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Leaching of yttrium, europium and accompanying elements from phosphor coatings

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ABSTRACT

The aim of this work was to study and describe leaching behaviour of Y, Eu and accompanying elements (Zn, Cd) from the phosphors of waste cathode ray tube (CRT) screens in low concentrated sulphuric acid solutions under both non-oxidizing and oxidizing conditions (H_2O_2). Thermodynamic study showed that non-oxidizing acid leaching leads to elemental sulphur and hydrogen generation followed by formation of $H_2S(g)$. In the presence of oxidant in the leaching system $SO_2(g)$ or H_2SO_4 formation is possible. $PbSO_4$ was formed during leaching independently from the presence of the oxidant. Y, Eu and Zn dissolution without using H_2O_2 in 0.4 M H_2SO_4 at 80 °C attained 6, 9 and 8% respectively. The appropriate content of H_2O_2 in leaching solution was determined as 3.9 v/v %. The highest leaching efficiency of Y and Eu (around 90–95% after 20 min) was achieved by using the leaching solution (400 ml 0.4 M H_2SO_4, 60 ml 30 v/v % H_2O_2) at 80 °C and L/S ratio 23. Under these conditions Zn extraction was relatively low (20%) in comparison with Cd extraction (80%). The study also reveals that high leaching efficiency of both Y and Eu (around 90%) was achieved with even more diluted leaching solution (400 ml 0.05 M H_2SO_4, 60 ml of 30 v/v % H_2O_2) at 60 °C, L/S ratio 23 after 20 min of leaching. Zn and Cd extractions reached 20% and 55% respectively. Activation energy values calculated for Y and Eu leaching in the solution (400 ml 0.4 M H_2SO_4 with 60 ml of 30 v/v % H_2O_2) refer to diffusion mechanism in the range 40–80 °C (Ea = 14.85 kJ/mol and 16.47 kJ/mol respectively). In contrast, Ea values for Y and Eu leaching in the solution (400 ml 1 M H_2SO_4, 60 ml of 30 v/v % H_2O_2) suggest a mechanism change at the temperature around 40 °C. The leaching of Y as well as Eu up to 40 °C is controlled by diffusion and at higher temperatures by chemical reaction.

1. Introduction

Rare earth elements (REEs) belong among the deficient and strategic metals in the European Union (EU). Secondary raw materials containing REEs are basically the only sources available (aside from direct imports). Recycling of these sources is the most convenient and reasonable way to preserve REEs in Europe. Despite this fact, the EOL (end-of-life) recycling rate (functional recycling) for heavy REEs represents only about 8%, falling to 3% for light REEs (Communication from the Commission (COM), 2017). In the coming era the demand for REEs is expected to rise, namely for Tb, Dy, Pr, La, Eu, and Y (Schuler et al., 2011; Communication from the Commission (COM), 2008). There is no REEs mining in Europe, and the EU is dependent on raw materials and high-tech metals including REEs import. REEs belong among the 27 critical raw materials from the accessibility point of view in Europe (Communication from the Commission (COM), 2017). Phosphors from displays and lighting technologies also represent important REE resources from the recycling point of view, as well as for magnets and accumulators. Phosphors from spent screens/displays are categorized as hazardous waste in compliance with the European Catalogue (Commission decision 2000/532/EC, 2014) with waste type numbers 16 02 15 or 16 10 03 due to heavy metals presence (e. g. Zn, Cd, Pb). In accordance with the EU legislation, the storage of waste prior to recovery is possible for a period of three years or longer, and the storage of waste prior to disposal for a period of one year or longer given special permission (Directive 2008/98/EC, 2008). However, this waste mostly ends up in landfills despite its great economic, environmental as well as social potential. Since the introduction of flat-screen displays onto the market, sales of CRT displays have rapidly decreased in Europe. Chanceler et al. (2012) modelled the consequences of this technology change on the present and future waste streams. Although the market for CRT screens is going down rapidly, the amount of this waste available for recycling was constant until 2013 and has slowly been decreasing since then. Even so, in 2020 it will represent half the amount generated in 2012. At present time the number of obsolete cathode ray tube screens is still accumulating on the waste market and require an

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Table 1
Elemental composition of the phosphor sample from spent CRT screens.

Element	Y	Eu	Al	Si	S	Ca	Cd	Pb	Zn	Fe	C	RH*	LOI**
Content [wt%]	3.43	0.24	0.30	27.38	6.75	1.43	0.30	6.62	6.77	0.87	3.13	0.19	4.51

* RH - Relative humidity

** LOI - Loss on ignition (at 1000 °C)

appropriate solution. Walk (2009) proposed a method available for analysts' consideration of how the time lag between production and discard could impact recycling options.

Phosphor in CRT screens contains mainly ZnS and around 10% Y and 1.5% Eu. Red phosphor is mainly composed of $Y_2O_2S{:}Eu^{3+}$, green contains ZnS:Cu and blue ZnS:Ag. For example, in plasma panels phosphor occurs approximately eight-times more than in CRT (Gruber, 2009; Kochmanova et al., 2011). Pilot plant tests carried out by the company Safina, a.s. showed possibilities for REEs recovery by leaching in nitric acid followed by solvent extraction. The process was covered by patent (Gruber, 2006). Although some studies have been published in this field, many aspects of phosphor leaching from CRT are still unknown. Precise study of material composition and description of REEs and accompanying elements` behaviour during acid leaching with and without an oxidant is still awaited. Furthermore the influence of leaching parameters and process optimisation has not been presented sufficiently clearly. Resende and Morais (2010) examined CRT phosphor leaching in H_2SO_4 and HCl at temperatures 25–90 °C. Sulphuric acid appeared more effective and selective than hydrochloric acid. Leaching efficiency of the interest elements (mainly Y and Eu) was 96%. From this solution it is possible to recover Y by solvent extraction using for example D2EHPA (di-2-ethylhexylphosphoric acid) selectively. Tedjar et al. (2010) dealt with phosphor leaching in 2 N sulphuric acid at 70 °C. After pH adjustment this solution was mixed with an alkaline fluoride solution and heated to 50 °C to obtain precipitates of Y and Eu. Precipitates were washed with industrial water, the solid was suspended in soda solution and whitish precipitates were prepared. Innocenzi et al. (2013) describe the process of Y recovery from CRT phosphor by means of sulphuric acid leaching with hydrogen peroxide addition. Firstly, Zn was removed from the leaching solution and then Y was recovered by oxalate acid precipitation. Yttrium oxalate was calcined at 600 °C to obtain yttrium oxide. Resende and Morais (2015) used two steps of leaching for Y and Eu recovery from CRT screens. In the first step, the phosphor was leached in concentrated sulphuric acid followed by dynamic leaching in distilled water at room temperature. The efficiency of this process was 98% Y and 96% Eu in the leach liquor after 15 min of concentrated H_2SO_4 leaching and 1 h of distilled water leaching.

Stationary and mobile hydrometallurgical plants (HydroWEEE) for recovery of metals from wastes from electrical and electronic equipment (WEEE) were constructed in Italy for REEs recovery from powder from CRTs and fluorescent lamps and for other elements (In, Li, Au) from various WEEE. The steps carried out in these plants are powder leaching with acid, filtration, selective precipitation of elements, water treatment, removal of acid vapours and dust formed during plant operations (Altimari et al., 2014).

There are also other studies dealing with recovery of Y and Eu from another type of phosphor, for example from spent fluorescent lamps (Nakamura et al., 2007; De Michelis et al., 2011; Miskufova et al., 2013; Xie et al., 2014; Wu et al., 2014; Tunsu et al., 2014; Kochmanova et al., 2016), but the chemical and mainly phase composition of input materials are different and could not be fully compared.

This paper describes Y, Eu, Zn and Cd behaviour during leaching in sulphuric acid without and with an oxidant in more details. The study focuses on examination of the influence of temperature, initial acid concentration and oxidant dosage on the leaching efficiency of the selected REEs. In comparison with other studies, this research emphasizes more detailed leaching thermodynamics and kinetics especially in low acid concentration range with an oxidant, and the behaviour of accompanying hazardous elements is also investigated.

2. Materials and methods

2.1. Sample characterization

For the experimental part the sample of phosphor from cathode ray tube screens removed by dry method was used. This procedure could also have led to cross contamination of the experimental sample with amorphous silica glass containing Pb, Ba, Sr and other metals (Santos et al., 2017). The sample contained coarse-grained impurities (mostly glass) which were first sieved out on a sifter with size of 1 mm, and then the experiments continued with the fraction of phosphor below 1 mm. The sample was subjected to granularity assignment by dry sieving on sifters with mesh size of 1, 0.71, 0.4, 0.125, 0.09 and 0.063 mm. The majority of the phosphor sample (70 wt%) had grain size below 0.063 mm, whereby the wet laser method (sedimentograph Sympatec Helos) indicated that approximately 50 wt% of grains were even below 0.010 mm. The density of the sample measured with a pycnometer was 2.31 $g{\cdot}cm^{-3}$.

