

Process development for the recovery of europium and yttrium from computer monitor screens



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ABSTRACT

This work describes the development of a process for the recovery of Eu and Y from cathode ray tubes (CRTs) of discarded computer monitors with the proposition of a flow sheet for the metals dissolution. Amongst other elements, europium and yttrium are presented in the CRTs in quantities – 0.73 w/w% of Eu and 13.4 w/w% of Y – that make their recovery worthwhile. The process developed is comprised of the sample acid digestion with concentrated sulphuric acid followed by water dynamic leaching at room temperature. In the CRTs, yttrium is present as oxysulphide (Y_2O_2S) and europium is an associated element – $Y_2O_2S:Eu^{3+}$ (red phosphor compound). During the sulphuric acid digestion, oxysulphide is converted into a trivalent Eu and Y sulphate, in solid form, with the liberation of H_2S . In the second step, metals are leached from the solid produced in the acid digestion step by dynamic leaching with water. This study indicates that a proportion of 1250 g of acid per kg of the sample is enough to convert Eu and Y oxysulphide into sulphate. After 15 min of acid digestion and 1.0 h of water leaching, a pregnant sulphuric liquor containing 17 g L^{-1} Y and 0.71 g L^{-1} Eu was obtained indicating yield recovery of Eu and Y of 96% and 98%, respectively. Both steps (acid digestion and water leaching) may be performed at room temperature.

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1. Introduction

Devices containing cathode ray tubes (CRTs), such as computer monitors and TV tubes, have been replaced by new technologies such as LCD display, plasma, LED and other flat screen technologies. As a result, there has been a concern about how to deal with the growing electronic waste being generated (Gregory et al., 2009; Ravi, 2012).

There is a general consensus that a major problem concerning the disposal of CRTs devices is the large amount of lead present in them as well as the limitation in reusing their glass components in other applications (Poon, 2008; Andreola et al., 2007; Menad, 1999; Ravi, 2012; Yamashita et al., 2010; Cui and Forssberg, 2007). Some research groups have worked on the closed-loop recycling, i.e. the usage of CRT glass in further production of cathode ray tubes (Andreola et al., 2007; Menad, 1999; Gregory et al., 2009), however, with the introduction of new technologies, the demand of CRTs has dropped significantly. Ceramic industries are a potential consumer for CRTs since the restrictions on hazardous elements are not so severe.

Among the parts that a CRT is composed of (neck, funnel and the glass of the panel), the panel glass used in the front screen that

shows the image, contains a small amount of lead (between 0 and 4 w/w%), the funnel contains between 22 and 28 w/w% and the neck glass contains 30 w/w% of lead (Gregory et al., 2009).

Besides the presence of hazardous metals, panel glass contains a luminescent material, also called phosphors, based on rare earth ions or rare earth host lattices (Ronda et al., 1998). Colour for television and computer screens was obtained through the use of three phosphors: a europium – yttrium compound for red, a terbium fluoride – zinc sulphide for green, and a cerium – strontium sulphide for blue. When activated by photons, these phosphors emit a luminescence that makes the screen attractively colourful (Gupta and Krishnamurthy, 2004). The main phosphors used in the industry are: $Y_2O_3:Eu^{3+}$, $Y_2O_3S:Eu^{3+}$, $YVO_4:Eu^{3+}$, $Y_2(WO_4)_3:Eu^{3+}$ (red colour); $Sr_5(PO_4)_3Cl:Eu^{2+}$, $BaMgAl_{11}O_{17}:Eu^{2+}$, $Sr_2Al_6O_{11}:Eu^{2+}$ (blue colour); $CeMgAl_{11}O_{19}:Tb^{3+}$, $(Ce, Gd)MgB_5O_{10}:Tb^{3+}$, $(LaCe)PO_4:Tb^{3+}$, $YSiO_5:Tb^{3+}$, $Y_3Al_5O_{12}:Tb^{3+}$ (green colour) (Ronda et al., 1998).

