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Rare earths from secondary sources: profitability study

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Abstract. The paper is focused on the economic analysis of two hydrometallurgical processes for recovery of yttrium and other rare earth elements (REEs) from fluorescent phosphors of spent lamps. The first process includes leaching with sulphuric acid and precipitation of a mixture of oxalates by oxalic acid, the second one includes leaching with sulphuric acid, solvent extraction with D2EHPA, stripping by acid and recovery of yttrium and traces of other rare earths (REs) by precipitation with oxalic acid. In both cases the REEs were recovered as oxides by calcination of the oxalate salts.

The economic analysis was estimated considering the real capacity of the HydroWEEE mobile's plant (420 kg batch^{-1}). For the first flow-sheet the cost of recycling comes to 4.0 € kg^{-1}, while the revenue from the end-product is around 5.40 € kg^{-1}. The second process is not profitable, as well as the first one, taking into account the composition of the final oxides: the cost of recycling comes to 5.2 € kg^{-1}, while the revenue from the end-product is around 3.56 € kg^{-1}. The process becomes profitable if the final RE oxide mixture is sold for nearly 50 € kg^{-1}, a value rather far from the current market prices but not so unlikely since could be achieved in the incoming years, considering the significant fluctuations of the Res' market.

Keywords: yttrium; fluorescent; rare earths; hydrometallurgy; lamps

1. Introduction

Fluorescent lamps, laser, TVs are examples of popular and technological equipments whose production depends on availability of REEs, such as yttrium and europium. The main issue is that the majority of REEs are extracted in China and other few countries under conditions of oligopoly market. The European Commission published a report in which fourteen elements, including rare earths, were defined as critical. For these reasons, in the last years, the interest in REs and the study of several processes to recover them from WEEE are significantly growing. In scientific literature many works can be found that describe REs recovery from this type of waste: nevertheless, in this manuscript only the main papers relevant to treatment of fluorescent powders from lamps were considered. The main researches in this field are summarized in two recent review articles by Binnemans *et al*. (2013) and Innocenzi *et al*. (2014).

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Exhausted fluorescent lamps contain the red phosphor (YOX) in which yttrium and europium are contained as oxides, green phosphor (LAP) based on La, Ce and Tb phosphates and blue phosphors (BAM) that is a mixture of Ba, Mg, Al oxides and europium. The amount of REs in fluorescent powders varies according to the type and year of manufacture, but in general the concentration of RE oxides in lamp phosphors can be even 27.9%wt, but the actual recycled fluorescent material contains about 10%wt of RE oxides (Binnemans *et al.* 2013). REEs can be recovered by hydrometallurgical processes that include leaching with several acids, precipitation or solvent extraction using the most common organic extractants. Those processes can include purification stages with some precipitating agents like sodium sulphide to remove impurities from leach liquors. In the patent WO 2011/106167A1 (Porob *et al.* 2011) a method to recover rare earths from fluorescent material is described: phosphors are calcined with an alkaline reagent, thus the oxidized material is leached by HNO_3, H_2SO_4 or HCl at high temperature, and, finally the RE salts are separated from the pregnant solution by solvent extraction, crystallization or precipitation processes. Patent US 20100062673 describes recovery of phosphors from cathode ray tubes (CRTs) by means of acid-alkaline treatments and further recovery of glass (Tedjar *et al.* 2010).

Processes that include solvent extraction are described in Shimizu *et al.* (2005), Rabah (2008) and Yang *et al.* (2013); REs recovery using selective precipitation is cited and reported in other papers such as Tooru *et al.* (2001), De Michelis *et al.* (2011), Innocenzi *et al.* (2013a, b) and Braconnier and Rollat (2010).

Shimizu *et al.* (2005) reported a method to recover REEs, including supercritical carbon dioxide (SF-CO_2)/tri-*n*-butyl phosphate (TBP) complexes extraction with HNO_3 and H_2O. The results showed that the extraction yields for Y and Eu increased to over 99% after the static extraction for 120 min at 15 MPa and 333K.

Rabah (2008) studied the recovery of Y and Eu from fluorescent lamps by sulfuric/nitric acid mixture leaching for 4 h at 398 K and 5 MPa. RE sulphates were converted to thiocyanate at low temperature and trimethyl-benzylammonium chloride solvent was used to selectively extract Eu and Y from the thiocyanate solution. The extraction phase was followed by stripping with N-tributylphosphate in 1 mol L^{-1} nitric acid solution at 398 K to produce nitrate salts of Eu and Y. Europium nitrate was separated from yttrium nitrate by dissolving that mixture in ethyl alcohol. Thermal reduction by hydrogen gas at 1123 K and 1848 K produced europium and yttrium metals, respectively. Experimental tests showed that such process conditions were very efficient to extract REs: in fact, leaching yields were 96.4% for Y and 92.8% for Eu.

