



Characterization and leaching of real fluorescent lamp waste for the recovery of rare earth metals and mercury



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ABSTRACT

Current resource issues and the growing demand for metals used in advanced technologies have focused attention towards more efficient processing of end-of-life products and waste streams. Fluorescent lamp waste is a viable target for the recovery of rare earth metals (REMs); specifically cerium, europium, gadolinium, lanthanum, terbium, and yttrium. Waste originating from a discarded lamp processing facility was investigated using Scanning Electron Microscopy/Energy Dispersive Spectroscopy and X-ray Diffraction. Total dissolution experiments were carried out with aqua regia at elevated temperatures in order to estimate an average metal content and assess the recycling potential of the material.

Leaching using different solutions (pure water, ammonium chloride, acetic acid, nitric and hydrochloric acid) and parameters (temperature, ultrasound-assisted digestion, solid:liquid ratio and leaching agent concentration) was investigated for the recovery of REMs and mercury. Cerium, europium, gadolinium, lanthanum, terbium, and yttrium were the REMs identified, with a total average content of 8.4 ± 0.4 g/kg dry waste. An average of 0.7 ± 0.1 g mercury/kg dry waste was quantified. Partial removal of impurities from the material raised the average REMs content to 105.7 ± 5.3 g/kg waste. Pure water and ammonium chloride solution (1 M) performed poorly as leachants. Efficient leaching of europium and yttrium (over 95%, respectively 97% dissolution) was achieved in less than 24 h at 20 ± 1 °C, using weak nitric and hydrochloric acid solutions (0.5 M). Leaching of cerium, gadolinium and terbium occurred slowly and did not reach equilibrium even after 96 h. An increased acid concentration and increased temperature, and ultrasound-assisted digestion improved the leaching efficiency for all investigated elements. Hydrochloric acid proved to be as efficient as nitric acid when it comes to solubilizing most REMs. The former showed better efficiency for mercury: $89.6 \pm 3.3\%$ vs. $23.2 \pm 0.3\%$, when using a 4 M solution. Acetic acid (25% v/v solution) dissolved approx. 50% of the europium, 75% of all yttrium, between 2 and 10% of the other REMs, and just over 2% of the mercury. Based on the observations, several processing methods are suggested for the samples investigated.

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1. Introduction

The metals known as rare earth metals (REMs) are a group of elements comprising lanthanum, the 14 lanthanides, yttrium and scandium. Many of these metals are essential in advanced technologies (phosphors, lasers, magnets, batteries, magnetic refrigeration, high-temperature superconductivity, safe storage and transport of hydrogen, etc.), being characterized by high specificity (USGS, 2002). This has led to an increase in their demand, with significant price fluctuations along the way. Several reports acknowledge REMs to be of critical importance (European Commission, 2010, 2011; UN Environment Programme and UN University, 2009; USGS, 2002) and many industrialized countries are facing problems securing sustainable supplies. Recycling of end-of-life products and processing of waste streams has made a positive contribution to this problem, providing both environmental and economic benefits.

Fluorescent lamps are one of the main targets when it comes to reclaiming REMs, especially when taking into account the large amounts sold and disposed of every year (Aucott et al., 2003; Durao et al., 2008; Tansel et al., 1998). Hundreds of millions of fluorescent lamps are sold every year; 397 million compact fluorescent lamps were sold in 2007 in the US alone, and about 288 million units were sold in Europe (McKeown and Swire, 2009; Travis, 2011; US Department of Commerce, 2007). Mechanical separation is already used for the easily recoverable components, such as aluminum end caps, plastics, circuit boards and glass, but it cannot entirely address the current resource issues. Further processing of the waste streams is required in order to recover all of the valuable constituents, which is a challenge due to the presence of mercury in the stream (Jang et al., 2005; Raposo et al., 2003) and the complicated chemical processes available. Thermal treatment (distillation), acid leaching followed by metal recovery from solution, and stabilization (e.g. chemical oxidation of elemental mercury to less volatile mercury compounds) are the methods currently used to deal with mercury in the end-of-life products (Durao et al., 2008). The first two methods have the advantage of removing the contaminant

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from the stream, and have been the subjects of several studies (Chang et al., 2009, 2010; Durao et al., 2008; Jang et al., 2005). Thermal treatment is generally preferred for treating the cullet (waste glass), and shows better efficiency (Jang et al., 2005).

The work presented here focuses on the characterization of industrial fluorescent lamp waste and the leaching of mercury and REMs from the material. The fact that real waste, originating from a discarded lamp processing facility, is used has distinctive advantages. Not all of the proposed processes described in literature have been tested on real samples. Parts of the experiments have been performed only on a laboratory scale, using clean materials such as unbroken lamps, artificial mixtures that resemble real samples, or pure commercial phosphors. A recycling process optimized for such streams may pose problems when applied to real waste simply because the composition of the system is different. Moreover, certain treatment steps tested by the recycler (such as the stabilization of elemental mercury via hypochlorite oxidation) may pose difficulties to the use of some of the already proposed methods. Adjustments to an existing process or the development of an entirely new one may be needed, depending on the chemistry of the stream.

2. Background

Fluorescent lamps use various mixes of red, green, and blue REMs containing phosphors to produce visible light (Table 1) (Cuif et al., 2005; Ronda et al., 1998; US Department of Energy, 2009).

While the recycling of certain elements, such as cerium, may not be desired at the moment (due to high availability and low prices), export quotas, scarcity, demand and price fluctuations make the recycling of other REMs contained in fluorescent lamps, such as europium, terbium and yttrium, worthwhile (European Commission, 2010). There are, however, several challenges associated with this. Aside from the mercury contamination, the rather low concentration of metals in the material, the high purity of the REMs required in certain applications (99.999%), as well as the difficulty of individually separating them (due to having similar properties and chemical behavior) make the development of a sustainable process difficult.

