



# Application of solvent extraction operation to recover rare earths from fluorescent lamps

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## ABSTRACT

The paper is focused on the application of solvent extraction for the recovery of rare earth elements from sulfuric leaching solutions obtained by the dissolution of fluorescent powders of lamps. The efficiency on rare earths extractions of three extractants, Cyanex 272, Cyanex 572 and D2EHPA in kerosene were investigated as a function of pH levels.

Similar extraction for all the rare earths elements were observed, but the tests performed with D2EHPA showed that for pH values less than 1, yttrium and terbium could be extracted with yields higher than the other rare earths. The orders of the extraction were determined: yttrium  $\geq$  terbium  $>$  gadolinium  $\geq$  europium  $>$  cerium  $\geq$  lanthanum. Further tests showed the optimal conditions, under the investigated ones, to extract yttrium with traces of terbium and cerium from sulfate leaching solutions. According to the experimental results, operating conditions of extractions were proposed in order to establish the guidelines for the following stripping and operation steps to recover rare earths selectively or at least in groups of them. A simulation of the proposed process was performed using a specific software in order to define the mass and energy balance of the entire recycling treatment of spent lamps.

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## 1. Introduction

Spent fluorescent lamps are hazardous waste, under the code 20 01 21\* included in the European Waste Catalogue (Commission of the European Communities). The powders contained in the inner wall of the exhausted lamps should be treated in order to remove mercury before their final disposal (De Casa et al., 2007). These powders are an important secondary source of rare earth elements (REEs) that in recent years have become even more crucial for the emerging technologies (electric/hybrid automobiles, mobile phones, magnetic refrigeration, wind turbines, flat screen televisions, disc drivers, compact fluorescent lights, water purification and defence technologies (New Mexico, Earth Matter, 2011; Xie et al., 2014). Hence in the last years many researchers focused their studies on the development of the processes for the recycling of this type of waste with the principal aim to recover these

valuable metals. The main components of the fluorescent lamps containing REEs are the red phosphors  $Y_2O_3:Eu^{3+}$  (YOX), the green phosphors  $LaPO_4:Ce^{3+},Tb^{3+}$  (LAP),  $(Gd,Mg)B_5O_{12}:Ce^{3+},Tb^{3+}$  (CBT),  $(Ce,Tb)MgAl_{11}O_{19}$  (CAT) and the blue phosphors  $BaMgAl_{10}O_{17}:Eu^{2+}$  (BAM) (Yu and Chen, 1995; Ronda, 1995; Justel et al., 1998; Ippolito et al., 2017b). The rare earth oxides content is within 10–20% (Binnemans et al., 2013). The processes for the recovery of valuable materials from lamps include physicochemical methods to recover the phosphors and reuse for the production of new lamps or chemical treatments in order to obtain a product rich in REEs. These methods are summarized in various reviews (Binnemans et al., 2013; Innocenzi et al., 2014; Tan et al., 2015). The hydrometallurgical processes are usually performed after physical and mechanical pretreatments to remove glass (88 wt%), metals (5 wt%), plastic (4 wt%) and phosphors powders (3 wt%) (Binnemans et al., 2013). The powders are leached using several acids: Tooru et al. (2001), Rabah (2008), De Michelis et al. (2011), Innocenzi et al. (2013a, b, 2016, 2017) and Ippolito et al. (2017a,b), studied the leaching process using diluted sulfuric acid. Otto and Wojtalewicz-kasprzac (2012) reported the efficiency of leaching by HCl. Diluted acid

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leads in solution only the red phosphors instead to dissolve green phosphors strong acid conditions are necessary, that is because these last phosphors have a higher chemical resistance. Wang et al. (2011) showed that hydrochloric acid solution (4 M) in presence of hydrogen peroxide (4.4 g/L) was a strong leachant to dissolve rare earth trichromatic phosphors containing yttrium, cerium, europium, terbium and lanthanum.

Alternatively, a mechanical activation by ball milling to destroy the crystal structure of the green and blue phosphors (Mio et al., 2001; Song et al., 2017) or a preliminary alkaline fusion (Zhang et al., 2013; Innocenzi et al., 2016; Ippolito et al., 2017a, b) can be performed in order to transform the phosphors into oxides that are more easily dissolved by diluted acid media. After leaching, REEs are recovered by precipitation and/or solvent extraction to obtain a REEs rich product.

The liquid–liquid extraction of individual REEs is a complex operation due to the fact that these elements have similar physical and chemical properties: many extractable ions are in solutions therefore it usually takes a considerable number of separation stages to produce a purified individual rare earth.

Three major classes of extractants are usually used to extract REEs from solutions: cation exchangers, solvating extractants and anion exchangers (Xie et al., 2014). The most used extractants, the organophosphorous acids, belong to the first category: di (2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (EHEHPA or HEHEHP), di-2-ethylhexylphosphinic acid (P299), di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272) and di-2,4,4-trimethylpentyl-monothiophosphinic acid (Cyanex 302).