Yang *et al.* (2013) studied REs recovery by solvent extraction after leaching from phosphor powders. *N*,*N*-dioctyldiglycol amic acid (DODGAA) was used to extract REs. An effective recovery of the rare earth metals (Y, Eu, La and Ce) from the mixture containing metallic contaminants like Fe, Al and Zn, was achieved.

Rhodia reported a process that foresees leaching with nitric or hydrochloric acid, followed by a treatment with sodium hydroxide solution or molten sodium carbonate. The rare earths were recovered by solvent extraction.

Tooru *et al.* (2001) studied a process for separation and recovery of RE contained in fluorescent lamp waste. Yttrium and europium were recovered by pneumatic classification, sulphuric acid leaching and oxalate precipitation. The final recovery was around 65% and the purity of the products was 98.2%. The best results in terms of dissolution were obtained in these conditions: 1.5 kmol m^{-3} of acid, 343 K, leaching time of 1 h and pulp density of 30 kg m^{-3}.

De Michelis *et al.* (2011) studied the efficiency of sulphuric, nitric, hydrochloric acids and ammonia to treat fluorescent powders from spent lamps. The best leaching agent was sulphuric acid that dissolved yttrium and achieved a lower co-extraction of calcium, lead and barium. Yttrium was recovered from leach liquors by precipitation with oxalic acid. Yttrium recovery was 90% and purity of final oxalate was around 99%.

In our previous researches (Innocenzi *et al.* 2013a, b) recovery of yttrium from fluorescent lamps was widely studied. The process includes leaching with sulphuric acid, purification of leach liquors using sodium hydroxide and sulphide, finally yttrium was recovered by oxalic acid and the precipitated oxalate was calcined to obtain yttrium oxide. Recovery of yttrium was 55% and the grade of the final oxide was greater than 99%. Hence, this process was optimized since the purification step was removed, and this led to greater recovery yields of yttrium and even other rare earths.

The present research was developed in the ambit of the HydroWEEE projects. These projects were funded by the European Union, under the acronyms ID FP7-SME-2008-1 HydroWEEE (2009-2012) and FP7-ENV-2012 - two stage HydroWEEE demo (2012-2016). The aim of these projects was to study innovative hydrometallurgical processes able to recover metals from WEEE, for instance fluorescent powders from spent lamps and cathode ray tubes, Li-ion and Li-polymer batteries, liquid crystal displays (LCDs) and printed circuit boards (PCBs). Recovery of REEs from secondary raw materials is an issue of increasing relevance to electronic manufacturing, due to scarcity of primary ores. Many processes were developed to recover that, especially the hydrometallurgical ones, like recovery of dysprosium (Dy), neodymium (Nd) and ytterbium (Yb) by means of new sorbents (Galhoum *et al.* 2015, Galhoum *et al.* 2016).

In the first project the hydrometallurgical processes were developed in lab-scale with good results, whereas for CRTs and lamps the processes were validated in pilot-scale. In the second phase of the project (demo's phase), two industrial plants were built in order to test all the processes developed so far. The first plant is stationary and treats fluorescent powders: it was built at the Italian company Relight Srl (Rho, Milano) with a capacity of 600 kg batch^{-1}. The second one is a mobile plant with a capacity of 420 kg batch^{-1} and is composed by two mobile units (two 40 ft standard containers) where all the required equipment is allocated.

The present paper is focused on an economic analysis of two hydrometallurgical processes developed to recover yttrium and rare earths from fluorescent spent lamps. Two flow-sheets are presented: the first was developed within the HydroWEEE projects and the second one includes solvent as an alternative process. In the following pages some outlines about the technological methods were reported with the main results of experimental data. The final products were oxides, for both processes, but in the first process the product was a mixture of rare earths (91.3%wt Y, 4.07% Eu, 0.28% Tb, 1.08% Gd, 0.01% La and 0.11% Ce as oxides) and the rest calcium oxide and calcium sulphate.

The second method was more selective to yttrium and the final product was composed by yttrium oxide with impurities having the following concentration: Eu oxide 0.56%wt, gadolinium oxide 0.31%, terbium oxide 0.26%, lanthanum and cerium negligible and the rest calcium oxide and calcium sulphate Y oxalate.

The economic analysis was carried out considering the capacity of the mobile HydroWEEE plant, and the relevant capital expenditure (CAPEX) and operating expenditure (OPEX) were considered. The second process had the advantage to recover yttrium oxide with higher grade over the first process, but it would be profitable only if the price of the final product is at least 50 € kg^{-1}; instead, the first process is profitable if the price of yttrium oxide is greater than 15 € kg^{-1}.

2. HydroWEEE processes and principal results

2.1 Yttrium recovery by precipitation

Yttrium recovery from fluorescent lamps was studied within HydroWEEE and HydroWEEE Demo projects. Experimental data obtained in the laboratory scale and described in previous works (De Michelis *et al*. 2011, Innocenzi *et al*. 2013a, b) were used to work out a flow-sheet for recycling of fluorescent phosphors from lamps, reported in Fig. 1.

