

Recovery of critical and precious metals from E-Waste

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Abstract

Waste of Electrical and Electronic Equipment (WEEE) is the fastest growing waste stream in Europe. This waste contains a high amount of critical and valuable metals as the rare earths defined critical materials from European Commission (2010) and the precious metals. Exhaust fluorescent lamps are examples of electronic wastes that have important percentages of rare earths elements (REEs). These types of WEEE represent an important secondary source of REEs. Moreover, they are classified as hazardous materials for the presence of mercury and need to be properly handled. Among the most valuable component of WEE there are printed circuit boards (PCBs) for their precious metals content. In the present paper a hydrometallurgical process for the recovery of REEs (yttrium, europium, terbium, gadolinium, lanthanum and cerium) from fluorescent powders and copper, tin, zinc, gold and silver from WPCBs. Hydrometallurgical process for rare earths recovery includes a preliminary roasting, acid dissolution and precipitation of a mixture of REEs oxalates. Alternately, a solvent extraction operation and stripping can be added after dissolution to selective recover rare earths. For the WPCBs treatment, a hydrometallurgical process consisting of two sequential leaching procedures (performed in counter and cross current ways) followed by selective precipitation/reduction of elements of interest from solution has been designed.

Keywords: spent lamps; waste printed circuit boards; hydrometallurgical processes; precious metals; rare earths.

1. Introduction

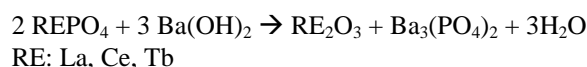
Waste Electrical and Electronic Equipment (WEEE) are significantly increasing for the rapid economic growth and also for a continuous development of technologies. The consumption of these equipment, and thus also the production of this waste, is expected in relevant increase in next years. Fluorescent lamps and PCBs at the end of their life, are included among these wastes. The world's interest in these wastes is growing, mainly thanks to the possibility of recovering strategic materials such as the rare earths that are contained in the powders of the fluorescent lamps (FL) and precious metals (Au, Ag, Pd) contained in PCBs. REE are currently extracted from minerals located only in China, which consequently holds the monopoly of production.

Rare earths are critical materials and have a high importance as they are used in different sectors: lighting, electronics and petrol-chemicals. Furthermore, the European Waste Catalogue classifies exhausted fluorescent lamps as hazardous waste due to the presence of mercury, so if not correctly recovered they should be disposed of in hazardous waste landfills. In literature there are several scientific articles regarding the treatment of fluorescent lamps, but mainly describe the recovery of yttrium, which being present as an oxide is more easily dissolved with an acid treatment.

2. Materials and Methods

2.1 Recovery of REE from fluorescent spent lamps

Powders of fluorescent exhausted lamps were supplied by Relight srl Italian company (Rho, Milan). Fluorescent powders were obtained by lamps crushing and further physical treatments in order to remove glass fragments. Different alternative pre-treatments, with the purpose to facilitate green phosphors dissolution in the following leaching step, were studied. The first solution includes a preliminary roasting at 950 °C (Merritt, 1990; Innocenzi et al., 2018) with the use of alkaline material as barium hydroxide, in order to transform the rare earths phosphates in oxides that are easier to dissolve according to the following reaction:



Alternatively, mechanical activation preliminary treatment was conducted using a steel rings mill, that introduces physicochemical changes, mainly an increase of amorphous content. The amorphization is considered as the most likely mechanism for the improved leachability of REE of green phosphors (Van Loy et al., 2018). Experiments were carried out according to factorial plans in order to evaluate the effect of main involved factors. Results were elaborated by analysis of variance, ANOVA.

2.2 Recovery of precious metals from WPCBs

Experimental works were performed using PCBs from waste computers (particle sizes < 2 mm) for gold recovery. Since the great concentration of copper in WPCBs has a negative effect on thiourea gold

extraction, a pre-treatment was investigated in order to remove copper and other base metals. Tests were planned according to factorial experimentation.

