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A HYDROMETALLURGICAL PROCESS FOR RECOVERING RARE EARTHS AND METALS FROM SPENT FLUORESCENT LAMPS

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Abstract

The recovery of raw materials from waste represents a sustainable growth opportunity for those countries with limited mineral resources availability. A case study for an integrated approach to recover raw materials from spent fluorescent lamps is presented, with the aim of improving the current treatments which are only able to recover the glass fraction. In particular a hydrometallurgical process was developed to obtain valuable metals such antimony, copper, and rare earths (yttrium and europium). Grinded powders were leached with several inorganic acids, then antimony and copper were recovered by electrodeposition; Y and Eu were finally precipitated as oxalates. The precipitate was dissolved and the rare earths were separated by solvent extraction. This approach, based on the holistic view of all elements contained in an End–of–Life complex product, ensures both environmental and economic sustainability since it allows waste reduction and materials recovery.

Key words: fluorescent lamps, hydrometallurgy, rare earths, WEEE

1. Introduction

The availability of raw materials (not-energetic and not coming from agricultural activities) for European industry is becoming problematic as shown in a recent report published by the European Commission (European Commission, 2014) and reported in Fig. 1. Great relevance was given to Rare earth elements (REEs), due to their economic importance and very high supply risk, becoming increasingly important in the transition to a green economy. In the next future demand for some of the rare earths is, in fact, expected to exceed supply. The substitution is the object of ongoing research, but REEs replacement by more common metals is still far from solution, due to their specific properties.

Many authors studied recovery of valuable materials from WEEE (Waste Electrical and Electronic Equipment) (Kumar et al., 2014). Also

rare earths are potentially recoverable from WEEE, but their recycling rates are still low (below 1%) (Graedel et al., 2011a, 2011b; Reck and Graedel, 2012), due to technological difficulties, low toxicities of the REEs, and, until recently, low prices and lack of incentives. Unfortunately, the REEs are often minor components of complex materials in consumer goods (Schüler et al., 2011), but they are still essential in a lot of complex products, i.e. permanent magnets, due to special electronic, magnetic, optical, and catalytic properties, but also in tyre industry (i.e. neodymium based catalyst for cis-1,4-polybutadiene synthesis). Their low content makes the recovery process often unsustainable, especially with focused-strategy only aimed at REEs recovering and considering the rest of materials as a waste. The current treatment technologies are only focused on glass recovery (Andreola et al., 2010; Taurino et al., 2012).

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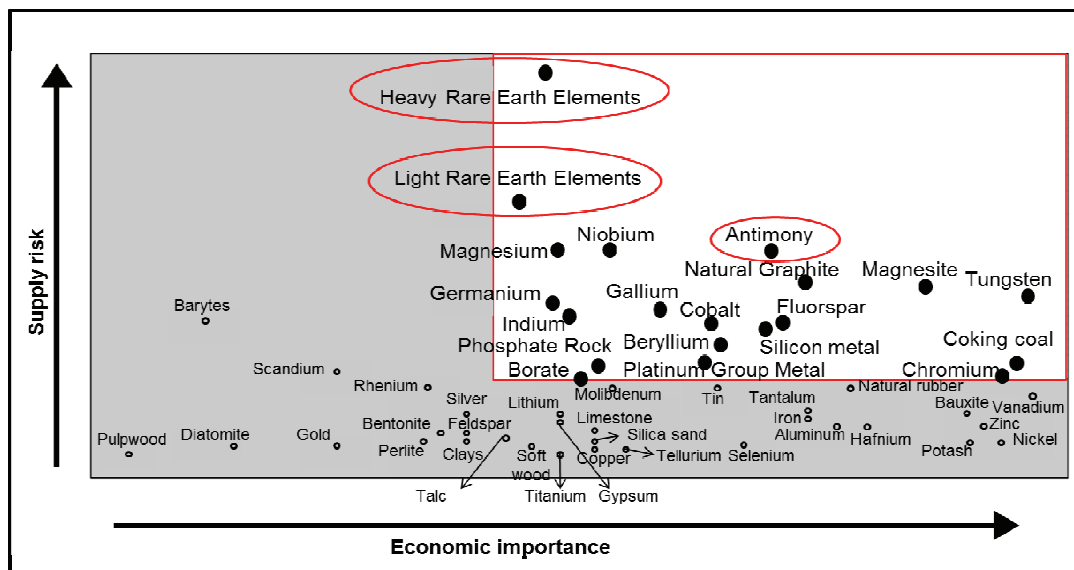
Fig. 1. Critical raw materials stated by the European Commission (May 2014)

In this work a product-centric approach is presented, aimed at recovering all the valuable components contained in an End-of-Life (EoL) product, i.e. REEs and other valuable metals.