The main elements in the initial fluorescent materials were silicon (around 9.0%wt) and calcium (13.0%wt). Rare earths were found in the following concentration, measured by atomic absorption spectrometry (AAS): 8.12%wt Y, 0.64% Eu, 0.26% Tb, 0.60% Ce, and 0.57% La. The original spent powders were leached with a sulphuric acid solution and the resulting suspension filtered, so that yttrium and other rare earths were recovered by precipitation with oxalic acid. The rare earth oxalates were calcined at 873 K for 1 h to obtain the corresponding oxides, but this phase was carried out in lab-scale only and not in the mobile plant because it is not equipped with a kiln. The process also includes the wastewater treatment: the residual solutions were treated with lime to adjust the pH to around 9: in this phase salts like sulphates, phosphates and oxalates were precipitated and removed for correct disposal.

Lab-scale results showed that yttrium and other rare earths, especially europium, can be recovered with a yield in the range of 80-90%, and the purity of the final oxides was around 90% with 1.6% of calcium oxide as main contaminant. Table 1 reports the average composition of the final oxides.

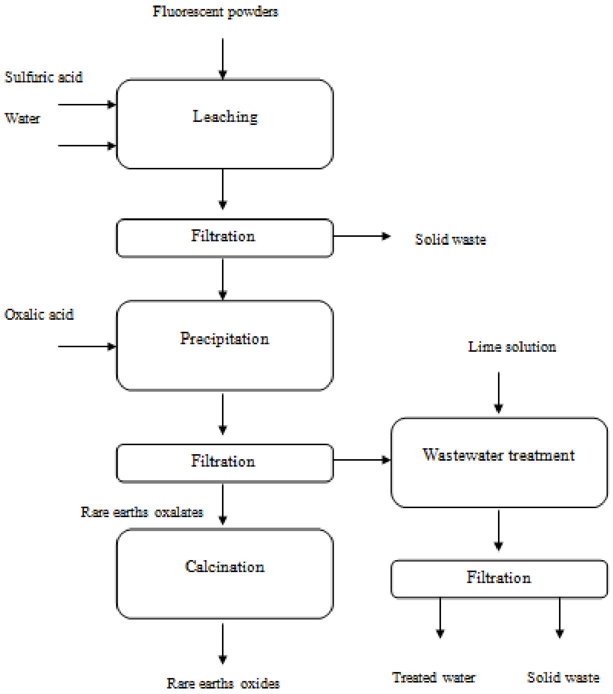

Fig. 1 Flow-sheet for yttrium recovery from fluorescent lamps by precipitation

Table 1 Average composition of the final oxides (lab-scale)

Compound	**%wt**
Y_2O_3	80-88
Eu_2O_3	4.0-5.8
Gd_2O_3	0.35-2.20
Tb_2O_3	0.5-1.1
Ce_2O_3	0.4-1.3
CaO	0.71 -1.60
Others	0-14

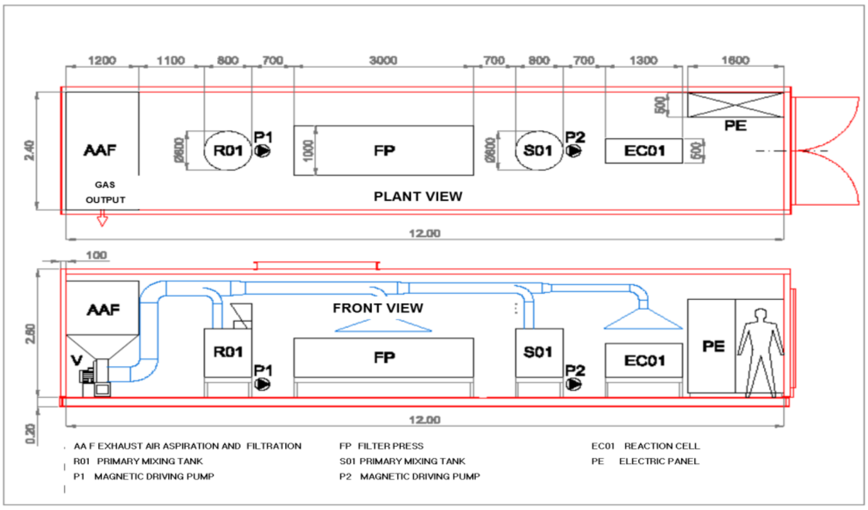

Fig. 2 Lay-out of the mobile HydroWEEE plant used to recover REEs

Fig. 3 Picture of the mobile HydroWEEE plant

Table 2 Rare earths' concentration as oxalates in the pilot-scale final products (by precipitation)

Compound	**Average value (%wt)**	**Maximum value (%wt)**
Yttrium oxalate	58.7	73
Europium oxalate	4.9	6.0
Terbium oxalate	0.5	0.8
Gadolium oxalate	3.2	5.1
Lanthanum oxalate	0.03	0.03
Cerium oxalate	0.5	1.1

The process was validated at pilot-scale using the mobile HydroWEEE's mobile plant. Fig. 2 shows the layout of the plant, whereas Fig. 3 shows a picture of the same mobile plant.