3. Results

3.1 Effect of preliminary treatments on REE acid dissolution and selective separation

The effect of preliminary thermal treatment on sulfuric acid leaching was studied. By experimental results, carried out according to a full factorial plan with 2 levels and 5 factors, the best operative conditions to maximize the dissolution yields of rare earths of green phosphors, were found. The maximum extraction of terbium was obtained with the following operating conditions: barium hydroxide - powders ratio 0.6, concentration of sulfuric acid 1 M, pulp density 5%, leaching temperature 80 ° C, reaction time 1 hour. Under the conditions listed was dissolved 99.8 % of yttrium and europium, 79.5 % of terbium and 60 % of cerium, lanthanum and gadolinium (Ippolito et al., 2017).

As an alternative preliminary treatment was tested mechanical activation of powders in order to evaluate an increase of REE dissolutions at subsequently leaching stage. By factorial experimentation was noticed a significant and positive effect of milling time of powders. In particular, at 30 mins of milling time, 30 % of terbium, cerium and lanthanum was obtained after leaching treatment, instead the extraction yields for yttrium and europium were almost 99%. At similar leaching operative conditions, without pre-treatment, were obtained the following extractions: 80 % for yttrium and europium, 20 % for gadolinium and no extractions for terbium, lanthanum and cerium (rare earths contained in green phosphors).

Further experimental studies have been carried out to selectively separate the rare earths present in acid solution. The capacity of different organic extractants as a function of pH was investigated. A possible route is to use D2EHPA in kerosene (20 % v/v) which allows to separate terbium and yttrium from other rare earths for pH values around 1. After acid stripping, precipitation with oxalic acid and subsequent calcination of rare earth oxalates, two products rich in rare earths were obtained. The first is a mixture of rare earth oxides with the following composition: 98.8% yttrium oxide, 0.6% terbium oxide and 0.6% cerium oxide. The second product instead consists of: 32.5% europium oxide, 17.9% cerium oxide, 17.1% yttrium oxide, 12.5% lanthanum oxide, 10.6% terbium oxide and 9.4% gadolinium oxide (Innocenzi et al., 2018).

3.2 Two leaching steps for base and precious metals recovery

Results of experimental tests showed a copper dissolution of 90 % after two oxidative leaching steps (1.7 M of H₂SO₄, 17 % v/v H₂O₂, 30 % w/v). The solid residue was used for gold dissolution with thiourea leaching treatment. Highest gold dissolution of 90 % was obtained at the following operative conditions: 20

g/L of thiourea, 6 g/L Fe³⁺, 0.1 M of H₂SO₄, room temperature. In the purified solutions obtained by the two leaching steps high recovery rates of both copper (almost 100 %), gold (larger than 80 %) and silver (50 %) were achieved by applying cementation process with Zn powder (Birloaga and Vegliò, 2016).

4. Conclusions

The present work reports the results obtained at the laboratory scale, performed for the recycling of e-waste, more in details for the treatment of fluorescent lamps and printed circuited boards. For FL, a preliminary alkaline thermal treatment at 950°C or as in alternative a milling process is necessary to improve the dissolution by sulfuric acid and hence the recovery of green phosphors from the initial materials. After leaching, REEs can be selectively recovered by solvent extraction using D2EHPA diluted in kerosene. The results confirmed the difficulty to separate the rare earths and two final products are obtained. Anyway, two oxides were obtained: the first rich in yttrium (98.8 %), and the second one a mixture of rare earths.

Regarding WPCBs treatments, the importance of a preliminary treatment for the recovery of copper has been highlighted as it competes with gold for the thiourea consumption. After the pre-treatment a gold dissolution of 90 % was obtained with thiourea leaching, compared with no gold dissolution in the case of direct thiourea leaching. After cementation processes on purified solutions the following recoveries were achieved: copper 99.5 %, gold 81% and silver 50 %.

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