A fluorescent lamp (Tan et al., 2014) is a sealed tube under vacuum conditions and works by exciting gaseous vapour, usually mercury, with electricity. Its inner surface is coated by a fluorescent film. In Fig. 2 a scheme of the fluorescent lamp is given.
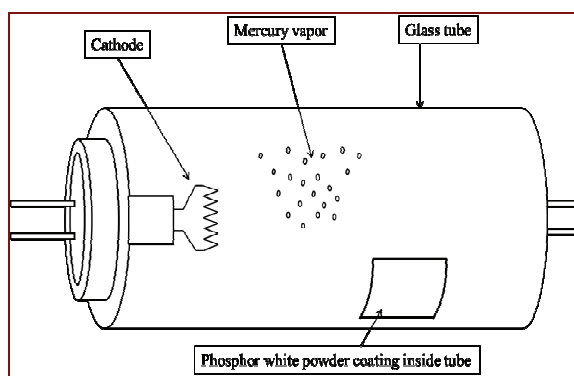

Fig. 2. Fluorescent lamp scheme

2. Experimental

2.1. Materials

Grinded powder without mercury was supplied by a recycling WEEE.

All solutions were prepared with analytical grade reagents and deionized water. The acids, standards and salts were purchased from Sigma Aldrich, the acidic organophosphorous extractant PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) was supplied from Daihachi, Chemical Industry co.

Metal ions concentration was determined by Microwave Plasma – Atomic Emission Spectrometer (4100 MP-AES, Agilent Technologies). Powder composition was determined by X-ray fluorescence spectrometer (Spectro X-LAB 2000 spectrometer).

The electrolysis device was supplied by Bicasa (mod. BE-47D, cathode surface: 55 cm^2).

2.2. Methods

2.2.1. Leaching

Samples were manually homogenized using a mortar. A 50 mL glass beaker was used for all the leaching experiments. Sample weight was fixed at 2.0 g; leaching was conducted at 25°C and under continuous agitation by a magnetic stirrer for 24 h. Leaching tests using different mineral acids at different concentrations and with a solid/liquid (S/L) ratio equal to 1/10 were carried out. The following conditions were evaluated: 15M, 7.5M and 1.5M HNO$_3$; 12M, 6M and 1.2M HCl; 1.8M and 9M H$_2$SO$_4$. After the leaching, the solid residue was separated from the leachate by a centrifuge, washed by distilled water and dried to assess the mass balance.

2.2.2. Electrodeposition

Electrodeposition of antimony on net platinum cathode at constant current intensity of 1A with magnetic stirring was performed, (t=2.5 h, T= 25°C). Metal ions in the liquid phase were then analyzed to check the process efficiency which was calculated according to Eq. (1), where C(fin) is the concentration after the treatment and C(0) is the initial one.

$$E\% = \frac{C(fin)}{C(0)} \times 100 \tag{1}$$

After the electrodeposition process, the cathode, coated by an antimony black layer, was washed, dried and weighed in order to verify the mass balance. Finally this layer was dissolved in HNO_3 to characterize the solution by MP-AES. In Fig. 3, the electrodeposition cathode is shown.
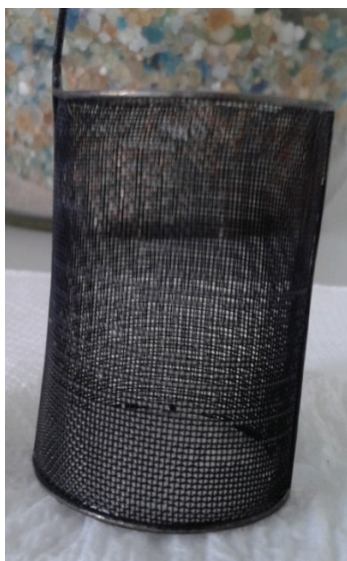

Fig. 3. Black layer of antimony on net platinum cathode

2.2.3. Precipitation and solvent extraction

After antimony electrodeposition, the solution was partially evaporated to increase yttrium and europium concentration, then a 1M $H_2C_2O_4$ solution was added in order to precipitate Y and Eu as oxalates. The RE oxalates were separated by filtration and treated with $KMnO_4$ 0.1N in acidic medium (HCl, pH 0.5-1) to oxidize the oxalates and completely remove them from the solution; this was done in order to avoid a calcination process that involves energy consumption to produce a mixed RE oxide and a further acidic dissolution step. The pH was raised to 2.0 by NH_4OH, then samples were filtered to separate manganese oxide.