The composition of the oxalates, before the final calcination, obtained in the pilot scale experiments was reported in Table 2.

The average grade was around 67% with a maximum peak of 80%. The total recovery for yttrium was 60%, with a maximum value of 90%; recovery of europium was around 55%.

2.2 Yttrium recovery by solvent extraction and precipitation

Another process for recovery of yttrium from fluorescent lamps was studied at lab-scale. The flow-sheet is shown in Fig. 4.

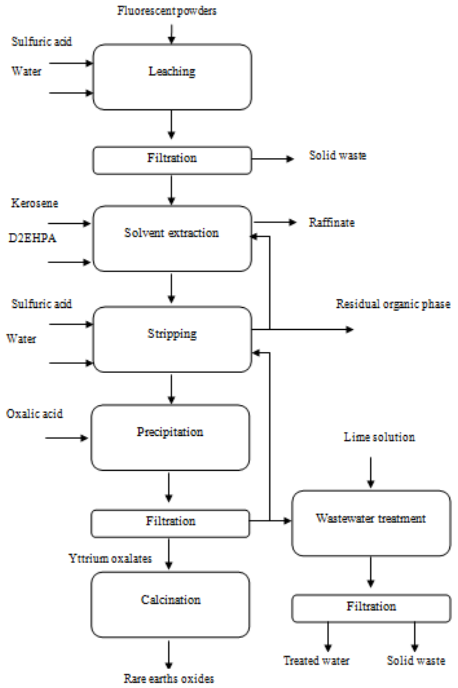

Fig. 4 Flow-sheet for yttrium recovery by solvent extraction

The original powders were treated with sulphuric acid solution. After reaction, the suspension was filtered, and the pregnant solution underwent solvent extraction with D2EHPA in kerosene. The aqueous phase contained the majority of europium, so that it could be treated to recover this important rare earth, whereas the organic phase was rich in yttrium that was stripped with a sulphuric acid solution; yttrium was finally recovered by precipitation with oxalic acid. The rare earth's oxalates were calcined to obtain the corresponding oxides. The process also included recycling of the organic phase after stripping with 2% of drain, recycling of solution after precipitation with oxalic acid in the same percentage of the drain and wastewater treatment: the residual solutions were treated with lime solution to increase the pH to around 9. The lab-tests showed that the final recovery is 80-90% from leach liquors and the grade of final oxides is: 97.8%wt yttrium oxide, 0.56% europium oxide, 0.31% gadolinium oxide, 0.26% terbium oxide, cerium and lanthanum negligible, and the rest being calcium oxide and sulphate.

In the following paragraphs the analysis of the processes presented in Figs. 1 and 4 was reported. Many assumptions were done and to estimate the feasibility of the processes the real mobile HydroWEEE Demo plant capacity was assumed (420 kg batch^{-1}). As mentioned above, this plant includes two units in which the main equipment was allocated, in order to carry out the first process already described (leaching reactor, precipitation reactor, wastewater reactor, two plate & frame filters, one tank and the scrubber unit). This plant is not equipped with solvent extraction devices; hence, in the economic analysis an additional mobile unit equipped with one mixer/settler for extraction and stripping tests was included with its relevant cost.

3. Process analysis

3.1 Precipitation process

A preliminary design and economic assessment of the recycling plant were carried out using experimental data. The plant was designed to operate in batch mode (420 kg batch^{-1} for two batches day^{-1} and 16 h day^{-1} as working time) with a capacity of 184.8 t y^{-1} of fluorescent powders from spent lamps. 185 t y^{-1} of fluorescent powder was estimated to be the maximum value of collected material in one year in Italy.

The annual mass balance is shown in Fig. 5, according to the flow-sheet reported in Fig. 1.

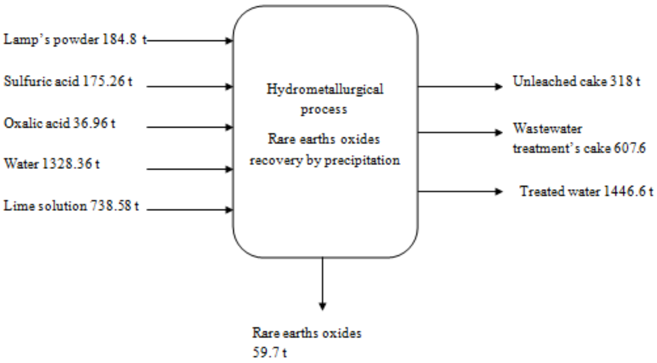

Fig. 5 Total annual mass balance for the first hydrometallurgical process (precipitation of REEs)

Table 3 Average composition of the final oxide mixture with the relevant prices of pure RE oxides (April 2016)

Compound	**Final product (%wt)**	**Price (€ kg^{-1})**	**Commercial grade (%wt)**
Yttrium oxide	91.3	4.5	99.999
Europium oxide	4.07	90.1	99.99
Terbium oxide	0.28	373.9	99.99
Gadolinium oxide	1.08	15.8	99.999
Lanthanum oxide	0.01	5.4	99.999
Cerium oxide	0.11	1.6	99.5-99.9

Fluorescent materials from dismantling of lamps was sent to a leaching reactor with sulfuric acid, and after filtration, the pregnant solution underwent yttrium recovery in one reactor where the required amount of oxalic acid was added: a concentrate of yttrium oxalate was recovered and thus calcined at 873 K for 1 h in oxidizing conditions. Laboratory- and pilot-scale tests showed that it is possible to obtain RE oxides with the average composition showed in Table 3. It has to be pointed out that the RE oxalate mixture obtained in pilot-scale tests was roasted in a laboratory muffle oven, since the mobile plant is not equipped with a calcination unit.