The content of elements in the phosphor sample was determined by means of atomic absorption spectroscopy (AAS) using Varian AA20+ spectrometer (Table 1). The amount of carbon was defined volumetrically.

The phase composition of the studied phosphor sample was analysed by X-ray diffraction phase analysis (XRD) using Phillips Xpert Pro (Co-Kα) diffractometer and identified by HighScore Plus software. The presence of the following phases was estimated: ZnS (cubic, JCPDS 03-065-1691), ZnS (rhombohedral, JCPDS 01-089-2199), ZnS (hexagonal, JCPDS 01-089-2174), SiO_2 (Quartz, JCPDS 01-081-0066 and 01-088-2487), Y_2O_2S (JCPDS 00-022-0993), $Y_4Al_2O_9$ (JCPDS 01-089-7002), $(Y_{0.964}Eu_{0.036})_2 0_2 S$ (JCPDS 00-052-1360), $Ca_3Al_2O_6$ (JCPDS 00-001-1051, CdS (JCPDS 01-080-0006) and PbS (JCPDS 00-005-0592) and with certain probability oxides of lead, barium and strontium which originated in glass. Fig. 1 shows the diffraction pattern of the input phosphor sample.

Along with the XRD phase analysis of the representative powder sample of phosphor, selected particles in the form of fine lustrous flakes, black fibres a few millimetres long and thin metal wires were also visually identified and then confirmed by XRD analysis. The analysis refers to the presence of elemental Al (from the light-reflecting coat), Fe thin wire, graphite fiber (Graphite, JCPDS 041-1487) and an amorphous substance most likely consisting of glass particle contaminants. Silicon oxide in crystalline form (Quartz, JCPDS 01-081-0066) could have originated from coatings on the screen in layers.

The sample was subjected to scanning electron microscopy (SEM) analysis along with Energy Dispersive Spectrometry (EDS). The analysis was carried out using a JEOL JSM-35CF with EDS analyser AN 10/85S fy LINK ANALYTICAL. From microstructure observation on the lowest enlargement it was possible to see that the morphology was miscellaneous and the material consisted of particles of different size and shape. Darker sharp particles with flat surface were identified as glass with content of Pb, Ba, Ca, K and Sr. Aluminum was present in its elemental form, visible as large-area, thin-walled, almost transparent units. Thin fibres found in the phosphor in the form of thin wires

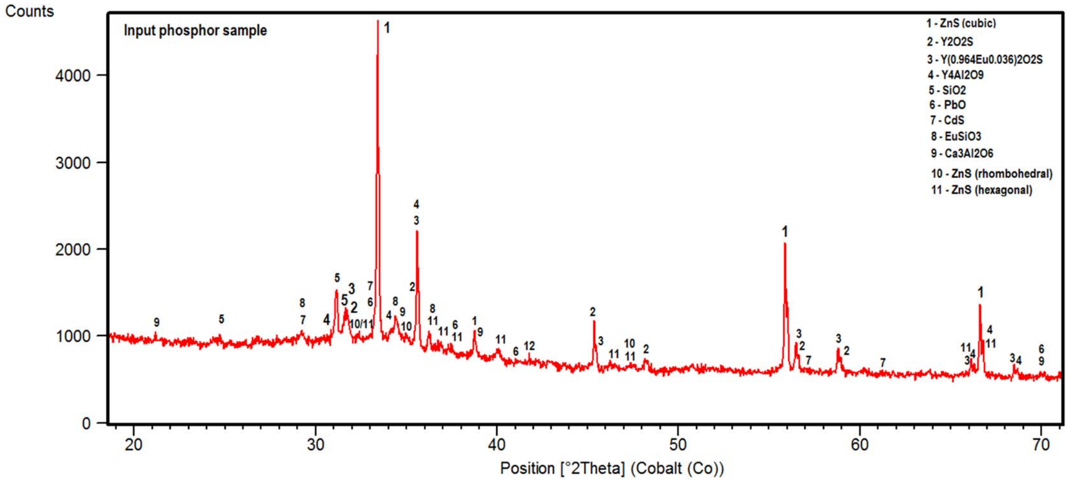

Fig. 1. XRD pattern of input phosphor sample (− 1 mm).

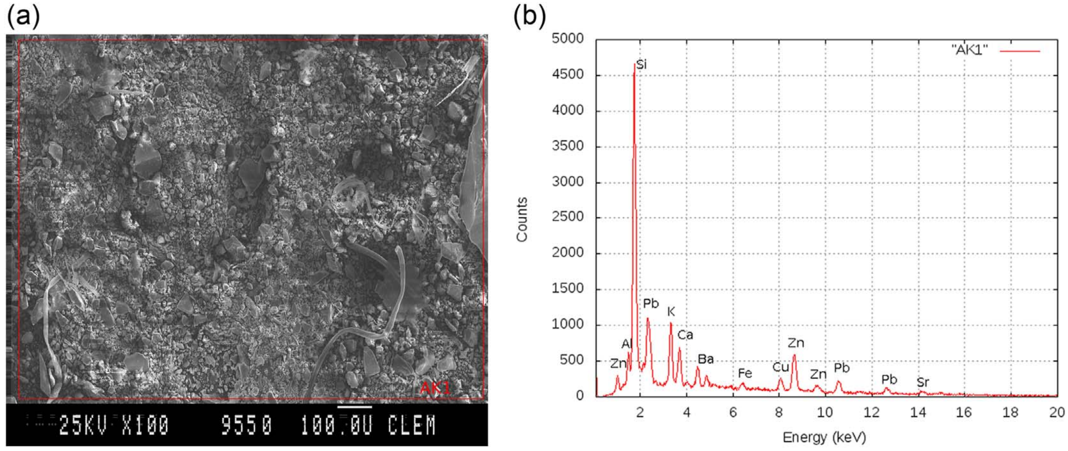

Fig. 2. a) SEM picture of phosphor and b) EDS spectra of the selected area (red area border).

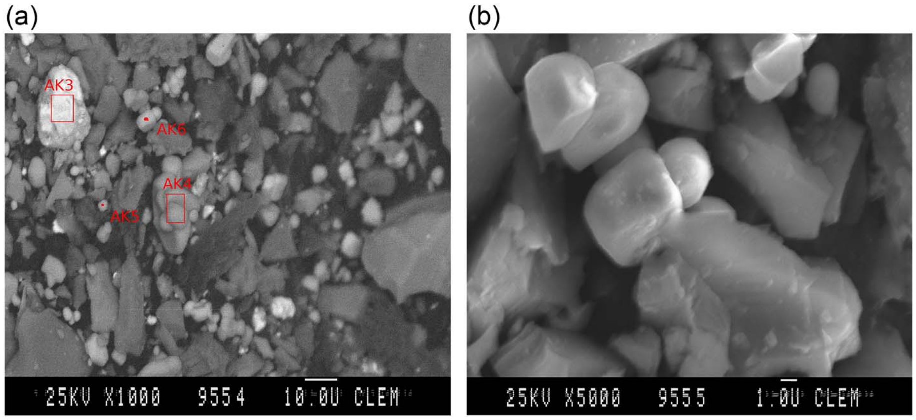

Fig. 3. a) SEM picture of phosphor sample at magnification 1000 ×; b) SEM picture of phosphor sample at 5000 ×.

consisted of Fe. From square EDS analysis (AK1) of the sample in Figs. 2–4 it was evident that the phosphor contained a major part of Si in the form of SiO_2 and the sample also contained Cu, Mn, Y, S. Eu and Cd were not identified in this EDS analysis probably due to their low content in the phosphor, but the elements were confirmed by AAS. The brightest particles (labelled as AK3) were formed by compounds of lead. ZnS created rounded particles and clusters of multiple "glued" particles with dark grey colour (AK4). Yttrium compounds (point AK5 and AK6) formed light pale grey grains.