Solvent extraction tests were carried out in order to selectively separate yttrium and europium from the leachate obtained as above described: preliminary extraction tests on simulated hydrochloric solutions were performed to find the optimal conditions for yttrium and europium extraction. 0.01M Y and Eu solutions were treated with 0.05M and 0.1M PC-88A in kerosene (aqueous phase/organic phase ratio (A/O): 1/1), then shaken for 1 h in stoppered glass tube at room temperature and allowed to settle for at least 30 min. Organic phase was stripped with HCl 2M with organic/aqueous volume ratio 1:1. Extraction efficiency was calculated according to Eq. (2), where *C(eq)* is the equilibrium ion concentration in the aqueous phase and C(0) is the initial one.

$$E\% = \frac{C(eq) - C(0)}{C(0)} \times 100 \qquad (2)$$

All tests were repeated on four samples; the error percentage was <5%.

3. Results and discussion

3.1. Characterization of spent fluorescent lamp powder

The metal content of spent fluorescent lamp powder is reported in Table 1.

Table 1. Spent fluorescent lamp chemical characterization by XRF analysis

Element	Mass of powder g/kg	Element	Mass of powder g/kg
Glass	820.0	Sb	1.4
Ca	135.1	Eu	1.2
Y	10.8	La	0.8
Ba	7.7	Tb	0.7
Pb	7.5	Ce	0.5
Al	6.3	Cu	0.4
Fe	2.7	Zn	0.2
Sr	2.6	Cd	<0.1
Mn	2.2	Ni	<0.1

3.2. Leaching

In Table 2 the results of the leaching tests are reported: the best leaching acid is HCl 6M, since it allows the highest recovery rates for the elements of interest. Lead is not leached out, suggesting that this element is not present into the coating but in the glass. It can be observed that Eu leaching efficiency is higher than Y: this different chemical behavior might be due to the fact that Eu is present not only as trivalent europium mixed with Y oxide (Y_2O_3:Eu^{3+}) but also in divalent form as an activator, while Y is only present as oxide (Tan et al., 2014). Furthermore a solid/liquid ratio equal 1:5 was tested on HCl 6M in order to verify the possibility of using a lower amount of reagents. In Fig. 4, a comparison between the leaching efficiency with S/L=1:10 and S/L=1:5 was reported, with leachate characterization obtained using S/L 1:5. The experimental data showed that S/L 1:5 allows comparable efficiency, then better conditions are obtained by leaching the powder by HCl 6M at S/L 1:5.

The pie chart on the right side of Fig. 4 shows the relative amount of each element compared to the total cation content in the leachate using S/L 1:5: it can be observed that calcium, probably present in the coating as $Ca_5(PO_4)_3(OH)$, $Ca_5(PO_4)_2(SiO_4)_6$, $Ca_4P_2O_9$ (De Michelis et al., 2011), represents a large part of the ions in solution despite its dissolution yield is only 50%. It was observed that lanthanum, terbium and cerium were not leached: these results agree with those found by Eduafo (2013). Moreover, Eduafo (2013) and Wang et al. (2011), testing different leaching agents, found hydrochloric acid as the best leaching agent, with europium and yttrium extraction efficiency equal to 90%.

