



Rare earth elements recovery from fluorescent lamps: A new thermal pretreatment to improve the efficiency of the hydrometallurgical process



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ABSTRACT

The literature is rich of scientific works regarding the recovery of yttrium and europium from red phosphors of lamps and it is poor of papers about the extraction of terbium, cerium and lanthanum from green phosphors. The red phosphors are constituted by rare earth oxides and they are more easily dissolved in the leaching step respect to the green phosphors that are rare earth phosphates. This paper was mainly focused on the recovery of rare earths from green phosphors, with major attention on terbium extraction that is the most valuable metal. Hence, an innovative process with a thermal pretreatment was proposed. Alkaline fusion with barium hydroxide and the following leaching were studied under various experimental conditions to optimize the process parameters. Statistical design of experiments and analysis of variance were performed in order to determine the main effects and interactions between the investigated factors (barium hydroxide/powders ratio, sulfuric acid concentration, leaching temperature, pulp density and leaching time) for the dissolution of each rare earth elements. The results, for most of REE considered, especially for terbium showed that barium hydroxide/powder ratio and temperature were significant with a positive effect. Concentration of sulfuric acid and pulp density were significant with a negative effect. Time of leaching instead had a very slightly positive effect. The best extraction yields, obtained under the optimal conditions, were: 99% for yttrium and europium, 80% for terbium, 65% for lanthanum, 63% for gadolinium and 60% for cerium. Therefore, rare earth oxides were produced after oxalic acid precipitation and calcination. The grade was 82.22% of yttrium oxide, 8.38% of europium oxide, 2.43% of cerium oxide, 2.29% of gadolinium oxide, 1.77% of lanthanum oxide and 1.52% of terbium oxide.

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1. Introduction

Rare earth elements (REE) are a group of metals used for several fields; one of the main applications is the production of the phosphors that have the optical phenomenon of phosphorescence. For this reason they are mainly used for the production of fluorescent lamps. In the last years the manufacturing of these devices significantly increased as consequence of the abolition of the traditional incandescent bulb. REE are present in the earth's crust in high

concentration however the extraction from ores of these metals is difficult. Moreover the open mining sites are concentrated only in a few countries of the world, mainly China, and often the market and exports are regulated by internal economic policies. The scarcity of the primary sources for European States it led to focus the attention on the extraction of REE from secondary sources as fluorescent lamps. At the end of their useful life the lamps are classified as hazardous materials for the presence of mercury (CER 200121) (Commission of the European Communities, 2000: Directive 75/442/EEC, Council Decision 94/904/EC, Council Directive 91/689/EEC) and need to be properly handled. The European Union has established the Directives for their disposal and recycling given their high concentration of REEs. Therefore more research groups

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are concentrated on the extraction and recovery of the metals from fluorescent lamps. The processes consist in the recycling of the phosphors for the re-use in new lamps and extraction of REE from phosphors by pyro and hydrometallurgical processes (Binnemans et al., 2013). According to Wang et al. (2011) the content of REE in the phosphors of lamps can reach 27.9% but only 10% are recovered. The recycling processes include a pretreatment of the spent lamps to separate the phosphors from the other part of the device, after the REE contained in the phosphors can be recovered by chemical process including dissolution with acids and recovery by several methods as precipitation. The low percentage of REE recovery from phosphors depends on the high acid resistance of some type of phosphors. In the lamps there are different phosphors: 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) (Justel et al., 1998; Yu and Chen, 1995; Ronda, 1995). The red phosphors are easily dissolved by diluted acid respect to the other ones. Tunsu et al. (2014) studied the leaching of the fluorescent powders of lamps using different solutions (pure water, ammonium chloride, acetic acid, nitric and hydrochloric acid) varying some parameters (temperature, ultrasound-assisted digestion, solid: liquid ratio and leaching agent concentration). Pure water and ammonium chloride solution (1 M) were not efficient to dissolve REE. 97% of extraction for yttrium and europium was obtained using weak nitric and hydrochloric acid solutions (0.5 M) in less than 24 h at 20 ± 1 °C. Leaching of cerium, gadolinium and terbium occurred slowly and did not reach equilibrium even after 96 h. Hydrochloric acid was an effective leaching agent as nitric acid. 50% of extraction for Eu, 75% for Y, 2–10% for the other REE was obtained using acetic acid solution (25% v/v solution).