2.2. Experimental methodology

In the experimental part the leaching behaviour of yttrium, europium and accompanying elements in the phosphor sample (Zn, Cd) in an acidic medium was studied. For leaching experiments a standard leaching apparatus was used. This consisted of a glass reactor with a stirrer inserted into a thermostatically controlled water bath. The sample (20 g) was poured into a leaching medium at the beginning of the experiment. At scheduled intervals liquid samples were taken and

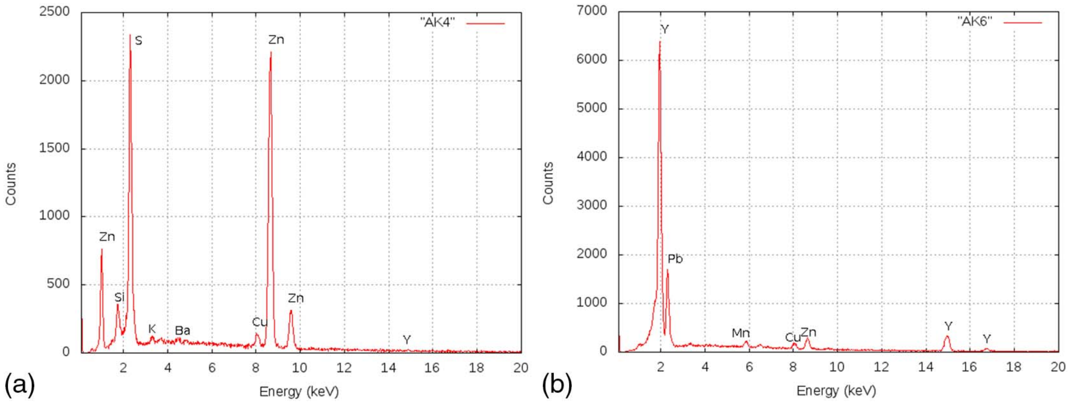

Fig. 4. EDS spectra of the selected spots (AK4 and AK6) seen through the SEM in Fig. 3a.

Table 2
Potential reactions of the phosphor phases and ΔG°_{298} values in the leaching system.

	Equations	ΔG°_{298} [kJ]
(1)	$Y_2O_3 + 3H_2SO_4 = Y_2(SO_4)_3(ia) + 3H_2O$	− 439.374
(2)	$Y_2S_3 + 4H_2SO_4 = Y_2(SO_4)_3(ia) + 4H_2O + 4S$	− 560.487
(3)	$Eu_2S_3(ia) + 4H_2SO_4 = Eu_2(SO_4)_3(ia) + 4H_2O + 4S$	− 681.837
(4)	$ZnS + 1.333H_2SO_4 = ZnSO_4(a) + 1.333H_2O + 1.333S$	− 102.853
(5)	$CdS + 1.333H_2SO_4 = CdSO_4(a) + 1.333H_2O + 1.333S$	− 73.357
(6)	$PbS + 1.333H_2SO_4 = PbSO_4 + 1.333S + 1.333H_2O$	− 112.903
(7)	$Y_2S_3 + 3H_2SO_4 = Y_2(SO_4)_3(ia) + 3H_2(g) + 3S$	− 301.839
(8)	$Eu_3S_4 + 4.5H_2SO_4 = 1.5Eu_2(SO_4)_3(ia) + 4.5H_2(g) + 4S$	− 522.989
(9)	$ZnS + H_2SO_4 = ZnSO_4(a) + H_2(g) + S$	− 16.455
(10)	$CdS + H_2SO_4 = CdSO_4(a) + S + H_2(g)$	+ 13.041
(11)	$PbS + H_2SO_4 = PbSO_4 + S + H_2(g)$	− 26.505
(12)	$ZnS + H_2SO_4 + 3H_2O_2(a) = ZnSO_4 + 4H_2O + SO_2(g)$	− 827.109
(13)	$Y_2S_3 + H_2SO_4 + 11H_2O_2(a) = Y_2(SO_4)_3(ia) + 12H_2O + SO_2(g)$	− 3353.976
(14)	$Eu_3S_4 + 1.5H_2SO_4 + 15.5H_2O_2(a) = 1.5Eu_2(SO_4)_3(ia) + 17H_2O + SO_2(g)$	− 4847.960
(15)	$CdS + H_2SO_4 + 3H_2O_2(a) = CdSO_4(a) + 4H_2O + SO_2(g)$	− 847.603
(16)	$PbS + H_2SO_4 + 3H_2O_2(a) = PbSO_4 + 4H_2O + SO_2(g)$	− 873.304

analysed for Y, Eu and other metals (Zn, Cd) by means of AAS. The resulting leaching efficiency values were corrected taking into account evaporation loss and sampling. The leaching efficiency "η" of metals was calculated using Eq. (1):

$$\eta = \frac{[m]t}{[m]o} \cdot 100\% \tag{1}$$

where $[m]o$ and $[m]t$ are respectively the metal content (in grams) in the input sample before leaching and the metal content leached out from the sample into the solution in the given time. Each experiment was repeated three times and leaching efficiency was calculated using arithmetic average values. The standard error of the mean was estimated to the value 8.39%. For the leaching experiments sulphuric acid (96 v/v % of analytical grade) and H_2O_2 (30 v/v %) as oxidant were used. The leaching liquor volume ranged from 400 to 500 ml, whereby the L/S ratio was 20–25 depending on the H_2O_2 dosage in the leaching solution. The experimental study monitored the influence of temperature in the range of 19–80 °C, the initial concentration of H_2SO_4 (0.05, 0.25, 0.4 and 1 M) with the constant volume of 400 ml used for leaching, and the oxidant dosage (0, 20, 40, 60, 80 and 100 ml of H_2O_2) on metal leaching efficiency. The content of oxidant in the individual leaching solutions represented 0, 1.5, 2.7, 3.9, 5 and 6 v/v % of the total volume in the final leachants (400–500 ml). The real concentration of the leaching solution used was then lower due to oxidant addition, and after recalculation it reached 0.04, 0.22, 0.35 and 0.87 M H_2SO_4. However, as the leaching solutions were prepared by means of mixing the diluted stock H_2SO_4 and H_2O_2 solutions (forming an original leaching agent), we preferred to use the expression "leaching solution" with the specification of concentration and volume of the sulphuric acid solution and oxidant dosage volume or "initial concentration" of the sulphuric acid solution in the text. The stirring rate was 200 rpm and leaching time was set to 120 min. After the experiment the leaching residue was washed and dried before being subjected to XRD qualitative phase analysis and morphology study using SEM-EDS.

3. Thermodynamic study

Before the leaching experiments a thermodynamic study was carried out in order to understand the principal behaviour of individual phases in the studied leaching systems. The thermodynamic study focused on mapping the progress of potential reactions and the presence of species in the leaching system under the given conditions. HSC Chemistry® 6.1 software (Roine, 2006) was used in this study. The most problematic aspects for detailed thermodynamic description and understanding of the heterogeneous system were the absence of thermodynamic data for some Y or Eu species or ions. For this reason Y and Eu sulphides served for description of the presumable chemical reactions instead of oxysulphides. The chemical reactions (reaction 1–11) which are likely to take place in the sulphuric acid medium are summarized together with values of ΔG°_{298} in Table 2.

The reactions of sulphides or oxides of the studied elements in the system (reactions 1–6) with generation of H_2O and S are more likely to proceed spontaneously to the right due to their negative standard Gibbs energy change value. However, without using the oxidant during leaching (represented by reactions 7–11), gaseous hydrogen sulphide is generated. H_2S (g) is formed according to reaction 17 where H_2 (g) reacts with elemental sulphur. Only the chemical reaction of CdS with H_2SO_4 (reaction 10) is non-spontaneous due to positive ΔG°_{298} value.

$$H_2(g) + S = H_2S(g) \qquad \Delta G^{\circ}_{298} = -33.323 \ \text{kJ} \tag{17}$$

When hydrogen peroxide is used for sulphide (or oxysulphide) leaching, water and SO_2 (g) could be produced according to chemical reactions 12–16. This should eliminate the formation of H_2S (g).

In the case that the reactants also produce solid intermediate products of sulphur, they can react with oxygen and water and create sulphuric acid according to reactions 18 and 19:

$$2H_2O_2(a) = 2H_2O + O_2(g) \qquad \Delta G^{\circ}_{298} = -206.377 \ \text{kJ} \tag{18}$$

$$S + 1.5O_2(g) + H_2O = H_2SO_4 \qquad \Delta G^{\circ}_{298} = -477.344 \ \text{kJ} \tag{19}$$

Lead sulphides and oxides can react in the studied system and form lead sulphates according to reactions 20 and 21.

$$PbS + 4H_2O_2(a) = PbSO_4 + 4H_2O \qquad \Delta G^{\circ}_{298} = -1129.17 \ \text{kJ} \tag{20}$$

$$PbO + H_2SO_4(a) = PbSO_4 + H_2O \qquad \Delta G^{\circ}_{298} = -171.61 \ \text{kJ} \tag{21}$$

When hydrogen peroxide is present in the leaching system with sulphuric acid, it leads to another reaction with the acid producing

