



Study of the recovery of rare earth elements from computer monitor scraps – Leaching experiments

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ABSTRACT

This paper describes the study of the coating powder leaching from computer monitors scraps with the view to obtain a liquor which can be treated by hydrometallurgical techniques to purify the metals studied. The technological development observed in recent years has stimulated the application of rare earth (RE) elements. TV tubes and computer monitors present as coating a powder containing some rare earth elements, mainly europium and yttrium. The recovery of the RE elements from electronics scraps is extremely important as the economic and environmental issues are concerned. The results of this study indicated the technical viability of the recovery of the metals. After the leaching process optimization, the europium and yttrium recovery was over 97% and a liquor containing 16.5 g/L Y, 0.55 g/L Eu, 59.0 g/L Zn, 0.20 g/L Fe, 131 g/L SO₄²⁻, 0.20 g/L Ca and 2.50 g/L Al was obtained.

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1. Introduction

The rare earths (RE) are a moderately abundant group of 17 elements composed of lanthanides, scandium and yttrium. Amongst the RE, promethium (Pm) is extremely rare, however several of the RE elements are not very rare and occur dispersed in a variety of forms (Greenwood and Earnshaw, 1984; Tyler, 2004; Abrão, 1994).

The innumerable applications of the RE elements are based on their particular properties, mainly their spectroscopic and magnetic properties (Martins and Isolani, 2005). They have been used in agriculture, electronics, superconductors, nuclear medicine, automobile industry, special inks – as those used in radar invisible airplanes, X-ray screens, high intensity mercury vapour light bulbs, neutron scintillators, charged-particle detectors and optical memory reading systems (Maestro and Huguenin, 1995; Nagaosa and Binghua, 1997; Sánchez et al., 2001).

The technological development of the last decades in the various sectors of the electronic industry has stimulated the replacement of obsolete gadgets. As a result, there is a growing disposal of obsolete computers and other electronic equipments into landfill sites throughout the world.

Tubes of colour TV sets and computer monitor present as coating, a powder containing a mixture of oxides and sulphides containing RE, mainly europium and yttrium. Despite the low amount recovered, the high commercial value of europium makes it worthwhile. The recovery of the RE from electronics scraps

(e-scaps) and other metals is extremely important as the economic and environmental issues are concerned and also it leads to the recovery of other metals, e.g. lead, zinc, strontium, zirconium and indium, which are also present in computer monitor and TV screen coating powders.

Morais et al. (2001) studied the recovery of europium and yttrium from colour TV screens using sulphuric acid as the leaching agent. In this study, the Eu and Y solubilisation was 90 and 95 wt.% respectively when conducted at 90 °C, 2 h of leaching, acid/sample ratio of 1000 kg/t and 40% solids. At 70 °C, 1500 kg/t acid/sample ratio, 2 h of leaching, and 40% solids, the solubilisation of both metals was 80%.

Rabah (2008) studied the recovery of europium and yttrium from fluorescent light tubes using a mixture of sulphuric/nitric acids as the leaching agent. At critical conditions i.e. autoclave digestion, at 125 °C, 4 h and 5 MPa using a mixture of sulphuric/nitric acids, the Eu and Y solubilisation was 92.8% and 96.4% respectively.

This work describes the study of the coating powder leaching from e-scaps aiming at obtaining a liquor which can be treated through metallurgical techniques to purify the metals. The parameters investigated were: leaching agent, acid/sample ratio, time of acid leaching, solids percentage and temperature of leaching.

2. Experimental

The coating powder used in this study was obtained by manually scraping the inner surfaces of computer monitor – on average 300 monitors are necessary to provide 1 kg of powder, considering

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different sizes. Sulphuric and hydrochloric acids (H_2SO_4 and HCl) were used in the leaching experiments. All solutions were prepared with analytical grade reagents and distilled water.

The sample was characterized by energy-dispersive X-ray spectrometer (Kevex system) (Morais and Ciminelli, 1998), atomic absorption spectrometry and X-ray diffraction. The X-ray diffraction indicated the zinc sulphide (ZnS) and yttrium oxide sulphide (Y_2O_2S) as the main constituents of the sample and the chemical characterization is shown in Table 1.

The leaching experiments were carried out in beakers of 150 mL, under mechanical agitation with controlled temperature. Hydrochloric and sulphuric acids were tested as leaching agents. The recovery was calculated based on the Eu and Y content in the sample and also on the leached residue. The measurements were taken by energy-dispersive X-ray spectrometry. Replications prepared from experiments randomly chosen indicated an experimental error of 2% at 95% of confidence level.

3. Results and discussion

As shown in Table 1, amongst the RE elements, Eu and Y are the ones present in the highest amounts in the sample, therefore the study of the RE leaching was based on these elements. Significant amounts of other metals such as zinc, indium, strontium, iridium and lead are present and can also be recovered.

The influence of the leaching agent, acid/sample ratio, time of leaching, solids percentage and the temperature in the dissolution of the RE from the powder were investigated. The dissolution of Eu and Y was very similar as the parameters investigated are concerned. Thus, in the discussion of the results they were regarded as a single element.

