Selective Reduction and Separation of Europium from Mixed Rare-Earth Oxides from Waste Fluorescent Lamp Phosphors

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Abstract Europium is a critical material required for LED, florescent lamp, cell phone screen, and flat panel display production. This process recycling europium from waste lamp phosphors is an innovative method to supply europium for high technology applications. Waste phosphor powder from recycled lamps is retorted, sieved, and leached to produce a europium/yttrium leach solution. The separation of europium and yttrium from the pregnant leach solution is conducted by selectively reducing Eu(III) to Eu(II) via zinc powder and precipitating europium (II) sulfate from solution using sulfuric acid as the precipitating agent. After one stage of selective reduction and precipitation, the purity and recovery of europium (II) sulfate was greater than 95% and 80%, respectively.

Keywords Waste Fluorescent Lamp · Phosphor Dust · Rare Earths · Recycling · Europium

Introduction

Recycled phosphor dust has the potential to supply a significant portion of US clean energy demand for europium. According to the DOE 2011 Critical Materials Strategy Report [1], the demand will increase from 200 to 220 tons per year in 2020. In 2007, 8000 tons per year of phosphor dust were discarded into landfills. Based a conservation calculation of concentration of 0.3% europium in the discarded dust, there is a potential to supply 240 tons per year. However, the concentration of europium is the dust will increase due to fewer halophosphate

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based T12 lamps being recycled and a greater ratio of newer T8 lamps being recycled.

Red phosphor is phosphor used to create the color red in fluorescent lamps. It is composed of Y_2O_3:Eu or yttrium oxide doped with europium. Based on the previous work presented by Eduafo et al. [2], europium and yttrium are leached at the same time into solution. Therefore, the goal of this research was to develop a process to separate europium from yttrium, in order develop a saleable europium oxide product. However, the product of this work is europium (II) sulfate—which can be converted to europium oxide in a few steps.

Originally, Molycorp [3], developed a process to recovery 99.9% pure europium oxide form Eu-Sm-Gd concentrates separated from monazite. More recently, Preston et al. [4], Morais et al. [5], and Rabie et al. [6] have used zinc metal and sulfuric acid to separate and purity europium from samarium and gadolinium concentrates. The paper proposes using the same method for europium and yttrium concentrates, as a product of waste lamp phosphor leaching. The equation below demonstrates the equation for converting Eu(III) to Eu(II) via selective reduction.

$$2\mathrm{Eu}^{3+} + \mathrm{Zn} = 2\mathrm{Eu}^{2+} + \mathrm{Zn}^{2+} \tag{1}$$

The equilibrium constant, K_c, can be used to describe the thermodynamics of a system. In the equation below the activities of species are replaced with their actual concentrations because there is no simple method to measure the activities of concentrated species in high ionic strength solutions.

$$aA + bB \Leftrightarrow cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

In addition, the formation of europium (II) sulfate precipitate, and intermediate in the europium separation experiments is demonstrated in Eq. 2.

HSC 5.11 was used to explore the possible reactions for the oxalic precipitation work and selective reduction and precipitation of europium (II) sulfate.

$$\mathrm{Eu}^{2+} + \mathrm{SO}_4^{2-} = \mathrm{EuSO}_4 \quad \mathrm{K_c} = 5.94 \times 10^8\ (\mathrm{T} = 25\,^\circ\mathrm{C}) \tag{2}$$

In all likelihood, europium (II) is part of chloride complex in a system with excess chloride ions, so the following equation better describes the actual conditions.

$$\mathrm{EuCl}^{+} + \mathrm{SO}_4^{2-} = \mathrm{EuSO}_4 + \mathrm{Cl}^- \quad \mathrm{K_c} = 3.01 \times 10^8\ (\mathrm{T} = 25\,^\circ\mathrm{C}) \tag{3}$$

Some of the possible by products of the reaction include europium (III) sulfate and yttrium (III) sulfate.

$$\mathrm{YCl^{2+}} + 1.5\mathrm{SO_4^{-2}} + 4\mathrm{H_2O} = 0.5\mathrm{Y_2(SO_4)_3} * 8\mathrm{H_2O} + \mathrm{Cl^-}\ \mathrm{K_c} = 4.90 \times 10^{-1}\ (\mathrm{T} = 25°\mathrm{C}) \tag{4}$$

$$\mathrm{EuCl^{2+}} + 1.5\mathrm{SO_4^{-2}} + 4\mathrm{H_2O} = 0.5\mathrm{Eu_2(SO_4)_3} * 8\mathrm{H_2O} + \mathrm{Cl^-}\ \mathrm{K_c} = 1.31 \times 10^{5}\ (\mathrm{T} = 25°\mathrm{C}) \tag{5}$$

Similarly, the process uses zinc metal to reduce $\mathrm{Eu^{III}}$ to $\mathrm{Eu^{II}}$ via $\mathrm{Zn^0}$. Next, the reduced solution is precipitated by the addition of sulfuric acid. As a result, europium (II) sulfate is precipitated and is separated via vacuum filtration. The product was quantified by X-Ray Fluorescence and SEM.

Experimental

Materials

Yttrium and europium oxide (99.99% pure) and zinc metal (99.8% 20–30 mesh) were provided by Alfa Aesar. Sodium hydroxide (Sigma Aldrich, USA) is dissolved in deionized water. Yttrium and europium were dissolved in solution using analytical grade (Sigma Aldrich, USA) hydrochloric acid and deionized water. The pH was adjusted with NaOH (Sigma Aldrich, USA) dissolved in deionized water. ACS grade 18 M sulfuric acid (Sigma Aldrich, USA) was diluted with deionized water.