The same Table 3 reports the current market prices of the RE oxides: values for yttrium, europium, terbium, gadolinium, lanthanum and cerium were found on the internet page of a well-established leading price reporting, business intelligence and news analysis agency (Argus Media, 2016).

To calculate the price of the final oxide mixture, the market price of each RE oxide was considered according to its concentration. To perform the economic balance in a conservative manner, the current price of each pure oxide (99.9%wt or higher) was reduced by 40%, hence the adjusted selling price of the final product was 5.40 € kg^{-1}.

The economic model was worked out with many assumptions and estimates coming from the analysis of the literature and data available from our real plant and other industrial plants. Table 4 shows the total cost analysis including fixed costs for equipment, construction, maintenance and variable costs for materials, labor and utilities.

Table 4 Total Cost Summary (*220 days year^{-1})

Total Cost of the precipitation process plant			
Fixed Cost	€	Per year*	Note
Equipment cost	€	138,083	Real data - mobile plant HydroWEEE Demo plus kiln
Construction cost	€	58,000	Real data - mobile plant HydroWEEE Demo
Insurance	€	2,762	
Others (Benefit, Installation fee, ..)	€	72,007	
Total Fixed Cost	**€**	**270,852**	

Table 4 Continued

Total Cost of the precipitation process plant			
Variable costs	€	Per year*	Note
Reagents	€	77,342	
Disposal	€	216,936	
Direct Labor	€	161,920	
Utilities - Electricity	€	16,080	Real data - mobile plant HydroWEEE Demo
Total Variable cost	**€**	**472,279**	
TOTAL PROCESS COST	**€**	**743,131**	

Table 5 Variable costs for the entire model (*220 days year^{-1})

Variable cost Breakdown of the precipitation process plant				
		Per year*	Per kg	Notes
Reagents				
Fluorescent lamp	€	---	--	
Sulfuric acid	€	33,299	0.19	Real quotation
Water	€	1,328	0.001	Real quotation
Oxalic acid	€	29,568	0.8	
Lime solution	€	12,556	0.086	
Total Reagent's costs	€	77,342		
Wastes				
Unleached cake (wet)	€	95,400	0.3	Estimated by real quotati-on of some company
Cake after wastewater treatment	€	121,536	0.2	Estimated by real quotati-on of some companies
Treated water	€	--	--	It is reused
Total waste's costs	**€**	**216,936**		
Labor costs				
Labor	€	161,920		Two workers per cycle
TOTAL VARIABLE COSTS	**€**	**472,278**		

Fixed costs were calculated taking into account the whole plant and included the real cost of equipment and construction (in the real case this cost is the total purchase of the mobile units and the performed works to make it suitable for the equipment installation, maintenance, etc..). The cost of equipment included the amortization share (for six years) with an inflation rate of 7%. The total real cost for the mobile plant was around 550,000 €. Other costs were considered in the list, such as insurance (2% of total equipment's costs), benefit (25% of the labor cost), installation fee (5% of total equipment cost) and others (10% total fixed cost). The variable costs included the purchase of materials, waste disposal costs, the variable labor cost and energy required by the

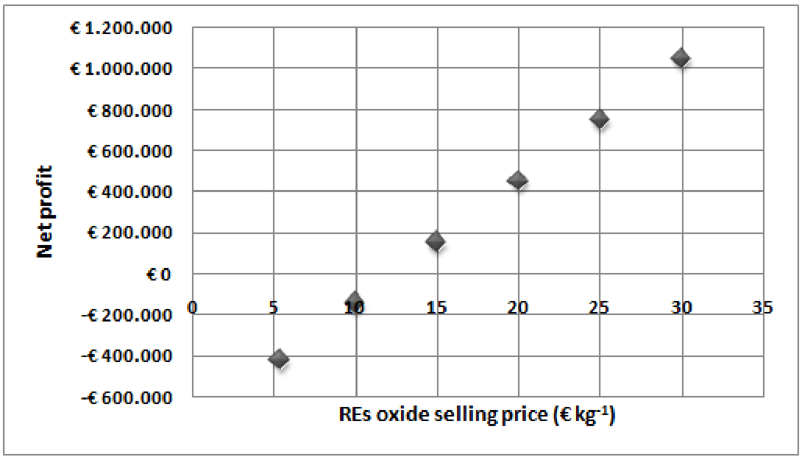

Fig. 6 Profit as a function of rare earths' price per kg (first year of activity, precipitation of REEs)

installed equipment. Four workers, two persons per shift, are required to operate the plant for 8 h day^{-1} at a gross cost of 23 € h^{-1}, (average value for one Italian worker). The specific list of variable costs is reported in Table 5.