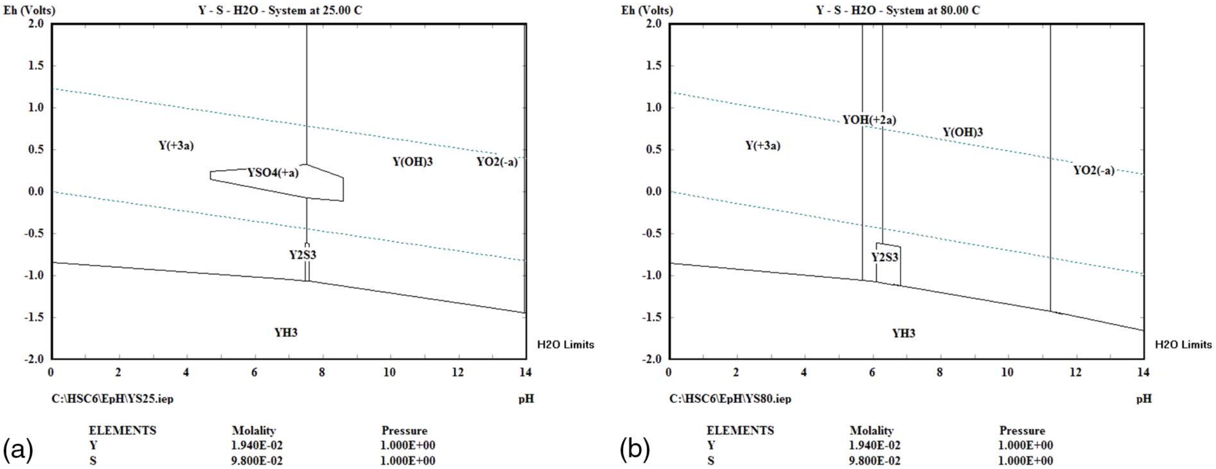

Fig. 5. Eh – pH diagrams of Y-S-H_2O system at $c_Y = 1.94 \cdot 10^{-2}$ mol/kg: a) 25 °C, b) 80 °C.

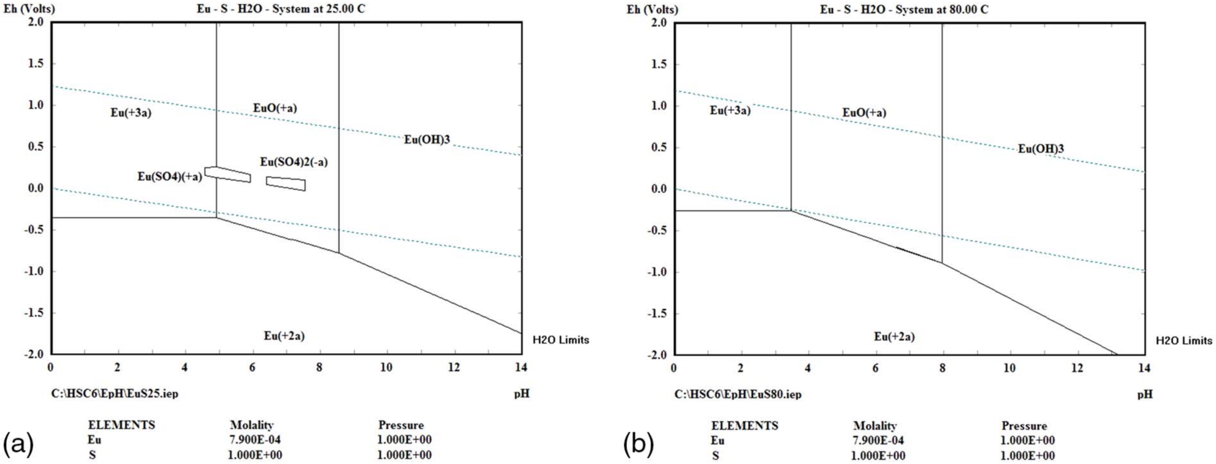

Fig. 6. Eh – pH diagrams of Eu-S-H_2O system at $c_{Eu} = 7.9 \cdot 10^{-4}$ mol/kg: a) 25 °C, b) 80 °C.

more aggressive peroxomonosulphuric acid (H_2SO_5), also known as Caro's acid (reaction 22). This fact should increase the efficiency of leaching metals from sulfidic and oxysulphide phases.

$$H_2O_2 + H_2SO_4 \rightleftharpoons H_2SO_5 + H_2O \tag{22}$$

The thermodynamic study implied that Zn and REEs from sulphides should be leached out in sulphuric acid without using an oxidant. However, for effective REE leaching from oxysulphides it is suitable to use an oxidizing medium. Thermodynamic results were also verified using experimental data obtained during a kinetic study of Y and Eu leaching efficiency, in both oxidizing and non-oxidizing media. Factors which could affect leaching kinetics of Y and Eu are mainly the formation of an intermediate phase of elemental sulphur (reactions 2–11), transformation of sulphur into hydrogen sulphide without the oxidant (reactions 7–11 and 17), or generation of sulphuric acid (reaction 19) in the oxidizing medium or generation of gaseous SO_2 (reactions 12–16).

Simultaneously, Eh – pH diagrams were calculated using HSC chemistry® 6.1 software, which is a suitable tool for determining the formation and stability of individual components, ions and species in studied solutions at various values of pH and redox potentials. The Eh-pH diagrams were constructed for systems Y-S-H_2O (Fig. 5), Eu-S-H_2O (Fig. 6), Zn-S-H_2O (Fig. 7) and Cd-S-H_2O (Fig. 8) at 25 and 80 °C under specific experimental conditions. Concentrations of metals were selected upon maximum concentrations of Y ($1.94 \cdot 10^{-2}$ mol/kg), Eu ($7.90 \cdot 10^{-4}$ mol/kg), Zn ($5.18 \cdot 10^{-2}$ mol/kg) and Cd ($1.33 \cdot 10^{-3}$ mol/kg) achievable in the leaching solution upon leaching with L/S ratio equal to 20.

Yttrium is leachable in an acid or strong alkaline environment as can be seen from the diagram in Fig. 5. Nevertheless, a higher temperature is evidently needed for leaching in an alkaline environment. In a very narrow range (pH = 13.8–14) Y is present in the $YO_2(-a)$ state at a temperature of 25 °C. This range is widens with increasing temperature. Y occurs in the stability region of water as + III ionic forms at 25 °C and molar concentration of $1.94 \cdot 10^{-2}$ mol/kg in the range of pH value from 0 to 7.5. With increasing leaching temperature the predominant area of Y^{3+} existence slightly shifts to the more acid area, and at 80 °C the pH boundary is around 5.5. At higher pH values over 7.5 and 6 at 20 °C and 80 °C respectively, yttrium hydroxide is present.

Yttrium exists at 25 °C in the pH range from 4 to 9 in the form of sulphate ions $YSO_4(+a)$ and $Y(SO_4)_2(-a)$. At 80 °C hydroxide ion YOH (+2a) is present and sulphate yttrium ion is absent. Change in the redox potential of the leaching media does not affect the ionic forms of Y in the stability region of water. Other forms of yttrium (sulphide and hydride) are present at both studied temperatures outside the stability region of water.

Fig. 6 presents Eh-pH diagrams of the system Eu-S-H_2O. Europium is stable in its ionic form at 25 °C up to pH = 8.5. In the pH range 4.5–8.5 Eu is present in the solution as EuO(+a) and in the form of sulphate ions. At 80 °C Eu is stable in its ionic form up to pH 8.0. Similar to yttrium, europium sulphate species disappeared in the system at a higher temperature. Europium hydroxide forms at higher pH values at both temperatures. Europium is present as the + II state out of the stability region of water.