In a previous work (Resende and Morais, 2010), it was found that the coating powder from computer monitors contains significant amounts of Eu and Y (0.76 w/w% and 17 w/w%, respectively), among other metals. Therefore, the recovery of Eu and Y present in these devices, besides offering an economic benefit – since these elements have a high value, is also advantageous from an environmental viewpoint – since its recovery can also contribute to the recovery of other metals present in the CRTs. The recovery of these elements also enables glass recycling, which can be used in the

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manufacture of fibres from glass and crystal, and can also be used as vitrifiers in ceramic manufacture and other applications. Resende and Morais (2010) studied sulphuric acid leaching of Eu and Y scrapped from computer monitors. The study showed that leaching efficiency depends mainly on the acid/sample ratio and the percentage of solids. The result was 96% of Eu and Y leached in 1.5 hours of leaching at room temperature. 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 dissolution reached 92.8% and 96.4% respectively. Morais et al. (2001) studied the recovery of europium and yttrium from the material scraped from colour TV screens using sulphuric acid as the leaching agent. In this study, Eu and Y dissolution was 90% and 95% respectively when conducted at 90 °C, 2 h of leaching, acid/sample ratio of 1000 kg/t and 40 w/w% solids.

The aim of this paper was to describe a much simpler process to recover Eu and Y from CRTs and highlight the parameters involved in the process, including the mechanism for metals dissolution that was not mentioned before.

2. Experimental

2.1. Sample and reagents

The coating powder used in this study was obtained by manually scrapping the inner surfaces of computer monitor panels – an average of 300 monitors are necessary to provide 1 kg of powder, considering different sizes. The experiments were performed using sulphuric acid and hydrochloric acid of analytical grade; (98 w/w%) and (37 w/w%) respectively and distilled water.

2.2. Analytical procedure

The concentration of Eu and Y was determined by energy-dispersive X-ray spectrometry KeveX Sigma (model X 9050) (Morais and Ciminelli, 2001), whereas the other metals were determined by flame absorption atomic spectrometry Varian (model AA240FS) and energy dispersive X-ray fluorescence spectrometer (SHIMADZU, model EDX-720). The identification of the compounds present in the sample was performed by X-ray diffraction with a Rigaku spectrometer (model D/Max Ultima).

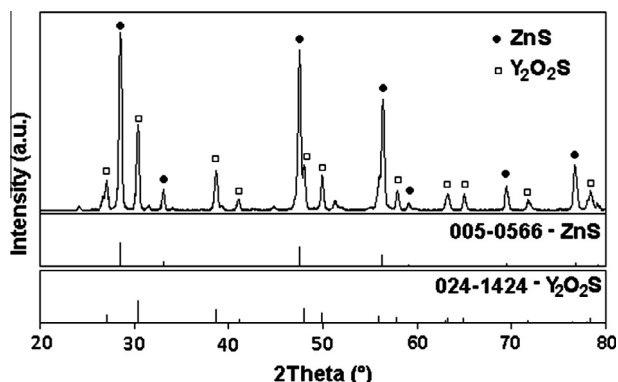


Fig. 1. X-ray diffractogram of the coating powder of computer monitors.

The percentage of recovery of Eu and Y was calculated by difference in weight of the metal in the initial sample and the remaining in the residue after leaching. As the dissolution of Eu and Y was very similar in all of the investigated parameters (variations of less than 1% in the percentage of dissolution), they were regarded together in the discussion. Replications prepared from randomly chosen experiments indicated an experimental error of 3% at a 95% confidence level for both steps.

Although the experimental procedure was similar to that described in our previous publication (Resende and Morais, 2010), it is important to emphasize that in this work the process of Eu and Y dissolution was achieved in two steps, namely acid digestion and water leaching, resulting in shorter operation time, water consumption minimizing and increasing metals content in the liquor. Others contributions over the previous work are the proposition of chemical reactions involved in acid digestion process and a flow sheet of the whole process.

2.3. Acid leaching experiments

Preliminary experiments aiming the dissolution of europium and yttrium from computer monitors screen coating powder were carried out by hydrochloric and sulphuric acid leaching. The leaching experiments were performed in beakers, under mechanical agitation and controlled temperature by a thermostatic water bath. The parameters investigated were reaction time, temperature and solid percentage.

2.4. Sulphuric acid digestion

The acid digestion experiments were carried out in beakers by adding concentrated sulphuric acid (H_2SO_4 – 98 w/w%) at a controlled temperature. The sample and the acid were mixed using a glass rod and were kept at rest during digestion time.

