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Rare earth elements recycling from waste phosphor by dual hydrochloric acid dissolution

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HIGHLIGHTS

- The article provides a new method for recycling rare earth (RE) from waste phosphor.
- When compared with the traditional methods, leach rate was much higher.
- Y–Eu concentrate and Tb–Ce concentrate were obtained successively.
- It would reduce the burden of later extraction, separation and purification.

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ABSTRACT

This paper is a comparative study of recycling rare earth elements from waste phosphor, which focuses on the leaching rate and the technical principle. The traditional and dual dissolution by hydrochloric acid (DHA) methods were compared. The method of dual dissolution by hydrochloric acid has been developed. The Red rare earth phosphor $(Y_{0.95}Eu_{0.05})_2O_3$ in waste phosphor is dissolved during the first step of acid leaching, while the Green phosphor $(Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19})$ and the Blue phosphor $(Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17})$ mixed with caustic soda are obtained by alkali sintering. The excess caustic soda and $NaAlO_2$ are removed by washing. The insoluble matter is leached by the hydrochloric acid, followed by solvent extraction and precipitation (the DHA method). In comparison, the total leaching rate of the rare earth elements was 94.6% by DHA, which is much higher than 42.08% achieved by the traditional method. The leaching rate of Y, Eu, Ce and Tb reached 94.6%, 99.05%, 71.45%, and 76.22%, respectively. DHA can decrease the consumption of chemicals and energy. The suggested DHA method is feasible for industrial applications.

1. Introduction

Rare earth elements (REEs) are becoming increasingly important in the transition to a green, low-carbon economy. Because the three-band phosphor (TBL) tubes have better color purity and higher luminous efficiency, fluorescent tubes with TBL have become a general trend in the World. Consequently, an amount of waste phosphor is huge. However, it is difficult to recycle the rare-earth phosphors from waste phosphor. The main challenges are as follows: firstly their emission intensities are sensitive to the concentrations and purities of rare earths, secondly the complicated contents of waste phosphor, and finally degradation of phosphors depends on the kind of phosphor (Eu^{2+} in Blue phosphor tends to be oxidized to Eu^{3+}) [1]. Waste phosphor is always mercury-contaminated, but now is landfilled or temporarily stockpiled, and recovery of rare earths from lamp phosphors could offer a total solution.

The improvement in recycling rates for REEs is a strategic necessity. It can only be realized by developing efficient, environmental-friendly and fully integrated recycling routes. In reality, commercial recycling of REEs from the waste phosphor is still extremely low. Despite the vast literature dealing mostly with lab-scale research efforts of REEs recycling from waste phosphor powders [2–8], less than 1% of the REEs was recycled in 2011 [9]. Only method for commercial recycling of REEs in China is the combination of alkali fusion [10] and the traditional extraction separation [11]. However, commercial recycling of REEs is not high.

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Table 1
Chemical composition of the waste phosphor, wt.%.

Y	Eu	Tb	Ce	Al	Si	Ba	Mg	Ca	P	Zn	Others
15.51	0.95	0.43	0.70	7.73	10.27	1.51	2.80	14.61	8.98	0.11	36.4

The improvement of REEs recycling rate is a necessity. This paper presents a new method for increasing rate of recovery.

2. Materials and methods

2.1. Materials

Waste phosphor, supplied by the Baogangxinli RE Co., Ltd, used in this research was collected from Ganzhou, China. Table 1 shows the chemical composition of the waste phosphor analyzed by ICP-AES, others mainly includes O, S, Cl, Mn, Sb and organic impurity, etc., the total content of REEs is 17.59 wt.%. Prior to analysis, samples were roasted and smelted with appropriate amount of sodium carbonate and H_3BO_3 at 1200 °C for 30 min, and then dissolved using 1:1 hydrochloric acid solution.