Figs. 7 and 8 show Eh-pH diagrams of system Zn-S-H_2O and Cd-S-

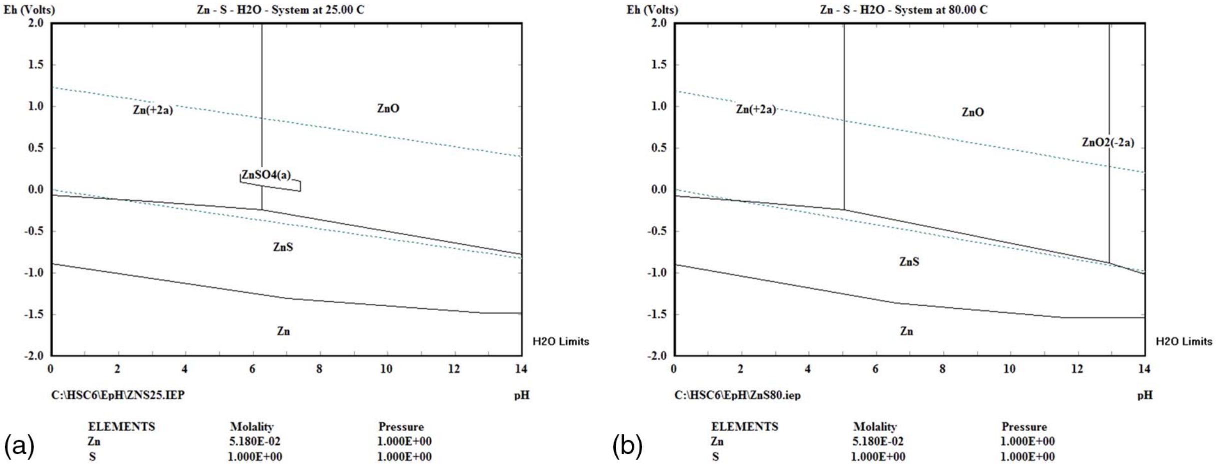

Fig. 7. Eh – pH diagrams of Zn-S-H_2O system at $c_{Zn} = 5.18 \cdot 10^{-2}$ mol/kg: a) 25 °C, b) 80 °C

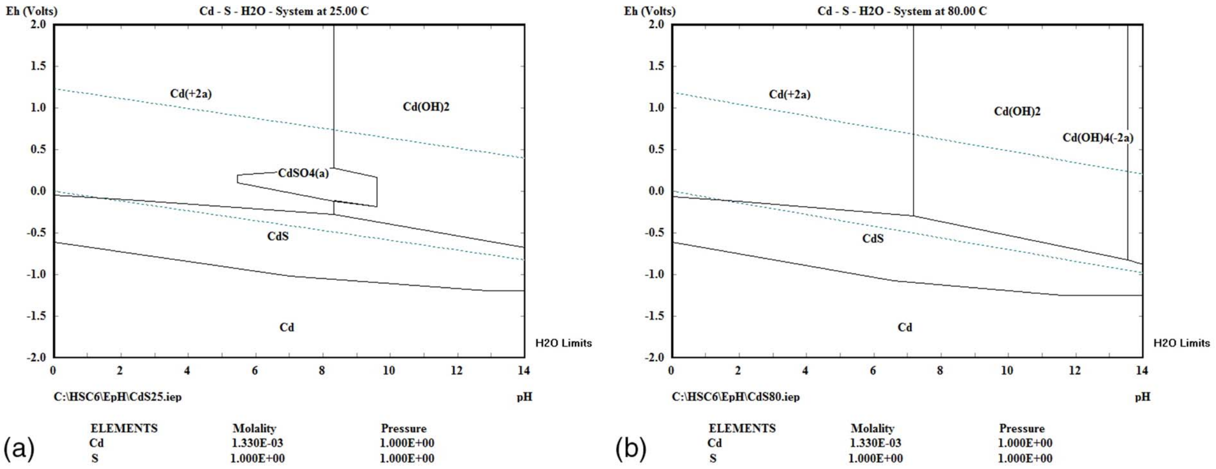

Fig. 8. Eh – pH diagrams of Cd-S-H_2O system at $c_{Cd} = 1.33 \cdot 10^{-3}$ mol/kg: a) 25 °C, b) 80°

H_2O at 25 and 80 °C respectively. Identically, at low temperatures the soluble sulphate phases ($ZnSO_4$ and $CdSO_4$) exist in both systems under the given conditions, but vanish at 80 °C. The anion species $ZnO_2(-2a)$ and $Cd(OH)_4(-2a)$ are present only at the higher temperature in the studied concentration regions.

4. Results and discussion

4.1. Non-oxidizing leaching of metals from phosphor

Based on the results presented by authors (Kochmanova et al., 2011) in different media (HNO_3, HCl, NaOH), it was decided that the process of retrieving Y into the solution was more effective in sulphuric acid, so this leaching medium was chosen as the proper one for this study. The first set of experiments focused on Y, Eu and Zn dissolution using sulphuric acid without the oxidant at temperatures of 60 and 80 °C and L/S = 20. It was desirable to verify first the leaching behaviour of these elements in sulphuric acid without oxidant in order to be able to evaluate the contribution of the oxidant itself to the leaching efficiency of REEs and other metals. The leaching efficiency of metals at both temperatures was very low (up to max. 9%). However, with increasing time (up to 120 min) even a small increase in leaching efficiency of Eu and Y was found (Figs. 9–10). Previous experiments by Kochmanova et al. (2011) and the leaching results in this study imply that increasing the temperature up to 80 °C for both used acid concentrations (0.25 and 0.4 M H_2SO_4) is not sufficient for effective Y and Eu dissolution. Also very low leaching efficiency of Y (< 7% after 60 min) was achieved through the use of 1 M sulphuric acid (Fig. 11), as well. Under the same conditions Cd exhibited the highest leachability of around 50%. However, the content of Cd in the phosphor is very low, representing around 0.088 g/l in the leaching liquor. Eu under these leaching conditions was not monitored because the same behaviour as Y was expected. Zn dissolution increased with rising concentration of sulphuric acid and the highest leaching efficiency of 10% was obtained in 1 M H_2SO_4 at 80 °C after leaching for 60 min. The extraction of Zn was more sensitive to acid concentration than to temperature in the studied range. On the other hand, Resende and Morais (2010) showed that by using more concentrated sulphuric acid solution (~3 M H_2SO_4) it was possible to achieve high leaching efficiencies (88–98%) even at low temperature (25 °C) and without oxidant depending on the solid to liquid ratio. Furthermore, the content of yttrium in their sample was at least five times higher than in the sample used in this study. It is necessary to note that non-oxidative leaching of this type of phosphor is accompanied with generation of toxic gaseous H_2S, making it unattractive as a practical recycling process, not only from the environmental point of view.

4.2. Oxidizing leaching of metals from phosphor

4.2.1. Influence of H_2O_2 dosage

Non-oxidizing leaching results lead to the conclusion that Y and Eu dissolution is inefficient under the given conditions (low acid concentrations), as well as being environmentally unfriendly. We therefore went on to perform further experiments under oxidizing conditions

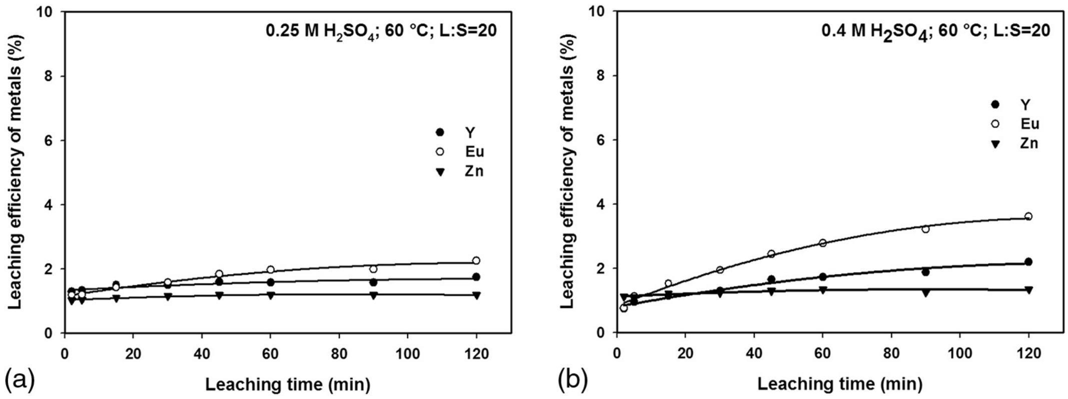

Fig. 9. Leaching of elements from phosphor in H_2SO_4 at 60 °C, L/S = 20: a) 0.25 M; b) 0.4 M.

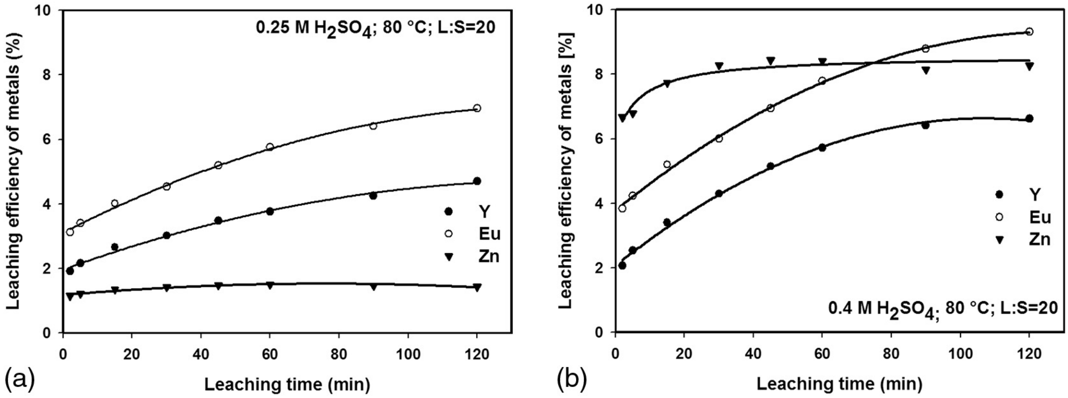

Fig. 10. Leaching of elements from phosphor in H_2SO_4 at 80 °C, L/S = 20: a) 0.25 M; b) 0.4 M.