3.1.1 Profitability analysis

The economic aspect of the recycling process does bring in some interesting conclusions for our research which could help to develop future recommendations for such recycling sector. The revenue from the recovered RE oxide mixture was calculated to be around 5.40 € kg^{-1} and the resulting revenue was around 322,000 € per year. Looking more in detail at the costing model, the greater items were the disposal cost (29%) and direct labor cost (22%). An economic simulation was carried varying the price of the final products (Fig. 6).

It is possible to notice that the prices of the final oxides influence significantly the feasibility of the hydrometallurgical process: the process was profitable if the price of the RE concentrate was greater than 15.0 € kg^{-1}; after six years the investment should be feasible if the price is greater than 10 € kg^{-1}, since the amortization rate is not present anymore as an annual operating cost.

3.2 Solvent extraction process

A preliminary design and an economic assessment of the recycling plant were carried out using experimental data. The plant was designed to operate in semi-continuous mode (24 h day^{-1}) with a capacity of 184.8 t y^{-1} of fluorescent powders from spent lamps: this means that two leaching batches should be carried out in one day. This amount was used to carry out economic simulation as the plant should work in semi-continuous mode and around 185 t y^{-1} of fluorescent powder could be collected in one year. The total leach liquor is around 7,100 kg that goes into the tank that feeds the solvent extraction section with a capacity of 297 kg h^{-1}. The total mass balance, referred to one year, is shown in Fig. 7, according to the flow-sheet in Fig. 4.

Fluorescent phosphors from dismantling of lamps were sent to a leaching reactor where sulfuric acid is used, and after this phase, the filtered liquid is sent to the solvent extraction section with D2EHPA, stripping by sulfuric acid and recovery of REEs by oxalic acid precipitation. Laboratory tests have shown that it was possible to obtain an oxide mixture from roasting of oxalates

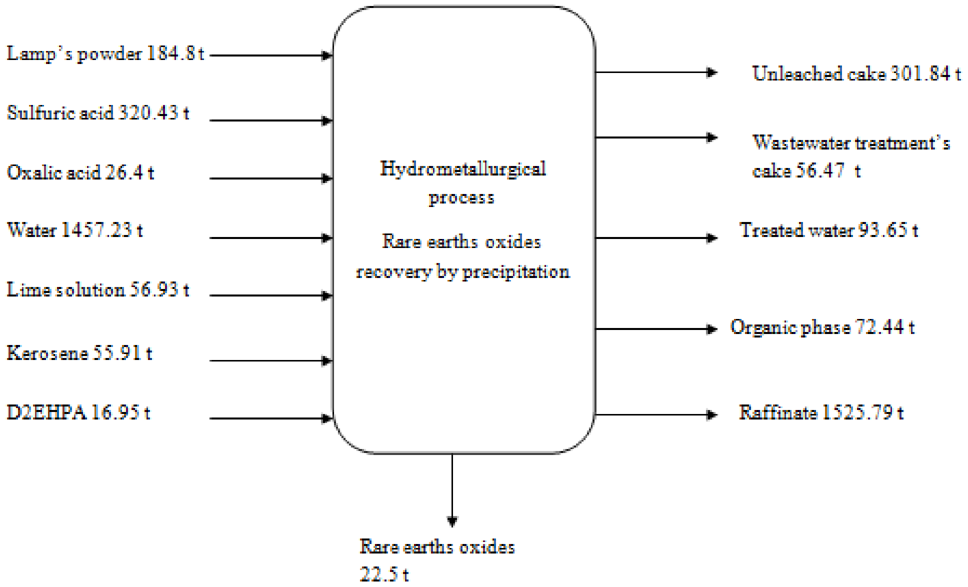

Fig. 7 Total annual mass balance for the second hydrometallurgical process (solvent extraction of REEs)

Table 6 Total Cost Summary (*220 days year^{-1})

Total Cost of the solvent extraction process plant			
Fixed Costs	€	Per year*	Note
Equipment cost	€	191,583	Mobile plant HydroWEEE Demo plus the cost for the solvent extraction section
Construction cost	€	87,000	Estimated according to mobile plant HydroWEEE Demo works
Insurance	€	3,832	
Others (Benefit, Installation Fee, ..)	€	105,571	
Total Fixed Cost	**€**	**387,986**	
Variable costs			
Reagents	€	203,821	
Disposal	€	123,578	
Direct Labor	€	242,880	
Utilities – Electricity	€	16,080	Estimated
Total Variable cost	**€**	**586,359**	
TOTAL PROCESS COST	***€***	**974,344**	

recovered by precipitation of REEs from the aqueous phase. Purity of this compound was higher in yttrium with respect to final oxide mixture obtained in the first process without solvent extraction.