The acid digestion product was leached using water as leaching agent. The leaching experiments were carried out under mechanical stirring (500 rpm). The pulp was filtered (8 μ m porosity) in a vacuum filtration system and the residue and filtrate were analysed. The residue was analysed after abundant (approximately 1 liter) scrubbing with distilled water. The influence of solids percentage was investigated in the interval between 10 w/w% and 40 w/w% at 25 °C (room temperature) and 3 h of reaction time. The influence of leaching time was investigated at the interval between 0.5 and 3 h at 25 °C and 10 w/w% of solids.

3. Results and discussion

3.1. Characterization of the sample

The X-ray diffraction indicated zinc sulphide (ZnS) (JCPDS 005-0566) and yttrium oxysulphide (Y_2O_2S) (JCPDS 024-1424) as the main compounds of the sample. Europium was not identified in the X-ray diffraction however it is present as ($Y_2O_2S:Eu^{3+}$), a phosphors consisting of Eu doped in an yttrium-containing host Eu^{3+} , commonly used to produce the red colour for television and computer screens. The X-ray diffractogram and the main constituents of the sample are shown in Fig. 1 and in Table 1 respectively.

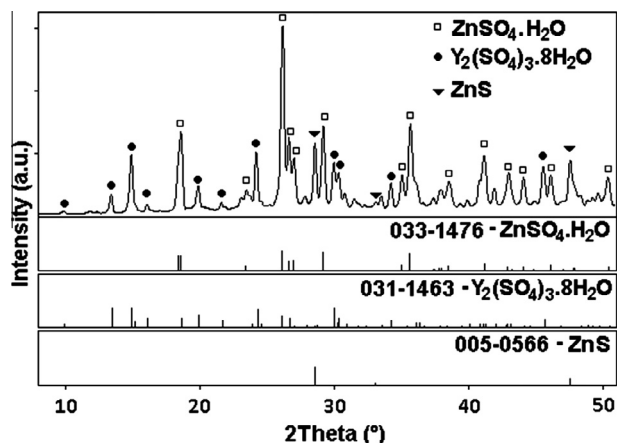
Table 1
Chemical composition of the powder scraped from computer monitor.

Specie	Y	In	Ce	Nd	Sm	Eu	Al	Si	S	K
Content (w/w%)	13.4	0.24	0.02	0.01	0.02	0.73	4.55	10.4	17.4	2.36
Specie	Ca	Mn	Fe	Zn	Sr	Zr	Ir	Pd	Ba	Pb
Content (w/w%)	0.80	0.39	0.54	31.4	0.82	0.15	0.42	0.07	2.15	7.53

Table 2

Effect of the leaching agent and acid-sample ratio on Eu and Y dissolution at 3 h of leaching at 90 °C.

<i>HCl leaching</i>			
Acid sample ratio (g/kg)	200	400	1100
Eu and Y leachate (%)	1.5	31	35
<i>H₂SO₄ leaching</i>			
Acid sample ratio (g/kg)	550	1100	
Eu and Y leachate (%)	14	51	

**Fig. 2.** Diffractogram of the acid digestion product.**Table 3**

Effect of the temperature on Eu and Y dissolution – 1250 g kg⁻¹ acid/sample.

Temperature (°C)	25	45	60	75	90
Eu and Y recovered (%)	98.5	98.1	98.9	98.1	98.0

Table 4

Influence of the percentage of solids on Eu and Y dissolution from digestion residue (1250 g kg⁻¹ acid/sample ratio, 0.5 hours at 25 °C) – 3 h of leaching at 25 °C.

Solids percentage (w/w%)	Content of Eu and Y in the sample (w/w%)		Content of Eu and Y in the leaching residue (w/w%)		Content of Eu and Y in the leaching residue after scrubbing (w/w%)	
	Eu	Y	Eu	Y	Eu	Y
23	0.73	13.4	0.46 (63% ^a)	5.9 (44% ^a)	0.05 (6.8% ^a)	0.74 (5.5% ^a)
16			0.27 (37% ^a)	3.7 (27.6% ^a)	0.04 (5.5% ^a)	0.51 (3.8% ^a)
10			0.07 (9.6% ^a)	0.78 (5.8% ^a)	0.04 (5.5% ^a)	0.64 (4.7% ^a)

^a Percentage of Eu and Y that were not leached.