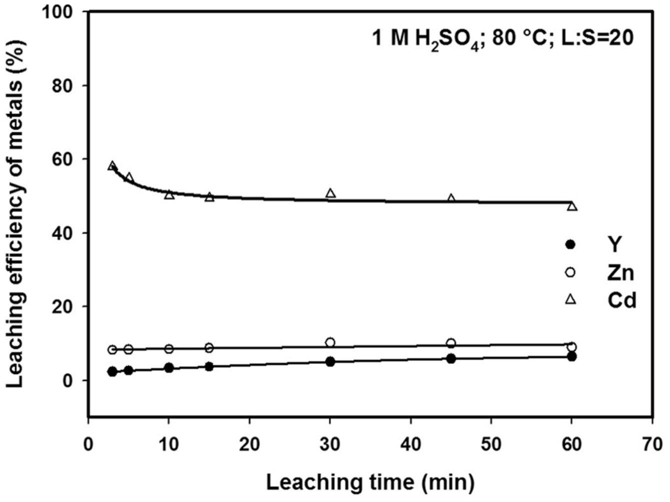

Fig. 11. Leaching of elements from phosphor in 1 M H_2SO_4 at 80 °C, L/S = 20.

using sulphuric acid with addition of hydrogen peroxide as the oxidant (30 v/v %). Preliminary leaching tests with use of the oxidant were carried out under the following conditions: L/S ratio = 20.5 (10 ml of 30 v/v % H_2O_2 was added to 400 ml 0.4 M H_2SO_4), temperature 80 °C, leaching time 10 min, stirring rate 200 rpm. These tests showed a strong positive effect on Y leaching. Around 20% of Y was leached out from the phosphor after 10 min. Additional tests were performed in order to optimize the sufficient volume of added oxidant at one selected initial acid concentration of 0.4 M H_2SO_4. The L/S ratio varied in the range of 21–25 depending on the H_2O_2 dosage (20–100 ml of 30 v/v % H_2O_2). The final real concentration of acid leaching solutions was slightly decreased due to the addition of a specific volume of oxidant and varied from 0.38 to 0.32 M H_2SO_4.

Y was completely leached out (Fig. 12) into the solution (400 ml of 0.4 M H_2SO_4 with dosage of 100 ml of 30 v/v % H_2O_2). In contrast, while the leaching efficiency of Eu also increased with the addition of H_2O_2, the efficiency achieved with 100 ml H_2O_2 was only 80%. Taking into account economic and environmental aspects, the content of H_2O_2 in the leaching solution 3.9 v/v % was chosen as being most appropriate. Moreover, it is assumed that with prolonged leaching time the leaching efficiency of Eu will increase, as well.

4.2.2. Influence of initial H_2SO_4 concentration

The influence of initial sulphuric acid concentration (with the same volume of 400 ml) on Y and Eu leaching efficiency in the presence of the identical H_2O_2 dosage (60 ml of 30 v/v % H_2O_2) at temperature 80 °C is shown in Fig. 13. Fig. 13a points out that the influence of sulphuric acid concentration on REEs dissolution under oxidizing conditions is not linear and the highest leaching efficiency of Y was obtained at initial concentrations 0.25 and 0.4 M H_2SO_4 at L/S ratio 23. The lowest leaching efficiency of Y at 1 M H_2SO_4 could be caused by different solubility of individual yttrium phases at various acid concentrations. Moreover, the solubility of yttrium sulphate decreased with temperature (7.3 g/100 g H_2O at 20 °C and 2.89 g/100 g H_2O at 80 °C (Gharib, 2012). This means that increased temperature promoted the precipitation of this compound. When dealing with Eu, the highest leaching efficiency was achieved through the use of 0.4 M H_2SO_4 after 10 min (Fig. 13b). One interesting fact was that the leaching efficiency of both Y and Eu was relatively high (85–90%) after 60 min in 0.05 M H_2SO_4 and stabilized during the whole leaching time. Kinetic curves also imply that leaching process is rather fast and maximum efficiency

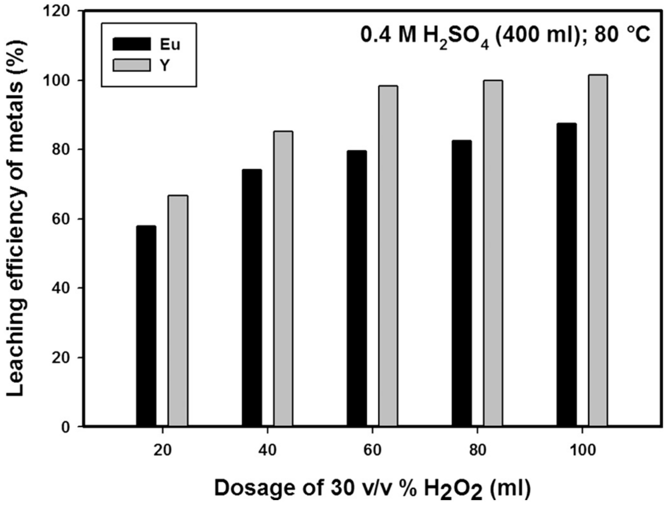

Fig. 12. Influence of H_2O_2 dosage (L/S = 21–25) in the leaching solution (400 ml 0.4 M H_2SO_4) on Y and Eu leaching efficiency (in 10 min of leaching).

is achieved already in 20 min. Such behaviour of REEs during leaching from phosphor has not been published so far and suggests the possible energy saving, though this will require further research as well.

4.2.3. *Influence of temperature*

In Figs. 14–17 the influence of temperature of 40 °C, 60 °C and 80 °C on the Y, Eu leaching at various initial concentrations of sulphuric acid solution (400 ml) is documented (0.05, 0.25, 0.4, 1 M) with the presence of hydrogen peroxide. Moreover, in the case of initial acid concentration 1 M H_2SO_4 the experiments were performed at room temperature. The H_2O_2 dosage was fixed to 60 ml of 30 v/v % H_2O_2, L/S ratio 23, leaching time 120 min and mixing speed 200 rpm. The aim was to find out if the temperature of 80 °C is optimal for both Y and Eu transfer into the solution and at the same time to identify the suitable initial concentration of used acid.

From the leaching results given in Figs. 14–17 followed that the temperature of 60 °C is also suitable for obtaining high leaching efficiencies (> 90%) of REEs in short time (in 20 min) especially in the case of leaching solution (400 ml 0.05 M H_2SO_4 and 60 ml 30 v/v% H_2O_2). The time of 60 min was needed for extraction of 90% of Y and 70% of Eu at 40 °C. The high leaching efficiency for Y and Eu is possible to achieve also in the leaching solution (400 ml 1 M H_2SO_4 and 60 ml 30 v/v % H_2O_2) at 80 °C. The results assume that the temperature and acid concentration are in strong relation. On the other hand, use of initial concentration 1 M H_2SO_4 is considered not to be suitable due to increased dissolution of Zn as well as from the economic and environmental points of view. This behaviour could be influenced by the heterogeneous character of the sample and the presence of various yttrium phases reacting differently in the leaching media, and the mutual influence of species created by leaching of other compounds such as ZnS, CdS, PbS.

Examination of the temperature influence on reaction kinetics (calculation of apparent activation energy, "Ea" using the Arrhenius equation; Eq. (2)) of yttrium and europium leaching from the phosphor indicated the diffusion mechanism in the temperature range 40–80 °C during leaching in the leaching solution 0.4 M H_2SO_4 (400 ml) with an oxidant addition (60 ml 30 v/v % H_2O_2).

$$k = A.\ exp\left(-\frac{Ea}{R\cdot T}\right) \tag{2}$$

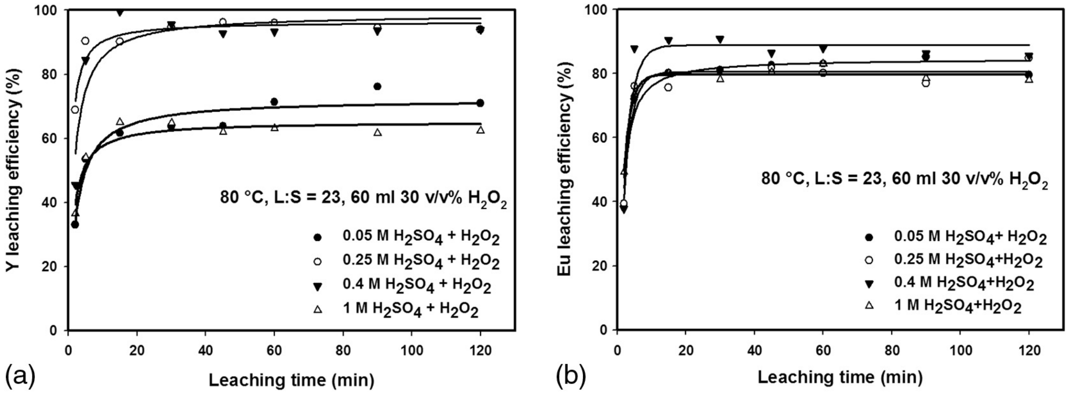

Fig. 13. Influence of initial H_2SO_4 concentration (400 ml) and leaching time on metals dissolution with H_2O_2 dosage (60 ml of 30 v/v %) at 80 °C: a) Y; b) Eu.