A critical review regarding the recycling of REMs from waste streams such as permanent magnets, car batteries and lamp phosphors was recently published (Binnemans et al., 2013). This reviewed proposed pyrometallurgical and hydrometallurgical routes for processing these waste streams. The relevance of Life Cycle Assessment for REMs was also discussed, with the authors emphasizing that, besides addressing the supply risk, REM recycling also reduces the environmental challenges associated with their mining and processing.

Dense medium centrifugation (Hirajima et al., 2005b), flotation recovery (Hirajima et al., 2005a) and solvent extraction based processes (Mei et al., 2009; Nakamura et al., 2007; Rabah, 2008; Shimizu et al., 2005; Yang et al., 2012) have been investigated for the separation of REMs. Acid leaching followed by precipitation using oxalic acid has been used to recover yttrium (De Michelis et al., 2011). For the moment hydrometallurgical processes appear to be the best approach. Leaching of the waste, typically using acidic solutions, followed by solvent extraction is suitable if individual separation of REMs is the goal.

Table 1
REM-based phosphors used in fluorescent lamps.

Phosphor type	Possible compounds
Red phosphor	$Y_2O_3:Eu^{3+a}$
Blue phosphor	$BaMgAl_{10}O_{17}:Eu^{2+}$; $(Sr,Ca,Ba)_5(PO_4)_3Cl:Eu^{2+}$
Green phosphor	$CeMgAl_{10}O_{17}:Tb^{3+}$; $LaPO_4:Ce^{3+},Tb^{3+}$; $(Ce,Tb)MgAl_{11}O_{19}$; $(Ce,Gd,Tb)MgB_5O_{10}$

^a The colon symbol specifies doped compounds, in this case yttrium oxide doped with europium.

Leaching and recovery of REMs from spent fluorescent lamps has been the focus of several studies but, although there is great interest, industrial scale applications are in an incipient stage (Meyer and Bras, 2011). Lab-scale leaching experiments have been carried out using various agents. A sulphuric and nitric acid mixture has been used to leach europium and yttrium from the fluorescent powder of spent lamps (Rabah, 2008). 92.8% europium and 96.4% yttrium were leached during 4 h at 125 °C, using 5 MPa pressure. Sulphuric acid has also been used to leach waste fluorescent lamp powder (Hong-mei, 2010). After 8 h at 37 °C, solid:liquid ratio of 1:50, 250 rpm stirring, 61.1% cerium, 71.5% europium, 66.9% terbium, and 75.3% yttrium were leached using a 2 M sulphuric acid solution. Nitric acid, hydrochloric acid, sulphuric acid and ammonia have been tested as possible leaching agents for yttrium (De Michelis et al., 2011), the latter showing poor efficiency. A 4 N sulphuric acid solution at 90 °C and a solid:liquid ratio of 20% leached out more than 90% yttrium and also led to the precipitation of the calcium, barium and lead present in the samples. Leaching with hydrochloric acid has also been investigated (Wang et al., 2011); under optimum conditions (4 M acid concentration, solid:liquid ratio of 100 g/L, 600 rpm stirring, 60 °C, 60 min contact time) 89.85% of all REMs were leached, with yttrium accounting for 96.28%.

3. Experimental

3.1. Characterization of the waste

The investigated material originated from a discarded lamp treatment facility. The company processes various types of fluorescent lamps in large batches, simultaneously. Crushing is used to reduce the volume of the waste and facilitate separation into different fractions: electronics, end caps, glass, phosphors, etc. Chemical oxidation using hypochlorite was carried out for the sampled batch as a possible containment method for elemental mercury during crushing. Due to the nature of the process the separation of pure phosphors powder is not possible. Sampling of waste was done on site. Drying and homogenization (manual mixing, grinding) were required to perform some of the investigations. Drying was carried out at room temperature (20 ± 1 °C), for 72 h, in a fume cupboard.

SEM/EDS (FEI Quanta 200F/Oxford Inca 300 EDS System) was used to magnify and analyze the appearance of the material, to obtain qualitative data about the elements present and to determine the occurrence and distribution of the components. XRD (Siemens Diffraktometer D5000) was used to identify the structure in which REMs are present and the atomic arrangement.

To estimate the metal content in the waste, dissolution experiments were performed using aqua regia at an elevated temperature. The solution was prepared before use by mixing hydrochloric acid solution (37%, puriss, Labasco) and nitric acid solution (64–66%, puriss, Sigma Aldrich) in a 3:1 v/v ratio. A triplicate test was made. Weighed amounts of dry waste (approx. 1 g) were heated with 10 ml aqua regia at 90 ± 3 °C for 2 h, using manual shaking at 15 min intervals. The solutions were left to cool, filtered using polypropylene syringe filters (0.45 µm, VWR) and syringes, and diluted with pure water (MilliQ, Millipore, >18 MΩ/cm) in 25 ml volumetric flasks. A 1 M nitric acid solution, prepared from concentrated stock solution (65%, suprapure, Merck) and pure water (MilliQ, Millipore, >18 MΩ/cm), was used to further dilute the solutions for analysis. The non-dissolved residue (mainly glass) was sampled and investigated with SEM/EDS to see if the attached phosphor particles had solubilised completely. The metal content was determined using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (iCAP 6500, Thermo Fischer).

Mechanical removal of large impurities from the stream (mainly glass) was tested by the recycler in order to concentrate the REMs and reduce the volume of the waste. The obtained material was also investigated, by subjecting it to the same procedure described above.

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