Analysis

X-Ray Fluorescence (XRF) (Thermo Fisher Scientific) and scanning electron microscopy electron dispersive spectroscopy (SEM-EDS) were used for quantification and identification.

Procedure

A 13:1 ratio of yttrium oxide to europium oxide was dissolved in concentrated 12 M hydrochloric acid. The alkalinity of the solution was adjusted with a dilute sodium hydroxide solution to pH 3. The solution was added to magnetically-stirred vessel. 4% Hydrogen was bubbled through the system. Next, 5 times the stoichiometric amount of zinc was added to the mixing vessel. After two hours, a the reduced europium solution and dilute solution of 1 M sulfuric acid, degassed with 4% hydrogen, were mixed together in a cylindrical vessel, bubbled with 4%

Table 1 This table enumerates the results of the europium (II) sulfate precipitation experiments

Experiment	Dry weight	$EuSO_4$ purity (%)	Y impurity (%)	$EuSO_4$ recovery (%)
1	1.26	95.00	1.84	85.50
2	1.25	95.33	1.46	85.12
3	1.29	95.30	1.73	87.81
4	1.35	96.00	1.43	92.57
5	1.35	95.80	1.30	92.38
6	1.23	96.80	0.74	85.05
Mean	1.29	95.71	1.42	88.07
Standard deviation	0.05	0.65	0.39	3.56

hydrogen. After two hours, the solution was filtered by vacuum filtration with Millipore 47 mm filter in a Pall vacuum filtration setup. The precipitate was washed with a 0.001 M sulfuric acid.

Results and Discussion

Analysis of Precipitate

The precipitate was analyzed by XRF. Based on the in 6 experiments listed in Table 1.

Based on the inputs of the system, the expected dry weight of the precipitate was 1.40 g of $EuSO_4$. However, the total weight was less than that value. The differences between the expected weight and the actual weight was likely to do incomplete conversion of Eu(III) to Eu(II). The incomplete version of the system may have been due to competitive reactions or Eu(II) reoxidizing due to incomplete isolation from oxygen during transferring or precipitation. The purity was determined from XRF by adding the values for sulfur and europium as shown in Table 2. This method is not quantitative in nature. The recovery was determined by multiplying the dry weight over the expected value multiplied by the europium sulfate purity.

In addition, SEM-EDS was run on the precipitate as shown in Fig. 1 and Table 3.

SEM-EDS is able to identify the major impurities such as chlorine, but cannot quantify yttrium. The nickel, manganese and aluminum values listed in the table are either due to misidentification or a mistaken introduction of impurities in the in the SEM.

Table 2 The table demonstrates the elements abundances determined via XRF for run #6

Element	Wt%	Est. error
Eu	85.39	0.18
Sx	11.43	0.16
Cl	0.971	0.048
Y	0.743	0.037
Na	0.579	0.029
K	0.102	0.0051
Al	0.095	0.0084
Sb	0.0927	0.026
I	0.0734	0.036
Hf	0.0633	0.021
Cs	0.0587	0.05
Ce	0.0522	0.016
Th	0.0492	0.033
Zn	0.0448	0.0072
Pr	0.0433	0.018
Ru	0.0418	0.015
Nd	0.0394	0.01
Mn	0.0322	0.014
Mg	0.032	0.024
Pt	0.185	0.016
Zr	0.018	0.014
Rb	0.0118	0.012
Ga	0.01	0.006
V	0.0055	0.0027

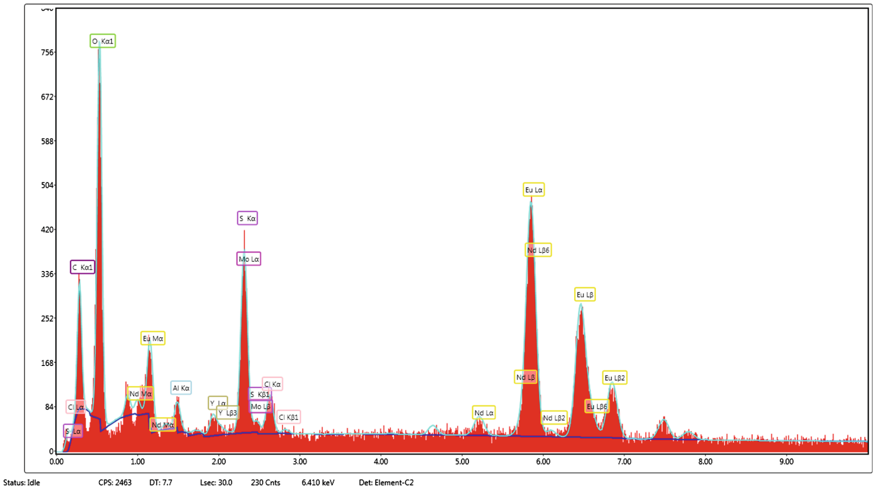

Fig. 1 This SEM-EDS spectrum was indicated for europium (II) sulfate

Table 3 The table shows the quant for europium (II) from SEM-EDS

Element	Weight %	Atomic %	Error %
C K	8.94	23.41	14.96
O K	27.24	53.57	9.32
AL K	0.85	0.99	25.97
S K	10.13	9.95	6.68
Cl K	0.95	0.84	20.98
Eu L	50.48	10.45	5.51
Mn K	0.73	0.42	49.75
Ni K	0.69	0.37	58.91

Conclusions

The selective reduction and precipitation is an interesting method to purify yttrium and europium rich solutions. Europium (II) sulfate purities greater than 95% and recoveries greater than 80% are easily attained.

Further work will be conducted using actual solutions with yttrium and europium attained from waste phosphor dust rather than pure powders. In addition, more attention will be paid to minimize disturbances from possible sources of oxygen so as to maximize recovery.

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