Table 5

Content of Eu and Y in the liquor of leaching process in different solid percentages and in scrubbing water. Digestion conditions: 1250 g kg⁻¹ acid/sample ratio, 0.5 h at 25 °C. Leaching conditions: 3 h at 25 °C.

Solids percentage (w/w%)	Product of acid digestion (g)	Volume of water added in the leaching step (mL)	Content of Eu and Y in the liquor (g L ⁻¹)		Content of Eu and Y in the water scrubbing – 150 mL (g L ⁻¹)	
			Eu	Y	Eu	Y
30	15	35	0.56	19.7	0.81	17.6
23	15	50	0.54	16.9	0.30	3.7
16	15	75	1.2	23.1	0.07	0.86
13	15	100	1.0	17.1	0.06	0.86
10	15	125	0.71	17.0	0.06	1.1

3.2. Acid leaching experiments

Preliminary leaching experiments using hydrochloric and sulphuric acids carried out under critical conditions indicated a low rate of Eu and Y dissolution. In these experiments, the performance of sulphuric acid was better than that of hydrochloric acids. When HCl was used at 90 °C, 1100 g kg⁻¹ acid/sample ratio and 3 h of leaching, the dissolution of Eu and Y was 32 and 31 w/w% respectively. For H₂SO₄, the metals dissolution was around 50 w/w% (Table 2). As results obtained with the acid leaching experiments were not satisfactory, the author decided to investigate the sulphuric acid digestion.

3.3. Acid digestion

In the study of the investigated parameters effect on Eu and Y dissolution by sulphuric acid digestion, the acid digestion product was leached by water using 3.0 h of reaction time and 10% of solids at 25 °C.

3.3.1. Chemical process

After a few minutes (~10 min.) of the addition of sulphuric acid concentrate on the coating powder of computer monitor panels, a liberation of H₂S gas was observed, indicating the sulphide decomposition. An X-ray diffraction study was made in order to investigate the behaviour of the acid digestion. The X-ray diffraction analysis of the solid formed after H₂S liberation showed the presence of zinc sulphate monohydrate (ZnSO₄·H₂O) (JSPDS 00-033-1476) and yttrium sulphate octahydrate (Y₂(SO₄)₃·8H₂O) (JSPDS 00-031-1463), confirming that the ZnS and Y₂O₂S present in the sample before the addition of H₂SO₄ were converted into sulphates. The diffractogram of the acid digestion product is presented in Fig. 2. As can be seen, a small part of the ZnS was not converted into ZnSO₄, remaining as ZnS.

The chemical reactions involved in acidic digestion process can be represented by the following equations:

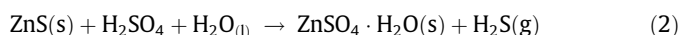
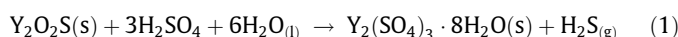


Table 6

Influence of the leaching time on the dissolution of Eu and Y from the digestion product (1250 g kg⁻¹ acid/sample ratio, 0.5 h at 25 °C) – 10 w/w% solid percentage at 25 °C.

Leaching time (h)	0.5	1.0	1.5	3.0
Eu and Y dissolved (%)	96.5	98.1	98.0	98.3

Table 7

Composition of the liquor obtained after the overall process.

Element	Y	Eu	Fe	Zn	Mn	Al	SO ₄ ²⁻	pH
Composition (g L ⁻¹)	17	0.71	0.076	21.8	0.21	1.0	82	0.71

The simple sulphates of trivalent rare earths, Y₂(SO₄)₃ and Eu₂(SO₄)₃, are soluble in water and their solubility decreases with increase in temperature (Gupta and Krishnamurthy, 2004). Thus, the authors were encouraged to proceed with the leaching using water at room temperature.

Table 8

Composition of residue after the overall process.

Specie	Y	In	Ce	Nd	Sm	Eu	Al	Si	S	K
Content (w/w%)	0.32	0.6	0.93	0.21	0.03	0.03	1.16	10.2	41	3.1
Specie	Ca	Mn	Fe	Zn	Sr	Zr	Ir	Pd	Ba	Pb
Content (w/w%)	1.1	0.03	0.24	4.2	1.9	0.72	0.22	0.014	3.19	16

3.3.2. Acid/sample ratio

The influence of the acid/sample ratio on Eu and Y dissolution was investigated in the interval between 750 and 2000 g kg⁻¹ at 90 °C for 3 h. The best results were achieved in an acid/sample ratio over 1200 g kg⁻¹. A higher amount of acid did not improve the rate of dissolution for either of the metals investigated, as described elsewhere (Resende and Morais, 2010).