3.1. Leaching agent

Preliminary leaching experiments were carried out using hydrochloric and sulphuric acids. The experiments were carried out under the same critical conditions. Sulphuric acid proved to be far more efficient and selective than hydrochloric acid in the dissolution of yttrium and europium, thus becoming the leaching agent chosen. At 90 °C, 3 h of leaching, 1500 g/kg acid/sample ratio and 10% solid, the Eu and Y recovery was 97% for H_2SO_4 and 30% for HCl.

3.2. Acid/sample ratio

The influence of the acid/sample ratio on the RE leaching was investigated in the interval between 750 and 2000 g/kg for two different solid ratios (10 and 30 wt%), using H_2SO_4 as leaching agent, at 90 °C and 3 h leaching time. Fig. 1 shows that the influence of the acid/sample ratio was the same for both solids percentage investigated. The efficiency of the leaching improved gradually with the increase of the acid/sample ratio, approaching a maximum of 98% for both metals at an acid/sample ratio of 1500 g/kg. A higher value of acid/sample ratio did not improve the rate of solubilisation of Eu and Y. The best acid/sample ratio is between 1200 and 1500 g/kg. The subsequent experiments were carried out with a 1500 g/kg acid/sample ratio.

Table 1

Chemical composition of the powder from computer monitor (wt.%).

Y	In	Ce	Nd	Sm	Eu	Al	Si	S	K
17.0	0.49	0.02	0.01	0.02	0.76	4.55	10.44	17.38	2.36
Ca	Mn	Fe	Zn	Sr	Zr	Ir	Pd	Ba	Pb
0.80	0.39	0.54	31.4	0.82	0.15	0.42	0.07	2.15	7.53

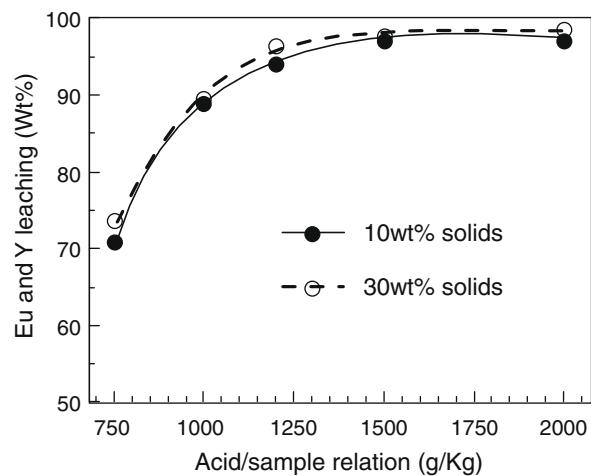


Fig. 1. Influence of the acid/sample ratio with 10 and 30 wt.% of solids on the leaching of europium and yttrium by sulphuric acid at 90 °C and 3 h leaching time.

3.3. Leaching time

The influence of the leaching time on the solubilisation of Eu and Y was investigated in the interval between 0.5 and 3 h in two different conditions: (i) at the temperature of 90 °C and 10% solids and (ii) at the temperature of 60 °C and 30% solids. The results are shown in Table 2. At 90 °C and 10% solids, no significant effect on the dissolution of Y and Eu is observed when the leaching period is over one hour. At 60 °C and at 30% solids, the efficiency of the leaching increased gradually over time, reaching the maximum Y and Eu dissolution – 98 wt% – in 1.5 h of leaching (Table 2). The subsequent experiments were carried out using 1.5 h of leaching.

3.4. Temperature

The influence of the temperature on Eu and Y dissolution was investigated at the interval between 25 °C and 90 °C at two different solids percentage (20% and 30%), 1.5 h of leaching and 1500 g/kg acid/sample. It was observed that for 30% solids, 60 °C is required to attain the maximum Eu and Y leaching (98 wt%).

It was also seen that when the solids percentage was reduced to 20%, no significant effect of temperature on the Eu and Y dissolution was observed. At room temperature (25 °C) the Eu and Y dis-

Table 2
Leaching of Eu and Y at different reaction time, temperature and solids percentage.

Leaching time (h)	Eu and Y leaching (wt%) 90 °C – 10% solids	Eu and Y leaching (wt%) 60 °C – 30% solids
0.5	91	87
1.0	97	90
1.5	96	98
2.0	96	99
3.0	97	98

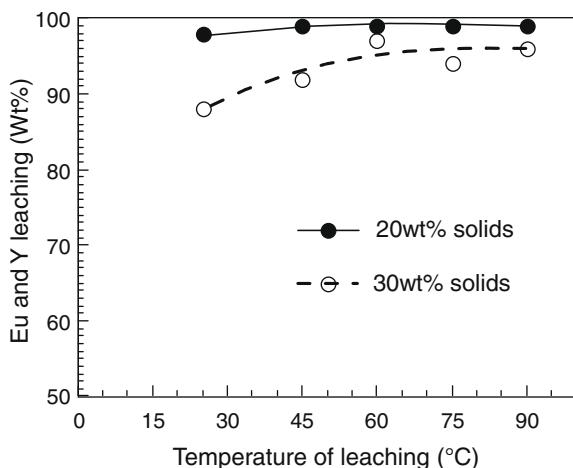


Fig. 2. Influence of temperature and solids percentage on europium and yttrium leaching with sulphuric acid at 1.5 h leaching time and 1500 g/kg acid/sample ratio.

solution was 98.5%, whereas at 90 °C the dissolution was 99 wt.% for both metals (see Fig. 2).