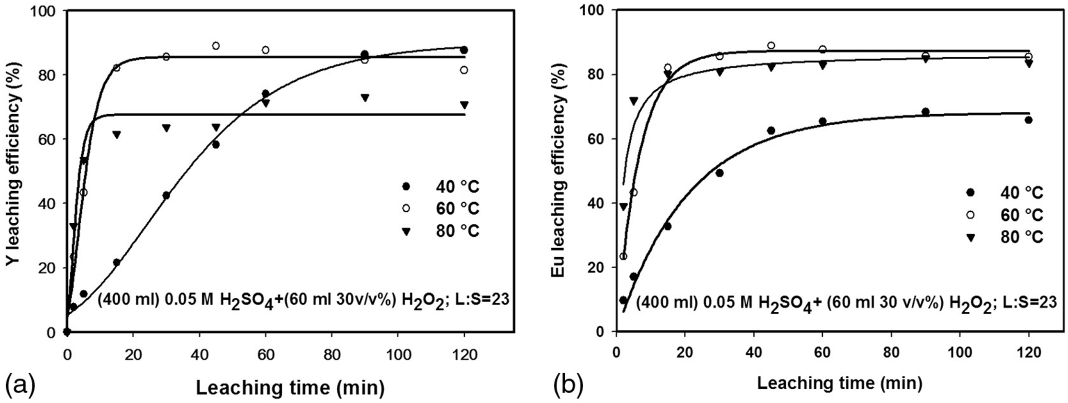

Fig. 14. Influence of temperature and leaching time in the leaching solution (400 ml 0.05 M H_2SO_4 + 60 ml 30 v/v % H_2O_2) on metals dissolution: a) Y; b) Eu.

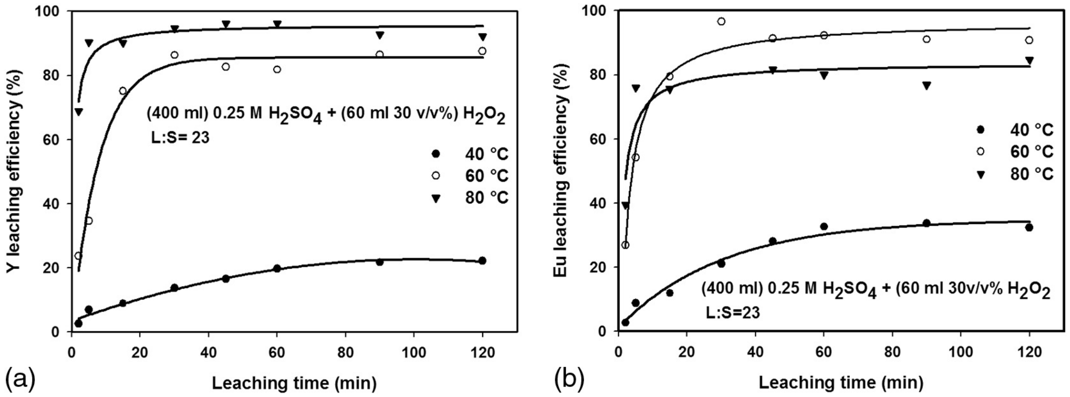

Fig. 15. Influence of temperature and leaching time in leaching solution (400 ml 0.25 M H_2SO_4 + 60 ml 30 v/v % H_2O_2) on metals dissolution: a) Y; b) Eu.

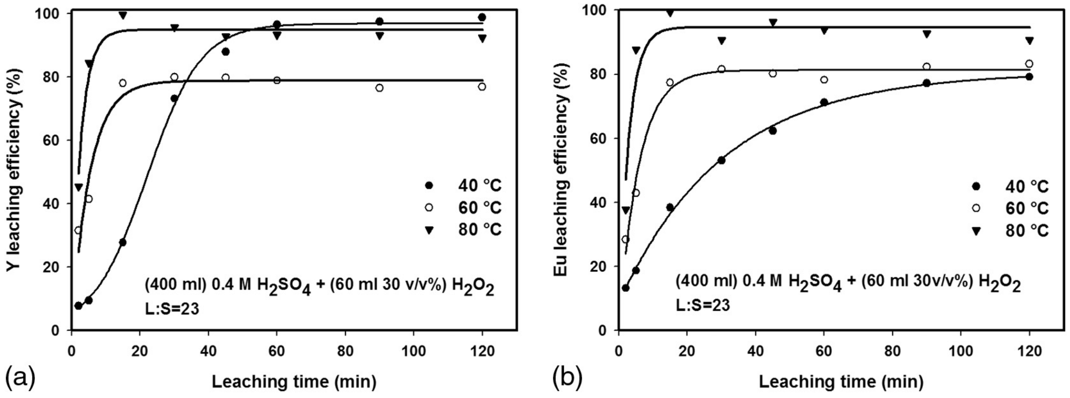

Fig. 16. Influence of temperature and leaching time in leaching solution (400 ml 0.4 M H_2SO_4 + 60 ml 30 v/v % H_2O_2) on metals dissolution: a) Y; b) Eu.

where k is the reaction rate constant, A is frequency factor, Ea is apparent activation energy (kJ/mol), R is a gas constant (8.314×10^{-3} kJ/mol/K), T is the absolute temperature (K).

The Ea values reached 14.85 kJ/mol and 16.47 kJ/mol, for Y and Eu respectively. On the other hand, during oxidizing leaching in the leaching solution (400 ml) 1 M H_2SO_4 with 60 ml 30 v/v % H_2O_2 the Ea values showed possible change in the mechanism of Y and Eu leaching in the temperature range 40–60 °C. The calculated Ea for Y and Eu leaching in that temperature range was 75 kJ/mol and 40.37 kJ/mol respectively, which suggested a chemical reaction as the rate controlling step. In contrast, in the temperature range of 19–40 °C the Ea values for Y and Eu leaching (6.34 kJ/mol and 9.46 kJ/mol) revealed a diffusion mechanism. At the higher temperature range 60–80 °C the Ea values showed a possible combined mechanism of leaching (20.15 kJ/mol and 24.68 kJ/mol for Y and Eu respectively). The leaching mechanism changes markedly depending on leaching conditions, confirming the complexity of the leaching system (solid-gas-liquid interface) as well as sample composition (various REEs and other metal phases) and its influence on the overall leaching process and mechanism. This also indicates the possible formation of solid intermediate products (sulphates) on the particle surface especially at the higher initial acid concentration and temperature (1 M H_2SO_4, 80 °C). At the same time, gas formation and diffusion through the product layer influences the overall kinetics of the process. These observations could then be utilized in further research and practice for adjusting the proper conditions for REEs leaching from this kind of phosphor. The temperature 19 °C was not sufficient, since Y and Eu leaching efficiency in the solution with initial acid concentration 1 M H_2SO_4 (with the H_2O_2

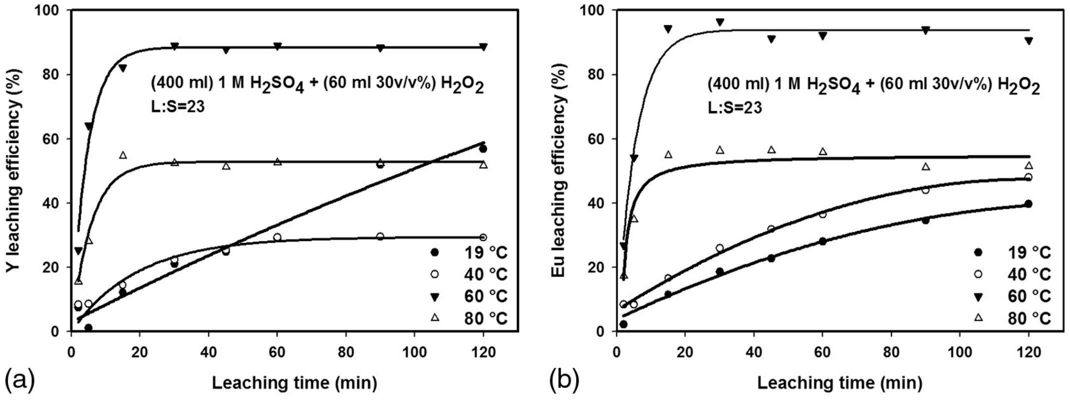

Fig. 17. Influence of temperature and leaching time in leaching solution (400 ml 1 M H_2SO_4 + 60 ml 30 v/v % H_2O_2) on metals dissolution: a) Y; b) Eu.