In this case, the price of the final oxides was calculated considering that it was almost completely composed by yttrium oxide with some traces of other rare earths and calcium, that is the main contaminant: under this hypothesis, that product price was set at 40% below the prices of pure commercial RE oxides of commercial grade. The estimated value was 3.56 € kg^{-1}. According to the amount of oxides produced annually, the revenue is around 80,000 € $year^{-1}$.

The cost model was worked out by making many assumptions and estimates using literature, calculated or real available data.

Table 6 shows the total cost analysis including the fixed costs for equipment, construction, maintenance and the variable costs for materials, labor and utilities.

The fixed costs were estimated according to real values reported for the mobile plant of HydroWEEE demo project that consists of two mobile units (two 40 feet standard containers). In the studied process another unit should be considered, where the equipment for solvent extraction should be allocated. The cost of equipments included the amortization share (for six years) with an inflation rate of 7%. The total cost for the mobile plant was around 850,000 € considering 550,000 € that was the real cost of two units of the mobile HydroWEEE plant plus 300,000 € as estimated cost for solvent extraction equipment allocated in a third unit of the plant. Moreover, further

Table 7 Variable costs for the Entire Model (*220 days $year^{-1}$)

Variable cost Breakdown of the solvent extraction process plant				
		Per year*	Per kg	Notes
Reagents				
Fluorescent lamp	€	---	--	
Sulfuric acid	€	60,881	0.19	
Water	€	2,477	0.0017	
D2EHPA	€	84,750	5	
Kerosene	€	33,546	0.6	
Oxalic acid	€	21,120	0.8	
Lime solution	€	1,095	0.086	
Total Reagent's costs	€	203,820		
Waste				
Unleached cake (wet)	€	90,552	0.3	Estimated by real quotation of some company
Organic phase	€	21,732	0.3	
Raffinate	€	--	---	To europium's recovery
Cake after wastewater treatment	€	11,299	0.2	Estimated by real quota-tion of some companies
Treated water	€	--	--	Could be reused
Total waste's costs	**€**	**123,578**		
Labor costs				
Labor	€	242,880		Two workers per cycle for 24 h day^{-1}
TOTAL VARIABLE COSTS	**€**	**586,358**		

40,000 € have to be included to purchase the kiln. Other costs were taken into account in the list: insurance (2% of total equipment cost), benefit (25% of the labor cost), installation fee (5% of total equipment cost) and other costs. The estimated value for the total capital cost on annual basis is around 974,000 €. The variable costs included purchase of materials, disposal costs, labor and energy consumption of the equipment. Considering that the plant should work 24 h day^{-1}, three shifts per day with two persons should be considered, hence a total of six workers per day with a hourly cost of 23 € h^{-1}. The specific variable costs are listed in Table 7.

3.2.1 Profitability analysis

The revenue of the material was calculated to be around 3.56 € kg^{-1} and the loss is around -894,000 € for the first six years of operation; after the sixth year this value should decrease since the amortization cost has not to be paid any longer. Looking more in depth at the costing model, the highest costs come from labor (25%) and reagents (21%).

The economic simulation was carried out varying the price of the final products (Fig. 8).

As for the first process, it is possible to highlight that the selling prices of the final oxides influence significantly the feasibility of the hydrometallurgical process: the process is profitable if the price of rare earths concentrate is greater than 50 € kg^{-1}; after six years the investment should be feasible if the price is more than 20 € kg^{-1}, that could be a possible future scenario considering the fluctuating price of REEs.

3.3 Comparison between economic simulations

Tables 8 and 9 summarize the main results of the two process simulations.

The main incidence on total cost was the disposal cost for the first process, instead for the solvent extraction treatment the direct labor cost and the reagent's cost were the main items. The recycling expenses were 4.0 € kg^{-1} and 5.2 € kg^{-1} for the first and second hydrometallurgical processes, respectively.

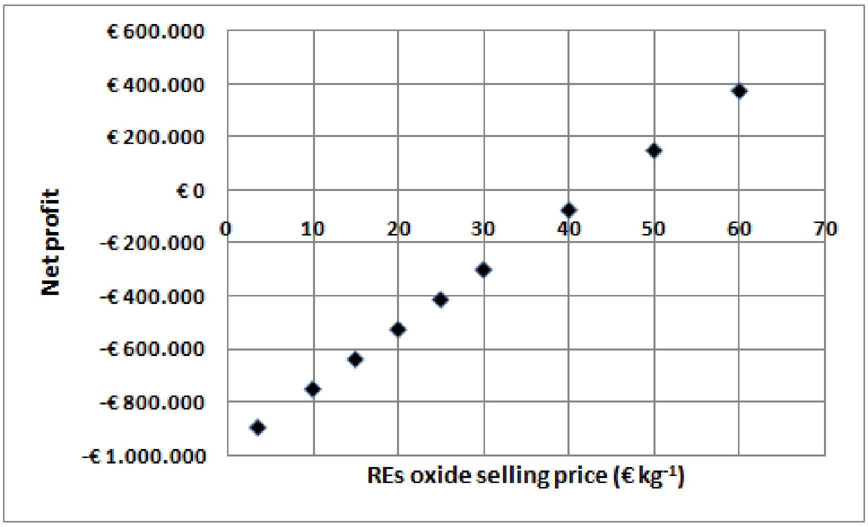

Fig. 8 Profit as a function of yttrium oxalate's price (throughout six years of activity, solvent extraction of REEs)