3.5. Solids percentage

The influence of solids percentage on the solubilisation of Eu and Y was investigated at the interval between 10% and 40% at 90 °C and at 25 °C. As shown in Fig. 3, at 90 °C the Y and Eu solubilisation was very high for values up to 30% solids. When the solid percentage was higher than 30%, the Eu and Y dissolution dropped steeply. At 25 °C it was observed that the applied solids percentage should not be greater than 20%. Under this condition, the Eu and Y dissolution was the same as obtained at 90 °C (98%) and dropping to 88% when 30% solids were employed (Fig. 3).

3.6. Optimised parameters

After investigating the leaching variables, the conditions selected were: 1.5 h of leaching, acid/sample ratio of 1500 g/kg, solids percentage of 20% and room temperature (25 °C). In these conditions, dissolution of 96 wt.% of Eu and Y was obtained. The condition achieved in this work results in a substantial energy saving and a reduced leaching time, thus making the metals recovery a rewarding process.

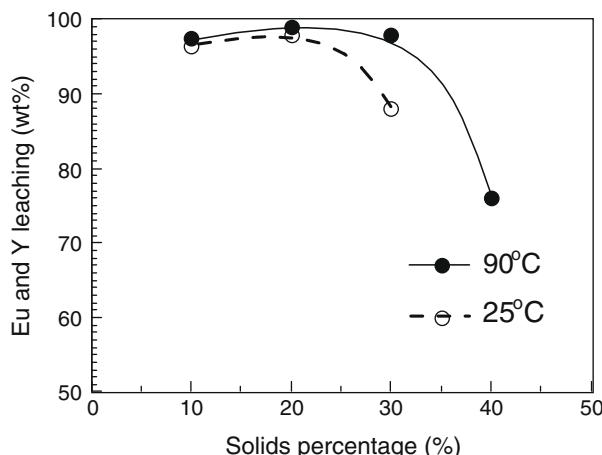


Fig. 3. Influence of the solids percentage on europium and yttrium leaching at 90 °C and 25 °C, 1.5 h leaching time and 1500 g/kg H₂SO₄/sample ratio.

Table 3
Chemical composition of the liquor obtained in the leaching step.

Specie	Y	Eu	Zn	Fe	SO ₄ ²⁻	Ca	Al
Content (g/L)	16.5	0.55	59.0	0.20	131	0.20	2.50

In similar reputable works Morais et al. (2001) studying the recovery of Eu and Y from colour TV tubes, reached 95% of the metals solubilisation in 2 h of leaching at 90 °C. Rabah (2008) carrying out the recovery of Eu and Y from fluorescent light tubes reached a metal solubilisation of 96.4% for Y and 92.8% for Eu by applying autoclave digestion of the powder in the acid mixture (sulphuric and nitric acids) for 4 h at 125 °C and 5 MPa.

The characterization of the main constituents of the sulphuric liquor obtained after the optimization of the leaching process is shown in Table 3.

4. Further steps of the process

In order to obtain pure Y and Eu, the following steps of the process will address the purification of the metal through solvent extraction technique, followed by the precipitation of the metals as hydroxide or oxalate and calcination of the precipitate in order to obtain Y and Eu oxides.

The separation of Eu and Y by solvent extraction is viable as Y presents similar behaviour to the heavy RE group while the Eu belongs to the medium RE group, thus, its chemical behaviour is slightly different. Therefore the separation of the elements individually can be carried out with the use of an organophosphorus extractant such as D2EHPA (di-2-ethylhexylphosphoric acid), which extracts preferentially Y rather than Eu (Morais and Ciminelli, 2004).

In a solvent extraction circuit, Y is extracted by the solvent and stripped by the stripping solution while Eu remains in the raffinate alongside other elements such as Zn, Fe, Ca and Al. The separation of Eu can be carried out through selective precipitation or by solvent extraction. By the solvent extraction technique, Fe (III) will be reduced to Fe (II) through addition of metallic zinc.

5. Conclusions

The coating powder sample collected from computer monitors shows significant amounts of europium and yttrium oxide, thus it can be considered a secondary source of the elements.

The study showed that sulphuric acid can be used as leaching agent in order to dissolve the RE metals. The efficiency of the Eu and Y dissolution depends mainly on the acid/sample ratio and the solids percentage. The experiments in this work showed that in 1.5 h of leaching at room temperature (25 °C), dissolution of 96 wt.% of Eu and Y was obtained.

The pregnant liquor obtained in the leaching step, containing 16.5 g/L of Y and 0.55 g/L of Eu and a pH near 0.3 can be processed by the solvent extraction technique without previous treatment.

This work leads to substantial economy, as time and energy are concerned, thus making the metals recovery a rewarding process.

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