Table 2. Spent fluorescent lamps leaching tests (t=24 h, S/L= 1:10, T=25°C; – Best leaching acid marked;
data reported with reference to XRF value)

	Leaching tests							
Metal	*HCl* *1.2 M*	*HCl* *6 M*	*HCl* *12 M*	*HNO₃* *1.5 M*	*HNO₃* *7.5 M*	*HNO₃* *15 M*	*H₂SO₄* *1.8 M*	*H₂SO₄* *9 M*
	Leaching %							
Y	75.9	87.4	82.6	71.4	72.4	73.0	62.8	53.5
Eu	92.7	97.0	98.3	92.1	90.7	96.9	54.1	42.2
Ca	47.1	47.0	46.4	38.9	46.4	47.7	15.0	15.1
Ba	34.0	36.9	37.6	30.6	35.8	38.4	<0.01	<0.01
Al	38.8	39.4	38.9	32.1	39.7	38.3	27.2	27.0
Sr	94.4	91.6	84.9	72.2	84.5	82.0	17.1	14.3
Mn	94.8	87.3	86.5	70.3	80.9	80.1	64.4	62.5
Fe	68.3	70.7	68.4	49.8	59.4	60.5	56.4	56.9
Sb	71.5	76.9	72.9	51.1	60.4	68.4	68.2	56.4
Cu	85.8	87.2	92.2	66.9	84.0	86.9	67.6	68.1
Zn	61.1	68.2	73.3	47.7	56.8	64.5	27.0	34.7
Pb	2.1	2.2	2.1	1.8	1.9	2.0	<0.01	<0.01
Cd	56.9	53.1	51.8	38.0	48.8	49.0	<0.01	<0.01
Ni	64.0	59.1	62.8	48.6	57.1	57.4	<0.01	<0.01

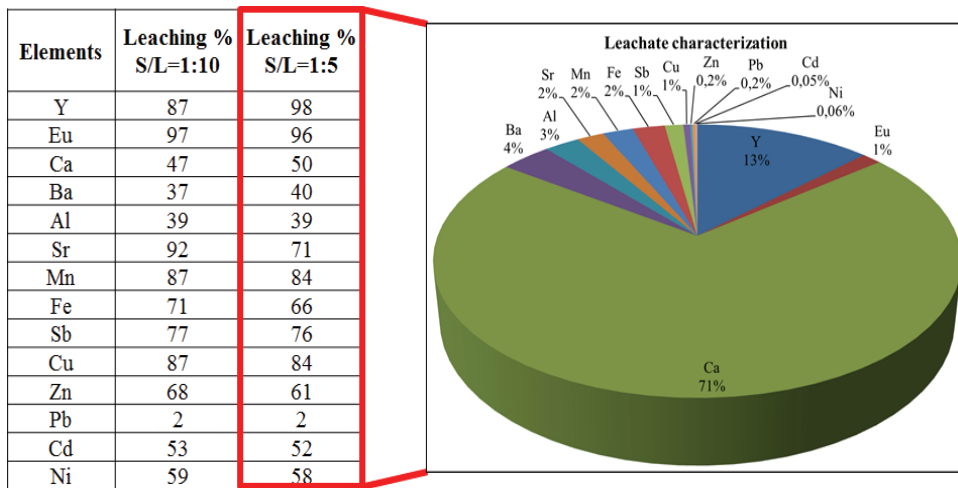| Elements	Leaching % S/L=1:10	Leaching % S/L=1:5
Y	87	98
Eu	97	96
Ca	47	50
Ba	37	40
Al	39	39
Sr	92	71
Mn	87	84
Fe	71	66
Sb	77	76
Cu	87	84
Zn	68	61
Pb	2	2
Cd	53	52
Ni	59	58

Fig. 4. HCl 6N leaching efficiency: comparison between S/L=1:10 and S/L=1:5, leachate elements being compared
to the total cation content

3.3. Antimony recovery

Electrolytic recovery of antimony from waste fluorescent lamp is not currently available in literature, but it can be found in metallurgic processes (Gupta and Krishnamurthy, 2004; Madkour and Salem, 1996) or in copper electrorefining (Ando and Tsuchida, 1997; Lin et al., 1994; Koparal et al., 2004).

The electrodeposition process only occurs for copper and antimony that are reduced in two distinct layers because of their Standard Electrode Potential:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = +0.34V$$

$$SbCl_4^- + 3e^- \rightarrow Sb + 4Cl^- \qquad E^0 = +0.17V$$
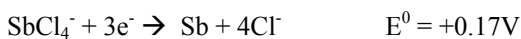
The layering of metals was verified by leaching them through HNO_3: copper was detected as an inner layer, while antimony was the outer: each layer was of purity grade > 98%. Sb and Cu are obtained respectively with a recovery rate of 81% and 31%. It is possible to separately reduce the two elements using two different cathodes and controlling the electrode potential.

