funnel glass with an average Pb-O distance of 22.4 nm. The PbO_3 polyhedrons are encapsulated firmly between SiO_4 tetrahedrons and high energy is needed to break the three-dimensional vitreous network [12–15]. A number of methods such as pyrometallurgy, subcritical hydrothermal, power ultrasound and mechanochemical processes have previously been developed and employed for the treatment of waste CRTs [16–21]. Among them, pyrometallurgy technology was proven an effective way of lead separation from funnel glass. Yot et al. [18] extracted 40 wt.% of total lead from waste CRTs by reaction with siliconcarbide after 60 min at 1223 K under the atmospheric pressure. Xing and Zhang [16] and Chen et al. [17] recovered more than 90 wt.% of total from funnel glass at 1273 K

* Corresponding author. Tel.: +86 10 62849488; fax: +86 10 62849515.
E-mail address: Zhujx@rcees.ac.cn (J. Zhu).

0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2012.02.041

Table 1
Chemical compositions (wt.%) of investigated CRT funnel glass by XRF.

Components	wt.%
SiO_2	52.45 ± 2.01
PbO	22.89 ± 0.91
K_2O	8.66 ± 0.62
Na_2O	5.67 ± 0.25
Al_2O_3	3.68 ± 0.04
CaO	2.74 ± 0.31
MgO	2.43 ± 0.66

via reaction with carbon powder under vacuum condition. These articles showed that the process is time-consuming (1–4 h) and needs a high temperature (>1200 K) to break the network structure of lead silicate and separate lead from funnel glass by the traditional pyrometallurgy method. The development of a novel high-temperature process with less energy and time consumption is necessary and meaningful to recycle CRT in an environmentally friendly way.

The self-propagating high-temperature synthesis (SHS) method is well known as an attractive alternative to the conventional methods for manufacturing advanced materials, such as ceramics, ceramic-composites and intermetallic compounds, since SHS provides advantages with respect to process economics, short reaction time and energy efficiency [22,23]. Previous researchers have explored the usage of SHS in the disposing various solid wastes [24–26]. The underlying characteristic of SHS relies on the highly exothermic reaction could be ignited in the form of self-sustaining combustion wave quickly from one side to another without additional energy, thus energetically efficient and procedurally short. Moreover, the high combustion temperature achieved during the SHS process is always above 1800 K, at which funnel glass could be easily melted and PbO in the waste CRTs could be effectively volatilized and separated. In addition, rapid cooling rate of evaporated phase might give rise to the formation of PbO nanoparticles.

This work aimed to investigate the possibility of preparing lead oxide nanoparticles from CRT funnel glass by the self-propagating process. The effects of elaborate parameters on the SHS combustion, lead extraction and crystallization process are described. The toxicity of the residues after SHS treatment was also studied by Toxicity Characteristic Leaching Procedure (TCLP).

2. Materials and methods

2.1. Materials

Funnel glass of wasted CRTs from Huaxing Environmental Protection Corporation (Beijing, China) was pulverized by the planetary ball-milling (through 80 sieve mesh) and dried at 378 K for 24 h prior to use, whose chemical composition was presented in Table 1. Commercial ferric oxide (purity 99%, particle size <5 μm) and magnesium (purity 99%, particle size 200 mesh) were used as the SHS reactants, and their contents were computed according to the stoichiometry of the following reaction:

$$3Mg + Fe_2O_3 = 3MgO + 2Fe, \quad \Delta H_{298} = 980.6\,\text{kJ/mol} \qquad (1)$$

The combustion enthalpy of reaction (1) was calculated from the formation enthalpies of Fe_2O_3 and MgO at 298 K. All the data needed were referred from the Lange's Handbook of Chemistry [27]. It could be found that the value of $\Delta H_{298}/C_{p298}$ is about 6061 K. Thus, this thermite reaction satisfies the experience criteria ($\Delta H_{298}/C_{p298} \geq 2000$ K) of high-temperature self-propagation reaction proposed by Merzhanov.

Table 2
Summary of the mixtures (wt.%) investigated.

Sample No.	Funnel glass (wt.%)	Fe_2O_3 (wt.%)	Mg (wt.%)
CRT10	10.00	61.79	28.21
CRT20	20.00	54.92	25.08
CRT30	30.00	48.06	21.94
CRT40	40.00	41.19	18.81
CRT50	50.00	34.33	15.67
CRT60	60.00	27.46	12.54

2.2. Self-propagating extraction process

CRT funnel glass, magnesium and ferric oxide powders were mixed as the contents shown in Table 2. Parallelepiped shaped samples with dimensions 40 mm × 8 mm × 7 mm and green densities in the range from 2.19 to 2.32 g/cm^3 were prepared by uniaxial pressing into a steel die with a pressure of 10 MPa for approximately two minutes. Each sample was located vertically in a small SHS reaction chamber with dimensions 100 mm × 100 mm × 100 mm, an electrically heated graphite rod at the top of the pellet initiated the reaction. A stopwatch was used to measure the combustion velocity and an infrared pyrometer (Raytek 3i series, Raytek, U.S.) was employed to measure the maximum combustion temperature. As observed in the experimental process, each sample self-propagated through the medium immediately after ignition in the form of a bright combustion front as a consequence of high energy generated from the exothermic reaction between Fe_2O_3 and Mg. Two solid products, residue and extract, were obtained. The extract was condensed on the reaction chamber walls due to the evaporation occurring during the SHS process while the residue remained where the original compact was placed inside the vessel.

2.3. Analysis

Crystalline compounds of the final solid products, both residues and extracts, were characterized by X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytical, Netherlands) using the Ni-filtered CuKα radiation over an angle of $10° < 2\theta < 90°$. The XRD data were identified by MDI Jade 5.0 software with ICDD PDF2003 database. The microstructures were observed by scanning electron microscope combined with energy dispersive X-ray spectroscopy (SEM-EDX, S-3000N, Hitachi, Japan) and transmission electron microscopy (TEM, H-7500, Hitachi, Japan). Quantitative analysis of metal contents was carried out by inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 2000, PerkinElmer, U.S.) analysis of the solution obtained after the solid products were fully dissolved into an aqueous mixture of HNO_3, HCL and HF. Leaching behavior of the obtained residues was determined according to the Toxicity Characteristic Leaching Procedure (TCLP, Method 1311, USEPA) [28].

3. Results and discussion

3.1. Separation of lead by SHS process

Fig. 1 shows the dependence of extraction ratio of lead and combustion temperature (T_c) on the amount of funnel glass added in the original mixture. It could be found that the self-propagating reaction in the presence of Mg and Fe_2O_3 can extract lead from funnel glass, and the extraction ratio changes with the content of funnel glass. Specifically, the extraction ratio of lead reaches over 90 wt.% when the funnel glass addition is no more than 40 wt.%. The lead extraction exhibits a significant negative correlation with the funnel glass addition, while it shows a positive relationship with the combustion temperature. This result indicates that the extraction