3.3.3. Reaction time and temperature

The results of the experiments where these variables were investigated indicated that in reaction time varying from 0.5 h to 3.0 h and temperatures varying from 25 °C to 90 °C, the dissolution of Eu and Y were not significantly affected. The results indicated that a reaction time of 0.5 h was enough to reach the maximum Y and Eu dissolution – 98% at 25 °C – room temperature. The results of the experiments carried out in 0.5 h and varying the temperature are shown in Table 3.

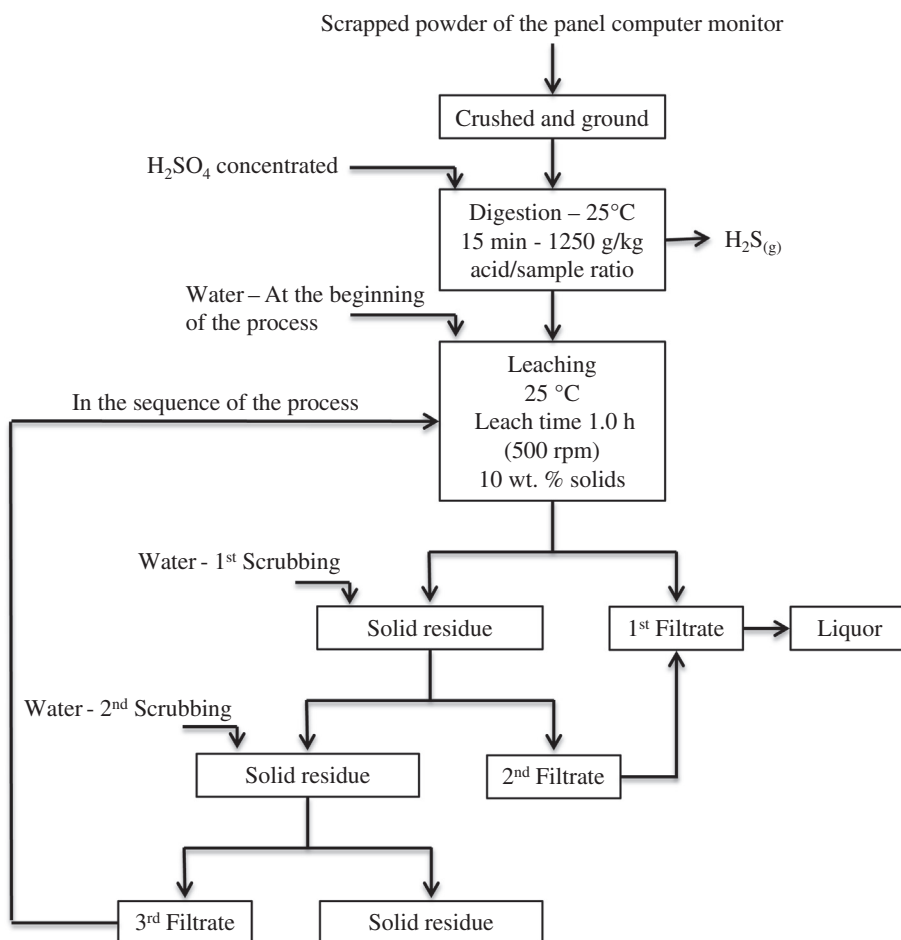


Fig. 3. Simplified flow sheet for the recovery of Eu and Y from CRTs of computers.

3.4. Leaching of the acid digestion product

3.4.1. Percentage of solids

The percentage of solids was investigated at the interval between 10 to 40 w/w%. When the yield of Eu and Y solubility was analysed through the metals content in the residue, no significant influence of the percentage of solids was observed in the interval investigated. However, when the liquor was analysed, it was observed that the dissolution yield of Eu and Y decreases as the solid percentage increases, due to the fact that the residue was washed prior to analysis, dissolving the europium and yttrium sulphates that remained insoluble. Table 4 shows the content of Eu and Y in the leaching residue after the leaching process in solid percentage of 10, 16 and 23 w/w% and the content of Eu and Y that remains in the residue after abundant scrubbing.

