



Research article

A hydrometallurgical process for the recovery of terbium from fluorescent lamps: Experimental design, optimization of acid leaching process and process analysis



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ABSTRACT

Terbium and rare earths recovery from fluorescent powders of exhausted lamps by acid leaching with hydrochloric acid was the objective of this study. In order to investigate the factors affecting leaching a series of experiments was performed in according to a full factorial plan with four variables and two levels (4²).

The factors studied were temperature, concentration of acid, pulp density and leaching time. Experimental conditions of terbium dissolution were optimized by statistical analysis. The results showed that temperature and pulp density were significant with a positive and negative effect, respectively. The empirical mathematical model deduced by experimental data demonstrated that terbium content was completely dissolved under the following conditions: 90 °C, 2 M hydrochloric acid and 5% of pulp density; while when the pulp density was 15% an extraction of 83% could be obtained at 90 °C and 5 M hydrochloric acid. Finally a flow sheet for the recovery of rare earth elements was proposed. The process was tested and simulated by commercial software for the chemical processes. The mass balance of the process was calculated: from 1 ton of initial powder it was possible to obtain around 160 kg of a concentrate of rare earths having a purity of 99%. The main rare earths elements in the final product was yttrium oxide (86.43%) following by cerium oxide (4.11%), lanthanum oxide (3.18%), europium oxide (3.08%) and terbium oxide (2.20%). The estimated total recovery of the rare earths elements was around 70% for yttrium and europium and 80% for the other rare earths.

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1. Introduction

In last years the use of fluorescent lamps is considerably increased as consequence of the decision of European Union to abolish the traditional incandescent bulbs in support of fluorescent ones for economic and environmental reasons. However in more recent time, the trend is to substitute the fluorescent lamps by LEDs and the consequence is that the amount of lamps to be disposed off is significantly increased. The question is sensitive considering that fluorescent lamps are classified as hazardous waste with CER code 200121* for the presence of mercury (Directive 75/442/EEC; Decision 94/904/EC; Directive 91/689/EEC), (Commission of the European Communities, 2000). The disposal of this type of waste

requires the recycling and re-use of the materials that they contain. Currently the recovery of only a few fractions of materials occurs, such as the glass tube and the parts in aluminum and copper. Moreover the lamps contain in the fluorescent powder valuable materials as the Rare Earths Elements (REEs), mainly yttrium, lanthanum, europium, cerium, terbium and gadolinium. REEs are a group of strategic chemical elements not only for several fields of application (e.g., magnets, catalysts, batteries) but also for their limited supply. The supply risk is not due to geographical distribution, in fact there are numerous REEs deposits over the whole world (up to 400 mine projects were initiated during the last years). The recent strong price decreases led to closure of the just opened deposits. Therefore the monopoly mainly resulted from economic and ecological reasons. This potential supply risk of REEs caused a fluctuation of REO and REEs prices that increased since 2010, reached their peaks in 2011 and already decreased significantly during 2012. For overcoming this problem, several countries are

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investing in research to develop innovative processes for their recovery from secondary raw materials. To identify the most suitable recovery process the characterization of the fluorescent powders coming from the dismantling of the lamps is absolutely required. In fact by the different characterization techniques it was found as 78% of the particles, including the phases containing the main elements of the rare earths, constituting the fluorescent powder has a size smaller than $38\ \mu\text{m}$ (Belardi et al., 2014). The phosphor powder is about 3% of the mass of a fluorescent lamp and the concentration of rare-earth oxides has been estimated as 27.9% (Binnemans et al., 2013; Wang et al., 2011). Yttrium is the rare earths most concentrated followed by lanthanum, europium, cerium and terbium (Belardi et al., 2014). REEs can be recovered by hydrometallurgical and pyrometallurgical processes. The hydrometallurgical treatments found in the literature analysis are mainly focused on the recovery of yttrium and europium that are dissolved from fluorescent powders using mild acidic solutions. It was estimated that the actual recycled phosphors is about 10% of REE oxide (Wang et al., 2011). The other rare earths are lost during the recycling processes and it causes an economic loss especially considering the economic value of the terbium equal to 736€/kg (02/2015) and 429 €/kg, (06/2016), (DERA). In order to have a better view on the state-of-the-art and to improve engineering possibilities of rare earth extraction from secondary resources, a review of the most technologies that are currently in use in REEs recovery is needed. Following a list of scientific works that describe mainly leaching treatments to recover REEs from fluorescent lamps is reported. Tooru et al. (2001) described a process consisting in a leaching with sulfuric acid and oxalate precipitation. Yttrium and europium recovery was about 65% and the grade of the products was 98%. Otto and Wojtalewicz-kasprzac (2012) pointed out a selective process finalized to the recovery of rare earths. The material was treated with a cold HCl leaching to remove halophosphates. A second leaching with hot hydrochloric and/or sulfuric acid leaching was carried out to remove the REEs. However, due to the easily solubility of $\text{Y}_2\text{O}_3\text{:Eu}$, some of them was lost during cold HCl leaching. De Michelis et al. (2011), Innocenzi et al. (2013) studied the recovery of yttrium from powders from spent fluorescent lamps. The research included characterization, leaching tests with several types of acids (nitric, sulfuric and hydrochloric) and recovery of yttrium by precipitation using oxalic acid. In the process worked out by Innocenzi et al. (2013) after leaching, a step of precipitation with sodium sulphide to remove impurities from leach liquors, such as calcium, was carried out. After this treatment of the residual solutions oxalic acid was added to precipitate yttrium oxalates. The final products were calcinated to obtain yttrium oxides. The process described by Rabah (2008) included firstly a step to decontaminate lamps from mercury by breaking the tubes under 30% of aqueous acetone. The powders were subjected to a leaching treatment using sulfuric/nitric acid mixture for 4 h at high temperature and 5 MPa. The leaching recoveries were 96.4% and 92.8% for yttrium and europium, respectively. The process described by Porob et al. (2011) provided that the initial material had to be burned with an alkaline material to transform phosphates into oxides. After this leaching using different acids (nitric, sulfuric and hydrochloric) at high temperature was performed. Finally the REEs could be recovered by precipitation and solvent extraction.

