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Optimized elemental analysis of fluorescence lamp shredder waste

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ABSTRACT

Fluorescence lamps contain considerable amounts of rare earth elements (REE). Several recycling procedures for REE recovery from spent lamps have been established. However, despite their economic importance, the respective recycling is scarce so far, with an REE recovery rate of less than 1%. A reliable analysis of REE and other relevant metals like Yttrium is crucial for a thorough and complete recovery process. This applies both to the solid matter and aqueous phase, since most of the recycling processes include wet-chemical steps. We tested seven different reagent mixtures for microwave-assisted digestion of fluorescent lamp shredder, including hydrofluoric acid, perchloric acid, and hydrogen peroxide. We determined the concentrations of 25 of the most relevant rare earth and other trace elements (Al, P, Ti, V, Cr, Fe, Ni, Cu, Ga, Ge, As, Y, Ag, Cd, Sn, Sb, La, Ce, Eu, Gd, Tb, W, Au, Hg, and Pb) in the respective dilutions. Two independent digestions, one a mixture of perchlorid/nitric/hydrofluoric acid and the other aqua regia, showed the highest concentrations of 23 of these elements, excluding only Sn and Tb. The REE concentrations in the tested lamp shredder sample (stated in g/kg) were 10.2 (Y), 12.1 (La), 7.77 (Ce), 6.91 (Eu), 1.90 (Gd), and 4.11 (Tb).

1. Introduction

The rare earth elements (REEs) are a group of 17 elements from the lanthanide series including scandium and yttrium that shares similar physical and chemical properties [1]. They are progressively important in transition to a green, low-carbon economy due to their vital role in electric cars, permanent magnets, phosphorus lamps, rechargeable NiMH batteries, catalysts and other applications [2]. In reality, the term of rare is misleading as these elements are widely present in earth crust. In contrast, the term relates to the effort of identification and refining of REEs with the challenge of cost-effective mining of sufficiently high ore grades at their geological occurrence [3].

REEs have a high supply risk due to the geopolitical situation resulting from limited Chinese exports. This, along with their importance in various clean and high-tech applications, has led the EU and the U.S. to label certain REEs, especially europium, terbium and yttrium as critical elements [4,5]. Recycling is often considered as one of the ways to reduce REEs criticality [6], especially the import dependency. Furthermore, REE mining and refinery have severe environmental impacts including ecological destruction, environmental pollution, soil erosion, and geological disasters [7]. Those can be reduced by REE recovery and recycling.

Fluorescent lamps are an important application for REE, especially Y, La, Ce, Eu, Gd, and Tb.

However, despite the vast literature dealing with lab-scale research efforts of recycling REEs from phosphor powders including selective extraction by ionic liquids [8], separation based on difference in magnetic properties of the phosphorus powder [9], liquid–liquid extraction [10], flotation [11], pneumatic separation [12], and gravity separation by dense liquids [13], less than 1% of REEs were commercially recycled in 2011 [2]. This low recycling rate can be as allocated due to technological difficulties (minor components of complex materials), inefficient collection, low toxicities of REEs and thus reducing the need for detoxification, and till recently low price and lack of incentives [1,2].

A large amount of phosphor material can be reclaimed from manufacturing residues and disposed devices. The disposed phosphor is a potential source of REEs, which can be recovered. It is ecologically and economically beneficial to recover REEs by recycling phosphor powder, as they are vital for many applications e.g. alloys, rare earth magnets or preparing catalysts. Therefore, it is necessary to develop new methods for efficient recovery of REEs from fluorescent materials, especially from waste phosphor [14].

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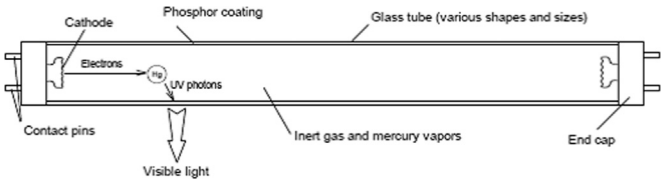

Fig. 1. Structure of double-capped linear fluorescent lamp [29].

1.1. Composition of lamp phosphor powder

Fluorescent lamps (Fig. 1) are internally coated by a thin layer of trichromatic phosphors to absorb the invisible UV energy emitted from the interaction of mercury (Hg) and electrons, and then convert it into visible light [15].

Standard tri-chromatic fluorescent lamps contain red, green and blue phosphor in standard chemical with a typical composition of 55%, 30% and 15%, respectively [15]. The chemical composition of pure tri-chromatic phosphors is a mixture of the rare earth elements Yttrium (46.9–51.2%), Europium (3.9–4.4%), Cerium (4.1–5.3%) and Terbium (2.2–2.6%). Next to these rare earth elements a chemical content of 29.9–35.9% Al, 2.7–4.0% Mg, 2.1–3.2% Ba exists in the pure tri-chromatic phosphors [15]. After collecting end-of-life fluorescent lamps containing this tri-chromatic phosphors are often treated by dismantling and crushing. The collected phosphor powder also contains impurities such as glass fractions, mercury and dust [16] analyzed the composition of phosphor powder from collected waste fluorescent lamps (Table 1). The elemental mass fractions were determined with X-ray fluorescence analysis of the air classifier fine fraction.

