Waste Management 79 (2018) 164–168

Contents lists available at ScienceDirect

Waste Management

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

Recovery of $LaPO_4$:Ce,Tb from waste phosphors using high-gradient magnetic separation ☆

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ARTICLE INFO

Article history:
Received 18 June 2018
Revised 13 July 2018
Accepted 15 July 2018

Keywords:
Waste phosphor
High-gradient magnetic separation
Magnetic susceptibility
Sedimentation
Recycle

ABSTRACT

$LaPO_4$:Ce,Tb (LAP) containing high terbium concentration was successfully recovered from waste phosphor from end-of-life fluorescent lamps by high-gradient magnetic separation (HGMS). In addition to HGMS, some contaminants in the waste phosphor, e.g., iron oxide and glass powder, were also removed by sieving and sedimentation. Repeating the magnetic separation procedure three times yielded LAP with a purity of 87%. Luminescence spectra intensities of recovered LAP were as high as 95% compared with virgin LAP. This recovery method will be useful during rare-earth crises.

1. Introduction

Fluorescent lamps are widely used for lighting around the world. Although they are being replaced by LEDs for conventional lighting, fluorescent lamps will continue to be used at present since they are cost efficient and have relatively high energy efficiency. Highly efficient three-band fluorescent lamps typically utilize $Y_2O_3:Eu^{3+}$ (YOX) as the red phosphor, $LaPO_4$:Ce,Tb (LAP) as the green phosphor, and $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) and $(Sr,Ca,Ba,Mg)_5(PO_4)_3Cl:Eu^{2+}$ (SCA) as the blue phosphor. These high-performance phosphors contain high concentrations of rare-earth elements such as lanthanum (La), cerium (Ce), europium (Eu), and terbium (Tb). The supply of rare-earth elements, in particular Tb, had once considerably reduced; therefore, the recycling of phosphors from end-of-life fluorescent lamps will be important to avoid a similar situation.

The recycling system for end-of-life fluorescent lamps was established from the requirements to recover mercury from the lamps and due to the established recycling system, waste phosphors were separated in the recycling plant. Directly reusing waste phosphors is the ideal way to close the recycling loop at a feasible cost; however, this cannot be realized because the efficiency of waste phosphor is considerably decreased compared with virgin tricolor phosphor. One reason for the decreased efficiency is that more than half of waste phosphor is composed of white phosphor ($3Ca_3(PO_4)_2Ca(F,Cl)_2$:Sb,Mn), which is used for low-cost fluorescent lamps and has a lower efficiency than tricolor type fluorescent lamps. Furthermore, unwanted materials, such as glass flakes, iron-related materials, and alumina fine powder for binder, are mixed in the waste phosphor. The heating process wherein mercury is extracted also lowers the efficiency of phosphor. Blue phosphor is deteriorated by heating in air due to the oxidation of Eu^{2+} ions (Oshio et al., 1998), while LAP and YOX show little degradation.

Many fundamental studies have been conducted to find a method for recycling waste phosphors, which can be classified into two categories. The first approach is chemical recycling whereby waste phosphors are completely decomposed in acid, and rare-earth elements in solution are recovered by solvent extraction or oxide precipitation (Takahashi et al., 2001; Yang et al., 2013; Otsuki et al., 2008; Mei et al., 2009). However, the main drawback of this method is that it is expensive. The other approach is physical separation in which the waste phosphors are separated into each species, e.g., by gravity separation (Hirajima et al., 2005a), pneumatic classification (Takahashi et al., 2001), and flotation (Hirajima et al., 2005b). A high-separation efficiency was achieved by gravity separation utilizing high-density liquids (Hirajima et al.,

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☆ This research was financially supported by New Energy and Industrial Technology Development Organization (NEDO). NEDO provided instructions to reduce the usage of terbium in any method. This project aimed to reduce the demand of terbium for fluorescent lamps.

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https://doi.org/10.1016/j.wasman.2018.07.038
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2005a). However, this method is not practical because the liquid used is toxic, whereas other methods do not yield sufficient separation efficiency for reusing phosphors.

Recently, we proposed a separation method by magnetic force that utilizes differences in magnetic susceptibility (Akai et al., 2013; Yamashita et al., 2014). We examined the magnetic susceptibility of commercial phosphors and found that LAP exhibits one order of greater magnetic susceptibility than that of the others (Yamashita et al., 2014). LAP is the most expensive phosphor used in lamps due to the high Tb content. Therefore, the separation of LAP is most important. Wada et al. separated phosphors by magnetic force using a magnetic Archimedes method in which paramagnetic materials are levitated in a medium that is placed in a superconducting magnet in order of the magnitude of magnetic susceptibility (Wada et al., 2013). However, the magnetic Archimedes method is not suitable for mass production because of the low working volume of superconducting magnets and the slow processing speed. In contrast, high-gradient magnetic separation (HGMS) is inexpensive, has a high-speed process, and has already been commercialized in industry (Yamashita et al., 2014; Nishijima, 2013; Nishijima and Takeda, 2006; Nishijima et al., 2003; Morita et al., 2011). HGMS comprises an outer electromagnet and matrices in a separator column placed in a gap of the outer magnet. An expanded metal or metal wire made of ferromagnetic metal is used as the matrix. In the HGMS system, paramagnetic materials are captured by a high-gradient magnetic field (more than 10^5 Tm^{-1}) produced on the ferromagnetic matrix due to magnetization.