It can be observed that when the process is conducted with 16 and 23 w/w% solids, the content of Eu and Y in the residue is reduced significantly after scrubbing. When the leaching is carried out at 10% of solids, the reduction of metal content in the residue after scrubbing was not so significant.

For the percentage of solids of 23%, the percentage of Eu and Y that were not leached was reduced by scrubbing from 63% to 6.8% and from 44% to 5.5%, respectively. However, for 10% of solids, the reduction in the percentage of Eu and Y that were not leached was not very significant, being reduced just from 9.6% to 5.5% for Eu and from 5.8% to 4.7% for Y. So, when a percentage of solids of 10 w/w% is used, only a small amount of water in the scrubbing step is required. The content of Eu and Y in the liquor and in the water used in the scrubbing was also assessed for different solid percentages. After the pulp filtration, the liquor was collected and the residue was scrubbed with 150 mL of water. A mass of 15 g of the acid digestion product was used in each experiment. The result of these experiments (Table 5) indicated that, for solids percentage smaller than 16%, it is not necessary a large amount of water scrubbing, which yields lower volumes of liquor with higher concentration of Eu and Y.

3.4.2. Leaching time

The influence of leaching time on the dissolution of Eu and Y was investigated within an interval between 0.5 and 3 h at 25 °C and 10 w/w% of solids. As shown in Table 6, the results indicated that 1.0 h of mechanical stirring was enough to reach the maximum Y and Eu dissolution of 98%.

4. Optimized conditions

The results obtained in the acid digestion and water leaching steps indicated the technical viability of recovering Eu and Y from the CRTs of discarded computer monitors. It was observed that 15 min of digestion time reached the same result that those carried out in 30 min. Accordingly, the best conditions established for the dissolution of Eu and Y from computer monitor screens are: sulphuric acid digestion at room temperature (25 °C), using an acid/sample ratio of 1250 g kg⁻¹ and a reaction time of 15 min (until the liberation of H₂S occurs); water leaching of the acid digestion product at room temperature (25 °C), with mechanical stirring, using a percentage of solids of 10 w/w% and 1.0 h of stirring. Under these conditions, a liquor containing 17 g L⁻¹ of Y and 0.71 g L⁻¹ of Eu was obtained. The composition of the liquor and of the residue after Eu and Y recovery from the sample are presented in Table 7 and 8 respectively.

After the overall process, there is a reduction of approximately 50 w/w% of the initial sample. As shown in Table 8, some elements present in the sample were not leached in the presented condition (In, Ce, Nd, Sm, S, Sr, Zr, Ba, Pb), concentrating in the residue. Some

of these metals, such as In, Ce, Nd, and Zn that remained in the residue, can be leached in another condition. The recovery of yttrium and europium was 98% and 96% respectively.

The flow sheet proposed for the recovery of Eu and Y present in the powder coating of computer monitors screens is presented in Fig. 3.

5. Conclusions

The study indicates the technical viability of the recovery of Eu and Y present in the coating powder of the inner surfaces of panel computer monitors. The recovery of Eu and Y can be done by employing sulphuric acid digestion followed by water leaching. The main factors influencing Eu and Y dissolution are the acid/sample in the digestion step and the solid percentage in the leaching step. The water used in the second scrubbing can be reused in the leaching step, minimizing water consumption and increasing the metals content in the liquor.

The process developed presents innovative aspects concerning the recovery of Eu and Y from the coating powder scrapped from panels of computer monitors, using a much simpler process than others cited in literature. The innovative aspects are: (i) sulphuric acid digestion at room temperature (25 °C), and a reaction time about of 15 min, (ii) water leaching of the acid digestion product at room temperature (25 °C) with mechanical agitation for 1.0 h. This is a substantial advantage in a chemical process, and also a considerable reduction in energy consumption as well as a reduction of operational costs and risks. Usually, metals leaching from sulphides involves high temperature and long leaching time.

At the conditions cited above, and using a sulphuric acid/sample ratio of 1250 g kg⁻¹ in digestion step and a 10 w/w% of solids in the leaching step, a dissolution of 98% of Y and 96% of Eu was reached and a liquor containing 17 g L⁻¹ of Y, 0.71 g L⁻¹ of Eu and 82 g L⁻¹ SO₄²⁻ at pH 0.71 was obtained.

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