Scientific literature is rich of works in which the recycling processes for the extraction of yttrium and europium are described, and it is poor of research for the treatment of the phosphate for the recovery of the other REE and in particular of terbium that is the most important REE, after europium, from an economic point of view. The extraction of yttrium and europium from fluorescent spent lamps was studied by several authors, for example Tooru et al. (2001) proposed a process consisting of three stages: pneumatic classification, sulfuric acid leaching and oxalate precipitation. Yttrium and europium recovery was about 65% and the grade of the final product was 98%. Shimizu et al. (2005) studied the yttrium and europium recovery achieving 99.5% of extraction by supercritical carbon dioxide working with tri-n-butyl phosphate, nitric acid and water. A few years later Rabah (2008) achieved a dissolution of 96.4% and 92.8% for yttrium and europium, respectively, with an acidic leaching for 4 h, at 125 °C and 5 MPa. Otto and Wojtalewicz-kasprzac (2012) described a process to recover selectively the REE from fluorescent powders. The treatment, after mechanical separation and sieving until 20–25 μm , included the leaching with hydrochloric acid at low temperature, less than 30 °C. In this step halophosphate phosphors were dissolved, after that a leaching with hydrochloric acid at 60–90 °C dissolved $Y_2O_3:Eu^{3+}$ instead $LaPO_4:Ce^{3+},Tb^{3+}$ were extracted by sulfuric acid at high temperature (120–230 °C). Finally aluminate phosphors were dissolved using 35% sodium hydroxide at 150 °C. In the past our research group studied a hydrometallurgical process for the recovery of yttrium (De Michelis et al., 2011; Innocenzi et al., 2013a, b). The first paper was focused on the recovery of yttrium from fluorescent lamps. The leaching efficiency of different agents was studied in particular of nitric, hydrochloric and sulphuric acids and ammonia. The experiments showed that ammonia was not suitable to recover yttrium, whereas HNO_3 produced toxic vapors. HCl and H_2SO_4 had the same efficiency to dissolve yttrium but the second one was chosen as leaching agent because allowed to reduce calcium

extraction with subsequent advantage during recovery of yttrium compounds in the downstream. 85% of Y extraction was obtained in the following conditions: 20% of pulp density, 4 N H_2SO_4 concentration and 90 °C of leaching temperature. In the other previous works (Innocenzi et al., 2013a, b) the research activities were focused on the recovery of yttrium from fluorescent material coming from dismantling of spent fluorescent lamps and cathode ray tubes. The experiments included leaching with sulfuric acid, purification step with sodium hydroxide to remove metal impurities like calcium and finally recovery of yttrium oxalates after precipitation with oxalic acid. Yttrium recovery was around 55% with a purity of the final yttrium oxide equal to 99%. Porob et al. (2011) described a method that included several steps. Initially, the powder was fired with an alkaline material to decompose the phosphor into a mixture of oxides. After the residue was dissolved in acid attack using nitric, sulfuric or hydrochloric acid at high temperature (150 °C). Therefore could be obtained REE salt from solution by solvent extraction, crystallization or precipitation. More recent studies were reported by Tunsu et al. (2016). In their paper the authors described a hydrometallurgical process for the recovery of yttrium and europium from fluorescent lamps. The process included: leaching of mercury by I_2/KI solutions (0.025–0.075 M, 1 h, 25% w/v of pulp density) with a decontamination efficiency of 98%; dissolution of the impurities as calcium using nitric acid (1 M nitric acid, 10 min, 10% w/v of pulp density) with removal yield for calcium > 90%; leaching of yttrium and europium using nitric acid (2 M nitric acid, 24 h, 10% w/v of pulp density) with yields more than 95%; solvent extraction circuit. This last circuit included three stages of extraction with 35% of Cyanex 923 in kerosene and organic phase/aqueous phase ratio of 2/1; four stages of stripping with hydrochloric acid and organic phase/aqueous phase ratio of 1/2 and finally a washing for the regeneration of the organic phase. The yields for the extraction and stripping of yttrium and europium were higher than 99.9%. Outputs of the process were: Y/Eu rich solution to send for further treatments for the recovery of yttrium and europium, and a residual solid obtained after leaching steps rich in cerium, gadolinium, terbium and lanthanum. Yttrium and europium could be recovered as oxides after precipitation with oxalic acid and calcination. The purity of the final product was 99.96% with 94.61% of yttrium oxide and 5.09% of europium oxide.

As it is possible to note the scientific literature is richer of yttrium and europium recovery from red phosphors than blue–green phosphors because the first REE are easier to dissolve respect to the others. Regarding the recovery of terbium, Takahashi et al. (2001) developed a process that included a first step in which the red phosphors were extracted with diluted acid. The residual solid was dissolved with acid, in a strongly oxidizing environment to dissolve also the green phosphors. The maximum extraction of terbium was around 73.61% in the following conditions: 1.5 M of hydrochloric acid, 30 g/L, 70 °C, 1 h, 200 rpm and 6 M of hydrochloric acid, 30 g/L, 90 °C, 1 h, 200 rpm. Tunsu et al. (2015) in their review cited another scientific work, Zhang et al. (2013), regarding the recovery of terbium from fluorescent powders. The process included two leaching steps. In the first extraction yields of 95.61% and 96.35% for yttrium and europium, respectively, were obtained using 3 M of hydrochloric acid, 60 °C, 4 h and solid/liquid ratio of 1/3. In the second leaching terbium and cerium were extracted using hydrochloric acid after alkaline fusion using sodium hydroxide at 800 °C for two hours. The leaching conditions were 5 M HCl, 60 °C, 3 h and solid/liquid ratio of 1/10. The total leaching rates were 99.06% Y, 97.38% Eu, 98.22% Ce, 98.15%.

In our previous work (Innocenzi et al., 2016) the terbium recovery from fluorescent lamps was studied. The process included a thermal pretreatment with potassium hydroxide, leaching with hydrochloric acid and precipitation adding oxalic acid. During the

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