The separation of LAP by HGMS would not be complete in principle compared with the magnetic Archimedes method or gravity separation because all phosphors are paramagnetic and the differences in their magnetic susceptibility are of the order of 1 magnitude, which is not very large. Hence, the repetition of separation and some combinations of other treatments would be necessary. In our previous study, we showed that high-purity LAP was separated from a mixture of virgin tricolor phosphor and calcium halophosphate phosphors (Akai et al., 2013; Yamashita et al., 2014). However, to prove the feasibility of HGMS in phosphor recycling, it is necessary to show that high-purity LAP can be recovered from actual waste phosphor containing various contaminates such as glasses, irons, and alumina. Herein, we studied the separation behavior of waste phosphor by HGMS. The effects of pre- and post-treatment on contaminant removal were also examined.

2. Material and methods

2.1. Materials

Waste demercurized phosphor was provided by Nomura Kosan Co., Ltd. The waste phosphors were sieved at 38 μm to remove large glass flakes, tungsten filament, and electrode metals. The typical composition of the waste phosphors after sieving is LAP (12.6 mass%), YOX (14.5 mass%), BAM (7.8 mass%), SCA (6.5 mass%), halophosphate (49.0 mass%), glass (9.4 mass%), and Fe (0.15 mass%). A total of 60 or 100 g of the sieved waste phosphor was used for magnetic separation, from which iron and majority of alumina were removed by sedimentation.

Deionized water was used to suspend and wash the waste phosphor. Surfactants were added to the washing solution to disperse phosphors in the water. The surfactants used were 0.15 vol% of a polycarboxylic acid ammonium salt surfactant (Nopcosant RFA, San Nopco Limited) as a non-foaming dispersant and 0.015 vol% of a nonionic polyether surfactant (SN-Wet 980, San Nopco Limited) as an antifoaming wetting agent. The phosphor suspension was stirred by an ultrasonicator.

2.2. Separator

HGMS was conducted using a high-gradient magnetic separator (HIW L4-20KI, Eriez Magnetics Japan Co., Ltd.) equipped with an electromagnet. An expanded metal made of SUS-430 was used as the matrix in the column. The internal volume of the column with the matrix was 200 mL (Fig. 1).

2.3. Separation procedure

Waste phosphor was suspended in the washing water and separated (Fig. 2).

2.3.1. Pretreatment

Iron metal flakes were separated prior to the HGMS process. The alumina fine powders were also separated before the HGMS process because they considerably increase the viscosity of the suspension, which would affect the separation efficiency.

The suspension with phosphor was separated by HGMS operation at low magnetic field (~0.02 T) to remove iron metal particles in waste phosphor. Ferromagnetic iron (Fe) particles were captured on the matrix by the weak magnetic field, while paramagnetic phosphors were not attracted to the matrix. In the waste phosphor, iron oxides (magnetite (Fe_3O_4, ferrimagnetic), maghemite (γ-Fe_2O_3, ferrimagnetic), and hematite (α-Fe_2O_3, weak ferromagnetic) were present along with metal flakes probably due to metal oxidation. The magnetic susceptibility of hematite ($\sim 1.7 \times 10^{-3}$) (Kataoka and Muranaka, 1974) is similar to that of LAP and cannot be removed by HGMS by this low magnetic field. Hence, hematite was removed by post treatment sedimentation (Section 2.3.3).

After using HGMS to remove iron at a low magnetic field, the suspension was left to stand for 3 h until the phosphors precipitated as a solid layer. After 3 h of standing, most of alumina fine particles were still suspended in the liquid and could easily be removed by separating the liquid and solid phases. This

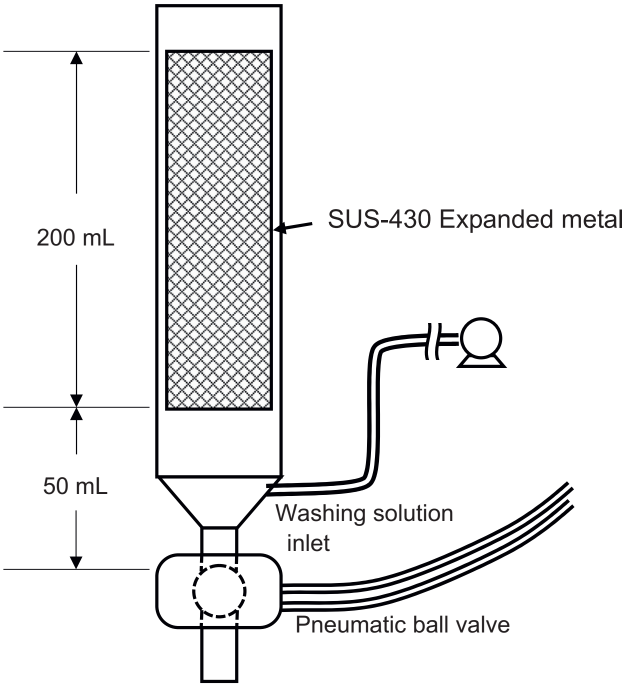

Fig. 1. Column structure with a ball valve below the column. The dead volume between the matrix and the valve was approximately 50 mL. The phosphor suspension was poured from the top.