The work of Tunsu et al. (2014) was focused on the dissolution process of rare earths from fluorescent lamps. The effect of several factors on extraction yields was investigated. The parameters studied were: leaching agent (pure water, ammonium chloride, acetic acid, nitric and hydrochloric acid) and its concentration, temperature, ultrasound-assisted digestion and solid/liquid ratio. Water and ammonium chloride solution were not efficient agents for leaching of REEs and mercury, instead a good extraction yields for Eu and Y

(over 95% and 97%) were obtained using nitric and hydrochloric acid solutions (0.5 M) for 24 h at $20 \pm 1\ ^\circ\text{C}$. Leaching of the other rare earths as cerium, gadolinium and terbium occurred slowly, required more time (96 h) and the efficiency was small (around 15%). Hydrochloric acid was an efficient agent to dissolve REEs as nitric acid. The acid concentration, temperature and ultrasound-assisted digestion had a positive effect on leaching extractions. Regarding acetic acid dissolution, the extractions were: around 50% for Eu, 75% for Y, 2–10% for the other REEs and over 2% for mercury.

This is a non-exhaustive list of scientific works relating to the recycling processes for lamps, while more complete reviews have been reported by Innocenzi et al. (2014), Wu et al. (2014), Tan et al. (2015) and Binnemans et al. (2013). As shown and summarized by reviews cited above, the researches are mainly focused on the recovery of yttrium and europium from red phosphors of fluorescent powders with a recovery that could reach more than 80%, while the scientific literature is poorer of the works about the recovery of other rare earths due their difficulties of leaching, mainly for cerium, lanthanum and terbium. In the present manuscript an innovative process for the treatment of fluorescent lamps, focused on green phosphors recovery, was presented. In particular the terbium extraction was studied because together with europium it is the rare earth with a highest economic value. Furthermore the presence of terbium in the final product increases the value of the mixture of rare earth oxides. This manuscript can represent a starting point for new researches focused on the recycling of green phosphors and recovery of critical metals as terbium. In the work, terbium dissolution with hydrochloric acid was studied using the technique of the design of experiments (Montgomery, 1997) in particular using a full factorial plan with four factors and two levels. The investigated factors were: temperature, hydrochloric acid concentration, pulp density and leaching time. The results of the experiments were analyzed by analysis of variance (ANOVA) and the significant effects were defined. Afterwards a mathematical model for terbium dissolution was proposed as a function of the main influenced factors. In order to complete the work a flowsheet for the treatment of lamps with a process analysis using Super Pro Design was proposed.

2. Materials and methods

2.1. Materials and waste characterization

A waste phosphor powder, collected from fluorescent lamps, was supplied by Relight Srl (Rho, Milan, Italy). Powders were treated with a cyclone to an approximately 1 mm cutoff grain size to reduce content of inert materials and increase the grade of REEs. The phosphor powder composition was analyzed by X-ray fluorescence analysis and by Agilent Technologies 5100 ICP-OES after acid attack of the initial materials. The acid attack was performed in a closed flask as follows: around 0.5 g of initial material was dissolved with 1:3 of nitric acid and hydrochloric acid at $90\ ^\circ\text{C}$.

Potassium hydroxide (min 85%, Merck) and hydrochloric acid (37%, Titolchimica) were used to carry out the calcination and leaching experiments, respectively.

2.2. Leaching tests

The phosphors of lamps can be divided in three main groups: green phosphors $\text{LaPO}_4\text{:Ce}^{3+},\text{Tb}^{3+}$, red phosphors $\text{Y}_2\text{O}_3\text{:Eu}$ and blue phosphors $(\text{Ce,Tb})\text{MgAl}_{11}\text{O}_{19}$ (Binnemans et al., 2013). Terbium is present in the green and blue phosphors. Leaching of these last phosphors required very aggressive conditions, in contrast of red phosphors that could be dissolved using sulfuric acid (Rabah, 2008; De Michelis et al., 2011; Innocenzi et al., 2013) or (Rabah, 2008) and

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