Table 8 Economic feasibility study of the two hydrometallurgical processes

184.8 tons year-1 of fluorescent phosphors				
Data	**Precipitation process**		**Solvent extraction process**	
Total Fixed Costs	€ 270,852		€ 387,986	
Total Variable Costs	€ 472,279		€ 586,359	
Revenue	€ 321,984	Estimated RE oxides price = 5.40 € kg^{-1}	€ 79,989	Estimated RE oxides price = 3.56 € kg^{-1}
Profit	€ -421,147		€ -894.356	
Minimum price to make the process feasible - first six years of activity	15 € kg^{-1}		50 € kg^{-1}	

Table 9 Incidence of the costs for the two hydrometallurgical processes

184.8 tons year-1 of fluorescent phosphors		
Incidence of the costs on total costs	**Precipitation process**	**Solvent extraction process**
Reagents	10.41%	20.92%
Disposal	29.19%	12.68%
Direct Labor	21.79%	24.93%
Utilities	2.16%	1.65%
Equipment amortization	18.58%	19.66%
Construction	7.80%	8.93%
Insurance	0.37%	0.39%
Others	9.69%	10.84%

The solvent extraction process has a greater cost since the organic liquid used (D2EHPA) is rather expensive. In this case the other REEs contained in the organic phase should be recovered and sold, but this will not improve the feasibility of the process. Both recycling processes are not feasible in the current market conditions since prices of REEs are very low: these processes are among the most simple currently available, so although they were able to recover and separate commercial grade oxides, the feasibility would not be guaranteed. In fact, consecutive solvent extractions are required to separate all the REEs contained in the phosphors, hence only plants with huge capacities and proprietary technologies can afford such technological challenge.

4. Value of the recovered materials

The feasibility of fluorescent phosphor recycling is mostly influenced by price of the rare earths. The products obtained in the mobile plant are a mixture of oxides. These products could be an intermediate compounds that could be further refined to increase the grade of rare earths, up to the commercial grades. For this reason, only 60% of the selling price of the commercial RE oxides was considered in the two profitability analyses. In the second process, in which liquid-liquid extraction was used, the purity of the final yttrium oxide was higher than the product obtained without solvent extraction. Nevertheless, it contains minor amounts of other REEs, so that the final selling price is lower. Anyway, the organic phase of the solvent extraction process containing the other REEs can be sold to enhance the economic performance of the second process.

5. Conclusions

The present research was developed in the ambit of the HydroWEEE projects. These projects were funded by the European Union, under the acronyms ID FP7-SME-2008-1 HydroWEEE (2009-2012) and FP7-ENV-2012 - two stage HydroWEEE Demo (201-2016). The aim of these projects was to study innovative hydrometallurgical processes able to recover metals from WEEE.

In this manuscript the influence of the rare earths' market on the feasibility of recycling of fluorescent lamps was evidenced. Two hydrometallurgical processes were considered: the first one includes leaching with sulphuric acid and precipitation by oxalic acid, the second one includes leaching with sulphuric acid, solvent extraction with D2EHPA in kerosene, stripping with sulfuric acid and yttrium recovery by precipitation with oxalic acid. In both cases, the RE oxalate salt is roasted in order to convert it into a RE oxide mixture, that can be further refined to produce high-grade commercial RE oxides.

For the first flow-sheet the cost of recycling came to 4.0 € kg^{-1}, while the revenue from the end product was around 5.40 € kg^{-1}. The operating costs were mostly due to equipment amortization and disposal costs; the first recycling process resulted to be not feasible at the current market conditions, since REEs prices are too low.

The second process was not profitable as well, considering the estimated selling price of the final oxides: the cost of recycling came to 5.2 € kg^{-1}, while the revenue from the end product was around 3.56 € kg^{-1} (estimated to be 60% of price for yttrium oxide). The costs were mostly due to direct labor and reagent purchase. The process should be profitable if the final oxalates are sold at 50 € kg^{-1}, far from the estimated value and the current market prices. In the first case, the recycling process would be profitable with a selling price of 15 € kg^{-1} of the final recovered product.

Recycling of spent fluorescent lamps, and more in general of WEEE, reduces the environmental impact of these waste at the end of their useful life; furthermore, they represent an important source for secondary materials like rare earths and it is clear that the research will not end at this stage of knowledge and continuous experimental activities, literature analysis and economical aspects should be deepened to reduce the costs of recycling and make it economically feasible through hydrometallurgical processes.

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