2.2. Proposed process flow

Fig. 1 shows the flow chart of the traditional and the new methods for recycling REEs from the waste phosphor. (a) Traditional method: 100 g of waste phosphor and sodium hydroxide were mixed as 1:1.5 waste phosphor/NaOH mass ratio. The mixture was placed into 100 ml iron crucible. Sintering was performed in a furnace at 800 °C ± 10 °C for 120 min. The fusion product was cleaned several times under stirring at 200 rpm for 20 min, with 500 ml of water at 60 °C. The insoluble matter was filtered and dried. 30 g of insoluble residue were employed. It was leached with 300 ml hydrochloric acid (5 mol/L) for 120 min with stirring (250 rpm) at 60 °C. The acidic leachate, called Filtrate 1, was obtained. Finally after oxalate precipitation and calcination, rare earth oxides (REOs) were obtained, and the Residue 2 was returned to the alkali fusion process. (b) The DHA method is a two steps acid hydrolysis method, where first 100 g of waste phosphor were leached with 300–500 ml hydrochloric acid (3–6 mol/L) for 4 h with stirring (250 rpm) at 60 °C, thus calcium in Filtrate 1 was removed by adding Na_2SO_4. Y–Eu chloride concentrate was obtained. Residue 1 and sodium hydroxide were mixed as 1:0.5–2 Residue 1/NaOH mass ratio. The mixture was placed into 100 ml iron crucibles. Sintering was performed in a furnace at 800 °C ± 10 °C for 2 h. The fusion product was cleaned as in the traditional method. The insoluble matter was filtered, and leached with 150 ml hydrochloric acid (5 mol/L) for 120 min with stirring (250 rpm) at 60 °C. The acidic leachate, called Filtrate 2, Tb–Ce chloride concentrate, was obtained, while the Residue 2, which could not be dissolved, was returned to the alkali fusion process. The advantages of the novel method can be quantified by calculating the leaching rates of both methods.

2.3. Analysis

X-ray diffraction (XRD) analysis was performed using Philips APD-10 X-ray diffractometer with Cu Kα radiation, 40 kV voltage and 150 mA current at 10°/min scanning rate, from 10° to 100° 2θ range. The morphology, aspect ratio and mean particle size were observed in the scanning electron microscope (Zeiss EVO-18, Germany). Chemical composition was analyzed by ICP-AES (Perkin Elmer Co., Ltd. OPTIMA 7000DV).

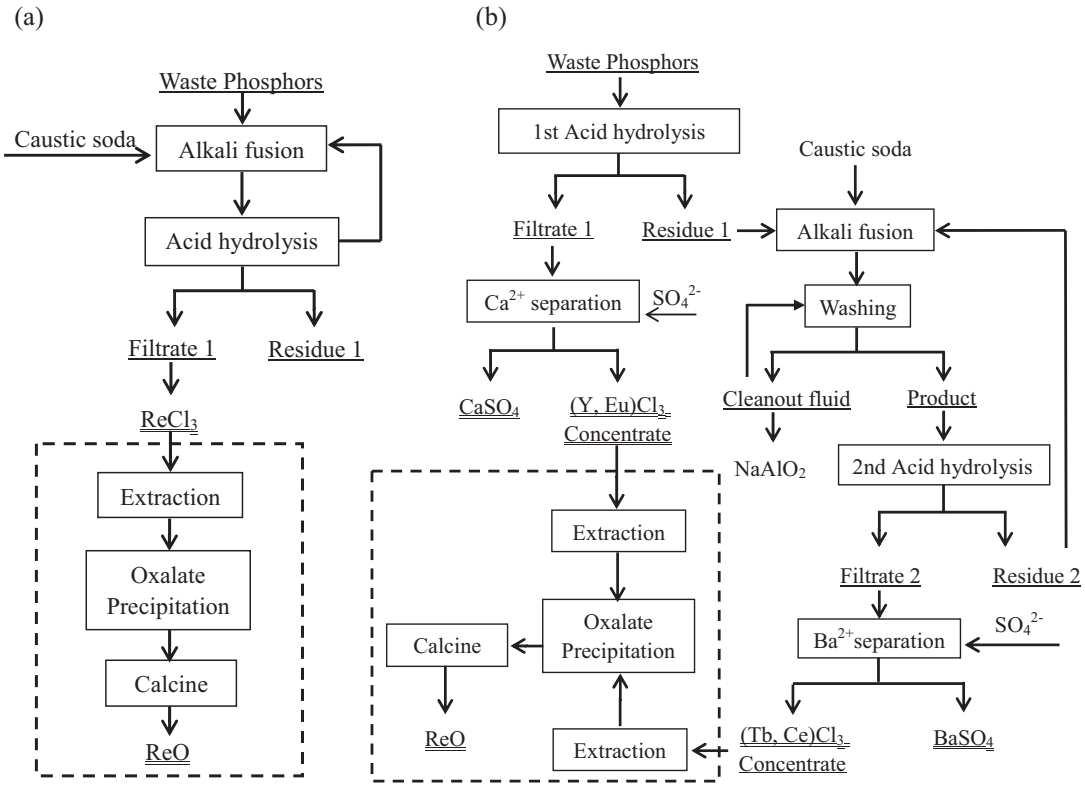

Fig. 1. Flow chart of REEs leaching from the waste phosphor: (a) traditional method and (b) DHA method.