3.4. Rare earths recovery

3.4.1. Precipitation

The rare earths oxalates Kps is equal to 5.1×10^{-30} and 4.2×10^{-32} for yttrium and europium respectively (Chung et al., 1998). Oxalic acid is commonly used as a precipitating agent for rare earths in fluorescent lamps, cathode ray tubes and spent nickel-metal hydride batteries (De Michelis et al., 2011; Innocenzi et al., 2013; Tan et al., 2014; Wang et al., 2011; Zhang et al., 1999).

Precipitation efficiency as oxalate was determined according to Eq. (1), showing 90% for Y and 80% for Eu (Fig. 5).

3.4.2. Solvent extraction

In this work PC-88A has been used as an extractant because of its selectivity for rare earths: it is a liquid cation-exchanger, the extracted metal being exchanged by the hydrogen ion of its hydroxyl group (Fernandes et al., 2013; Fontana et al., 2009; Wu et al., 2009).

The PC-88A solvent extraction efficiency, calculated according to Eq. (2), is shown in Fig. 6. It can be observed that the best condition to extract Y from Eu is pHeq = 1.45. At this pH rare earths extraction by PC-88A from solutions containing oxalates as anions is not feasible, due to their precipitation. For this reason oxalate oxidation is required, as explained in 2.2.3. The other elements in solution, except for iron, in these conditions are not extracted.

Using a 0.1M PC-88A solution, an organic phase loaded by 91.6 % of Y and 8.5 % of Eu is obtained, the aqueous phase still containing 76.8 % of the initial Eu. Stripping treatment with 2M HCl is not selective since both Y and Eu are stripped with an efficiency of 95.0%: taking into account the efficiency of the previous processes, the stripping liquor solution contains 76.7% and 6.2% respectively of the initial Y and Eu.

By increasing the number of extraction/stripping steps, it is possible to achieve further purification.

3.5. Proposed flowsheet

According to the experimental data, a block diagram for the hydrometallurgical recovery of Sb, Y, Eu and glass is shown in Fig. 7, starting from an electromagnetic separation of the crushed lamps to recover ferrous and ferromagnetic materials.

After a milling process, the powder is leached by HCl, then is filtrated to recover the glass; the leaching liquor is treated by electrodeposition to recover metallic Sb and Cu. Rare earths are precipitated as oxalates from the residue solution and extracted by PC-88A after oxidizing reaction by $KMnO_4$.
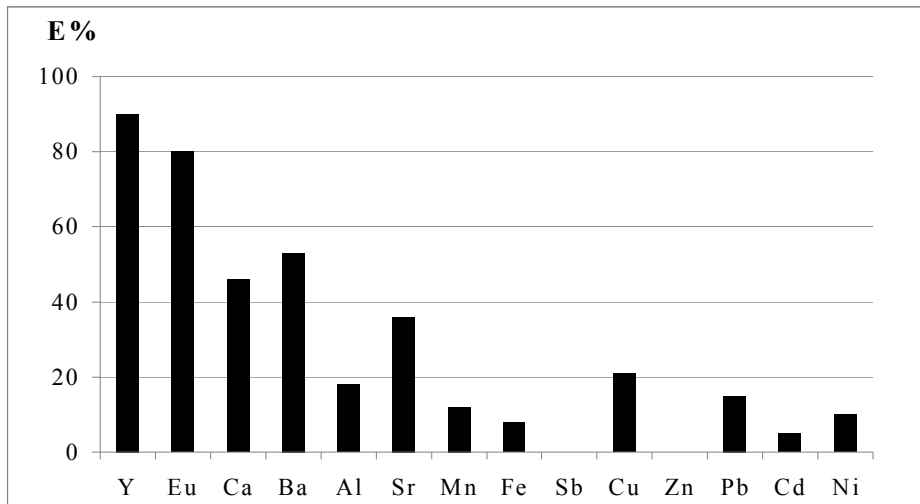