Considering the selective separation and recovery of REEs from leach liquors after dissolution of spent fluorescent lamps, several extractants were studied such as dibutyl butylphosphonate (DBBP), HEHEHP (Nakamura et al., 2007), Cyanex 923 (Tunsu et al., 2014), tributylphosphate (TBP) (Shimizu et al., 2005) and D2EHPA. Nakamura et al. (2007) studied the efficiency of PC 88 A diluted in kerosene for the separation of rare earths from nitrate leaching liquors. Using a process simulation, a possible flowsheet was proposed according to the experimental results. In particular, the process included two extraction steps, at pH = 2 and pH = 2.6, different scrubbing steps and rare earths precipitation by oxalic acid. Finally, the total recoveries were 97.8% Y, 58.1% Tb, 52.8% Eu and purity of the final product was 98.1%, 85.7% and 100% for yttrium, terbium and europium, respectively.

Rabah (2008) proposed a process that included autoclave digestion of the fluorescent powders in the H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> acid mixture as leaching agent for 4 h at 125 °C and 5 MPa. The leaching dissolutions were 96.4% for Y and 92.8% for Eu. Europium and yttrium sulfates were converted to thiocyanate, then the circuit included solvent extraction with TBP extractant and stripping with nitric acid. Europium nitrate was separated from yttrium by dissolving in ethyl alcohol. Y and Eu metals were recovered after thermal reduction using hydrogen gas at 850 °C and 1575 °C, respectively.

Tunsu et al. (2016a, b) reported their study in laboratory and pilot scale for the recovery of yttrium and europium from fluorescent powders of lamps. Mercury was leached using I<sub>2</sub>/KI solutions obtaining yields more than 96%. The other elements, impurities and rare earths were dissolved using nitric acid, especially calcium was leached over short time periods. The REEs contained in the residue were dissolved in two steps. The leaching was followed by solvent extraction of Y and Eu using 35% v/v Cyanex 923 in kerosene in a mixer settler system with three extractions and four stripping steps. After stripping, oxalic acid was added in solution and a final oxide with 94.61% of Y, 5.09% of Eu and 0.26% of other REEs was obtained. The same authors (2016b) reported another series of experiments in which solvent extraction of yttrium and europium

from nitrate leach liquor was discussed. Yttrium was extracted using Cyanex 572 at pH = 0 while europium was extracted in a second step at pH = 1. Yttrium and europium were separately recovered, as oxide, by adding oxalic acid.

Yang et al. (2012) studied instead the efficiency of the ionic liquid, in particular of N,N-dioctyldiglycolamic acid in 1-butyl-3-methylimidazoliumbis (trifluoromethylsulfonyl)imide. According to the literature, the main advantage of the solvent extraction operation is that it is more effective than other techniques as for instance selective precipitation, since the final product can achieve high purity (99%). Certainly, the main disadvantages are: the high cost of some types extractants; the high dangerous of these substances, that require specific arrangements from the safety of the operators and the high plant cost for the purchase and installation of several equipment for the solvent extraction operation. For these reasons, from an industrial point of view solvent extraction technology is not widely used anyway the cost of the process can be balanced by the high price of the final products that in this case are concentrates of rare earths with high purity.

The present work describes the experimental tests carried out to recover REEs from fluorescent powders using liquid–liquid extraction. The study is part of a research European project (HydroWEE demo 305489, FP7 Work Program) on the development of a process to recover valuable metals from spent fluorescent lamps (Innocenzi et al., 2016; Ippolito et al., 2017a,b). The main features of these previous works were 1) characterization of fluorescent powders of lamps; 2) thermal pretreatment of initial material in order to improve the efficiency of the leaching; 3) dissolution of rare earths with sulfuric acid and 4) recovery of REE oxides by precipitation with oxalic acid and calcination. The previous research showed that the rare earths, including REEs in the green phosphorus, could be leached with sulfuric acid after thermal treatment at 950 °C, and recovered by precipitation with oxalic acid. The final product was a mixture of oxides containing yttrium, europium, terbium, gadolinium, lanthanum and cerium. Moreover, in this present paper solvent extraction is studied to investigate the possibility to selectively separate the rare earths from leaching solutions, in order to produce more oxides of REEs with high purity. The efficiency of three extractant (D2EHPA, Cyanex 272 and Cyanex 572) on the rare earths extractions was studied.

The novelty of the present work is the application of solvent extraction for the recovery of all rare earths including terbium from fluorescent lamps using real solutions coming from dissolution of powders with sulfuric acid. Experimental tests performed with real leach solutions allow to study the solvent extraction operations under conditions as close to the possible industrial process.

A comparison of the results in term of separation factors with literature data highlighting the analogies and differences is also reported. Finally, a suitable recovery process with mass and energy balance is described according to the experimental results including thermal pretreatment, leaching with sulfuric acid, solvent extraction with D2EHPA in kerosene, stripping with sulfuric acid and final recovery of two rare earths concentrates, one rich in yttrium and the other rich of all rare earths.

## 2. Material and methods

### 2.1. Materials

The leaching solutions of fluorescent powders of lamps were used for solvent extraction experiments. These solutions were prepared according to the best leaching optimal conditions identified in the previous work (Ippolito et al., 2017a,b). Sulfuric acid (CARLO ERBA, 96%) was used as leaching reagents while sodium hydroxide (FLUKA, ≥ 97%) was used to adjust pH during the solvent

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