By now the focus is on recycling REMs. Rabah used spent fluorescent lamps (SFLs) for recovery of europium and yttrium. The SFLs were washed, cleaned and the two ends were removed mechanically. To prevent the escape of mercury vapour into the atmosphere, the SFLs were opened under 30% aqueous acetone. A rotating brush was moved through the inside of the lamp along its length under a stream of recycled water to collect the luminescent phosphor powder. The cleaned glass tube was used in the manufacture of new lamps. The water used for washing was filtered and evaporated at 110 °C to collect the powder. A mixture of sulphuric acid and nitric acid was used to leach rare earth metals. Calcium was precipitated from the leaching mixture as oxalate. Potassium thiocyanate was used to convert yttrium and europium sulphate to thiocyanate which were then extracted by organic solvent. From the solvent, the yttrium and europium were recovered as nitrate salts using N-tributyl-phosphate as solvent. The nitrate salts were dissolved in ethyl alcohol to separate europium nitrate from yttrium nitrate. Thermal reduction using hydrogen gas resulted in free metals. The isolated powder contained 61.52% calcium orthophosphate, 34.48% calcium sulphate, 1.65% yttrium oxide, 1.62% europium oxide and 0.65% metal impurities by weight. The Analysis was conducted by chemical methods and the usage of an atomic absorption spectrometer, direct current plasma (DCP) and a laser induced optical emission spectrophotometer. The acid mixture leached 96.4% of yttrium and 92.8% of europium. After stripping with organic solvent 99% of the REM were recovered achieving a metal separation factor of 9.4 [17].

Table 1
Elemental composition of waste phosphor powder [17].

Element	Wt%	Element	Wt%	Element	Wt%	Element	Wt%
Si	17.89	Mn	0.30	Na	4.94	Gd	0.09
Ca	12.44	F	0.38	Ba	5.79	Tb	0.12
P	5.56	Ce	0.30	Y	2.88	Eu	0.14
Al	4.32	La	0.31	Mg	1.02	Fe	0.38
Sb	0.19	K	0.47	Sr	0.73	Pb	0.21
Cl	0.22	–	–	–	–	–	–

Table 2
Chemical composition of fluorescent powder focused on REMs [18].

REM	mg/kg Dry solid
Y	49,260 ± 594
La	4583 ± 73.6
Eu	3957 ± 77.2
Ce	3383 ± 49.9
Tb	1320 ± 42.4
Gd	114 ± 1.70
Lu	8.8 ± 0.22
Sc	3.0 ± 0.47
Nd	1.40
Yb	1.00
Pm	0.99
Pr	0.99
Sm	0.33
Dy	0.30
Er	0.20
Ho	0.10

Additionaly, Belardi characterized powder of spent fluorescent lamps by determing the particle size and the chemical characterization has been done by thermal analyses, X-ray powder diffraction analysis, scanning electron microscope, electron microphobe analysis and electron microphobe analysis. The results for concentrations of REMs are summarized in Table 1.

Belardi characterized powder of spent fluorescent lamps by determining the particle size and the chemical characterization has been done by thermal analyses, X-ray powder diffraction analysis, scanning electron microscope, electron microprobe analysis and electron microprobe analysis [18]. The results for concentrations of REMs are summarized in Table 2.

Innocenzi et al. recoverd yttrium from cathode ray tubes [19]. They collected fluorescent powder from Relight, Rho, a company that processes fluorescent lamps and cathode ray tubes. From an industrial point of view, it is important to investigate the potential of treating the phosphor collected from two different types of electronic wastes-fluorescent lamps and cathode ray tubes (CRT) simultaneously in the same treatment facility. X-Ray Fluorescence (XRF) was used to characterize the powders. The lamp powder consisted of 4.57% of yttrium by weight and the CRT powder consisted of 13.74% of yttrium by weight. Atomic Absorption Spectroscopy (AAS) analysis shows that the lamp powder contains 2.77% and CRT powder contains 7.8% of yttrium by weight. Leaching tests were carried out on three types of powders: Lamp, CRT and Mix (a mixture of lamp and CRT) under the following operating conditions – 20% weight-to-volume pulp density, 2 M sulphuric acid, 70 °C, 3 h. For CRT and Mix powders 10% volume/volume hydrogen peroxide solution was used. All three powders exhibited 100% leaching of yttrium when subjected to leaching for 3 h. After leaching for 24 h, CRT, Lamp and Mix powders exhibited a leaching rate of 91%, 99% and 100%, respectively. Purification of leaching solution was done in two steps – (1) leach liquor basification with NaOH and (2) Precipitation of impurities with sodium sulphide. In Mix and Lamp leach liquors, yttrium was precipitated along with zinc and calcium during the basification step and was analysed using XRF and XRD (X-ray Diffraction). The CRT leach liquor did not exhibit precipitation. pH 2.5 was the most suitable for yttrium precipitation after purification with yields of 45%, 35%, and 0% for lamp, Mix, and CRT, respectively. Calcination at 600 °C results in 95% pure yield of yttrium oxide. This research shows that the same process can be used to treat yttrium containing WEEE adapting the experimental parameters accordingly [19].

In 2014 Zhang compared the rare earth recycling efficiencies by