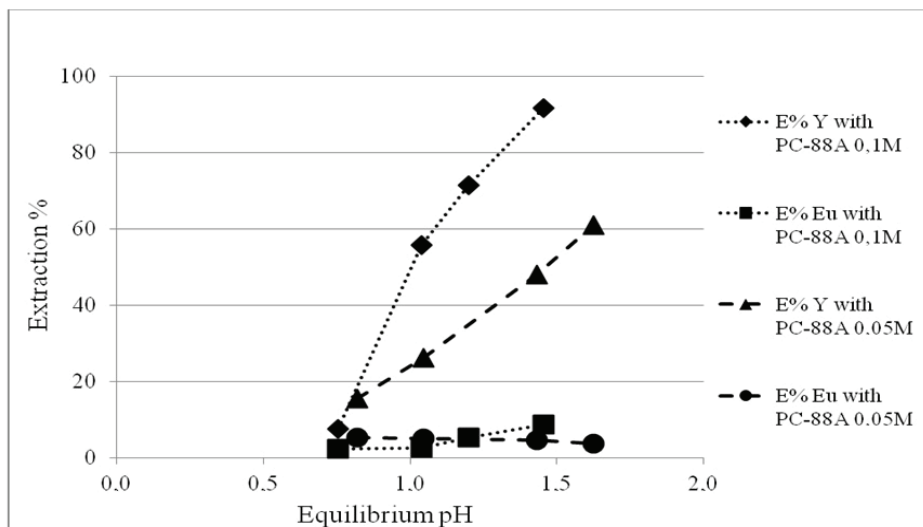**Fig. 5.** Element precipitation efficiency by oxalic acid at 25°C

Fig. 6. Solvent extraction efficiency ([Y] = 0.01M; [Eu]=0.01M; extractant: PC-88A)
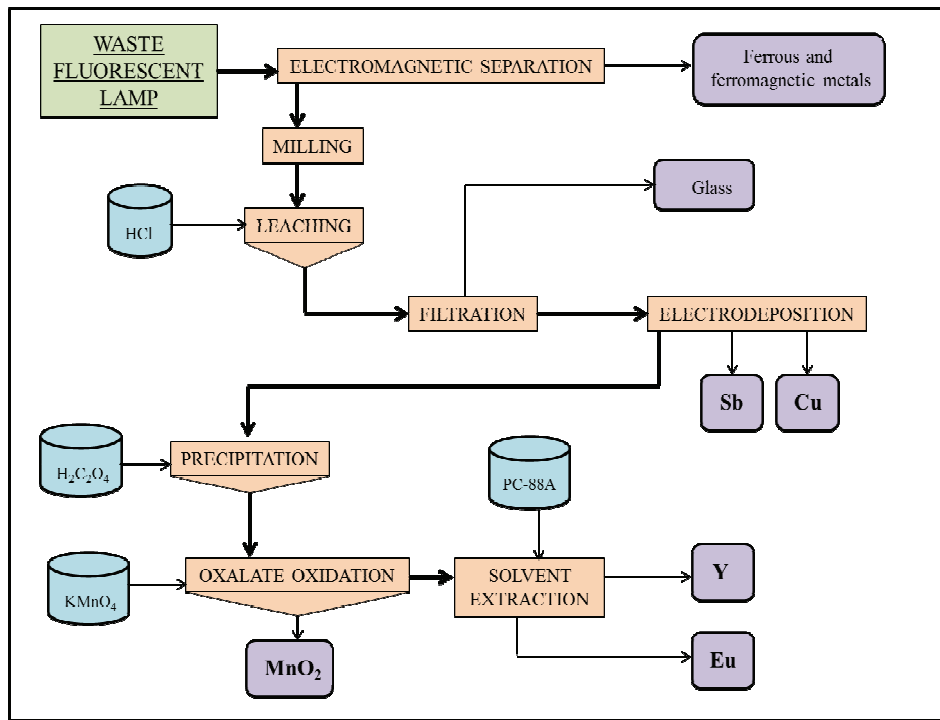
Fig. 7. Proposed process flowsheet

4. Conclusions

A hydrometallurgical process was developed to recover valuable metals from spent fluorescent lamps. Antimony is recovered by electrodeposition with recovery rates up to 80% and purity grade up to 98%; yttrium and europium, after a precipitation process as oxalates and a subsequent dissolution step by $KMnO_4$, are recovered and separated by one stage solvent extraction/stripping process with an efficiency up to 78% for yttrium and 76% for europium. The product-centric approach focuses environmental sustainability by reducing the waste, and supports economic sustainability of strategic materials process recovery.

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