Table 3
Comparison of conditions and leaching efficiency from available studies.

Author	Conditions	Leaching efficiency
Resende and Morais (2010)	1500 g/kg sulphuric acid/sample ratio, 25 °C, 1.5 h, 20% of solids	> 96% Y and Eu
Tedjar et al. (2010)	2 N H_2SO_4, 70 °C, neutralization, fluoridation at 50 °C, hydroxylation	NA[a]
Innocenzi et al. (2013)	2 M H_2SO_4, 10% H_2O_2 (30 v/v %), 70 °C, 10% w/v pulp density	95–99% Y, 90% Zn
Resende and Morais (2015)	1. digestion: H_2SO_4 (98%), 1250 g/kg acid/sample ratio, 15 min., 25 °C, 2. leaching: distilled water, 1 hod., 25 °C, 10% solids	98% Y, 96% Eu
Miskufova et al. (2013)	(400 ml) 0.4 M H_2SO_4 + (60 ml) 30 v/v % H_2O_2, 80 °C, L/S = 23, 20 min	90–95% Y and Eu, 20% Zn, 80% Cd

[a] NA – not available.

content 3.9 v/v % in final leaching solution) attained only 60 and 40% after 120 min respectively. The available literature provides no comparative detailed study or data about the leaching behaviour of yttrium oxides, oxysulphides or sulphides in sulphuric acid. Table 3 compares the data between available studies reporting on the leaching of REEs from CRT phosphor and the results obtained in this work. Table 3 shows clearly that leaching of spent phosphor under conditions presented in this study (for REEs recovery) offers some advantages over other studies, namely decreasing of acid consumption, shorten the leaching time and partial hindering zinc leaching.

4.2.4. Leaching of accompanying elements

The leaching behaviour of other heavy metals (Zn, Cd) contained in the phosphor in selected leaching solutions (400 ml 0.05 M H_2SO_4 with 60 ml 30 v/v % H_2O_2; 60 °C) and (400 ml 0.4 M H_2SO_4 with 60 ml 30 v/v % H_2O_2; 80 °C) were monitored as well. Under these conditions the highest leaching efficiency for REEs was achieved. The results (Fig. 18) show that Cd was already leached in the leaching solution with low initial acid concentration (0.05 M H_2SO_4) and hydrogen peroxide presence at 60 °C (Fig. 18a). The leaching efficiency for Cd reached around 55% after 20 min. In the case of Zn dissolution, the efficiency was only 20% under the given conditions. When the initial sulphuric acid concentration was increased to 0.4 M at 80 °C the leaching efficiency of Cd increased too, to 80% after 20 min. The leaching of Zn under these conditions (Fig. 18b) was comparable to that obtained at lower sulphuric acid concentration (Fig. 18a). The experimental results showed that it is possible to partially hinder Zn leaching from the phosphor by selecting the appropriate leaching conditions, e.g. low initial concentration of sulphuric acid with the proper H_2O_2 dosage (up to 0.4 M H_2SO_4; the content of H_2O_2 in leaching solution 3.9 v/v %). Thermodynamic study (in Section 3) confirmed the obtained experimental results, and indicated that sulphuric acid in the presence of H_2O_2 would be predominantly consumed by REE sulphides (oxysulphides) in contrast to CdS and ZnS (reactions in the order $Eu_3S_4 > Y_2S_3 > CdS > ZnS$).

Table 4 presents the comparison of Zn leaching efficiency in different leaching solutions (400 ml of 0.05, 0.4 and 1 M H_2SO_4 with 60 ml of 30 v/v % H_2O_2) after 120 min of leaching at temperatures of 40, 60 and 80 °C. From Table 4 it is evident that the leaching efficiency of Zn is similar during oxidizing leaching with initial acid concentrations of 0.05 M and 0.4 M H_2SO_4 at all studied temperatures. Under these conditions the dissolution of Zn does not depend on the initial sulphuric acid concentration or the temperature. The critical temperature for maximum zinc dissolution was 60 °C and initial acid concentration 1 M H_2SO_4, when the Zn leaching efficiency doubled after 2 h.

4.2.5. Leaching residues characterization

Solid residues obtained after leaching of phosphor under optimal conditions (400 ml 0.4 M H_2SO_4 + 60 ml 30 v/v % H_2O_2 at 80 °C and 400 ml 0.05 M H_2SO_4 + 60 ml 30 v/v % H_2O_2 at 60 °C) were analysed using XRD and EDS to evaluate the efficiency of the process. Comparison of XRD patterns of leaching residues under optimal conditions and their analyses (Fig. 19) suggested the possibility of efficient leaching of Y_2O_2S and Eu doped phase $(Y_{0.964}Eu_{0.036})_2O_2S$ at low initial sulphuric acid concentrations. In the studied leaching residues diffraction peaks of residual phases $Y_4Al_2O_9$ and $EuSiO_3$ were also identified, indicating that Y and Eu were not easily leached from these more stable yttrium and europium phases under the given conditions. These assumptions were confirmed by the leaching efficiencies of those elements, which were < 100%. The XRD pattern in Fig. 19 also confirmed that Zn was present in the phosphor in three ZnS structures (cubic, rhombohedral, hexagonal). Zn is probably primarily leached from ZnS (cubic) and not from other ZnS structures as the XRD pattern analysis of leaching residue shown in Fig. 19 indicated. XRD pattern also showed possible presence of solid $PbSO_4$ and/or $(Ba_{0.4}Sr_{0.6})SO_4$. $PbSO_4$ could be formed by reaction of PbS or PbO present in the input material according to the reactions (20 – 21). Other components from glass, Ba and Sr oxide could react similarly, for example according to reactions 23–26.

$$BaO + H_2SO_4 = BaSO_4 + H_2O \qquad \Delta G^{\circ}_{298} = -374.832 \text{ kJ} \tag{23}$$

$$BaO + H_2SO_4 + 2H_2O_2(a) = BaSO_4 + 3H_2O + O_2(g) \qquad \Delta G^{\circ}_{298} = -581.209 \text{ kJ} \tag{24}$$

$$SrO + H_2SO_4 = SrSO_4 + H_2O \qquad \Delta G^{\circ}_{298} = -330.420 \text{ kJ} \tag{25}$$

$$SrO + H_2SO_4 + 2H_2O_2(a) = SrSO_4 + 3H_2O + O_2(g) \qquad \Delta G^{\circ}_{298} = -536.979 \text{ kJ} \tag{26}$$

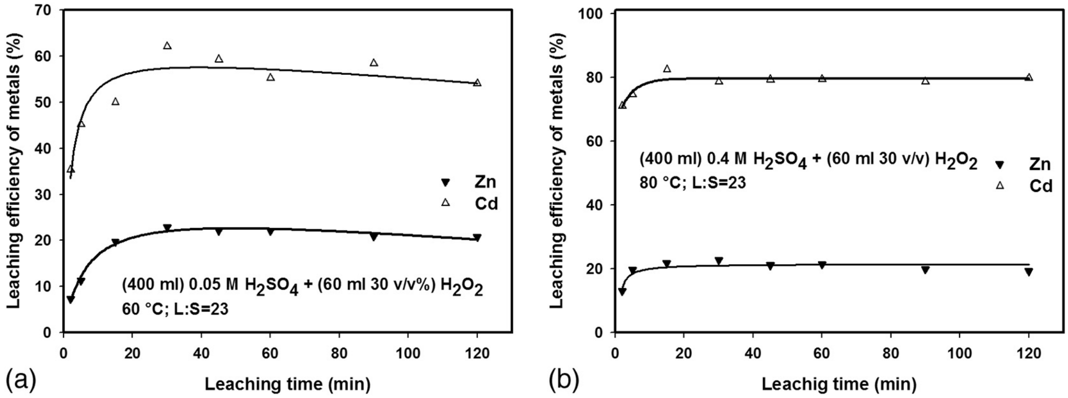

Fig. 18. Leaching efficiency of Cd and Zn in leaching solutions: a) 400 ml 0.05 M H_2SO_4 + 60 ml 30 v/v % H_2O_2, 60 °C; b) 400 m 0.4 M H_2SO_4 + 60 ml 30 v/v % H_2O_2, 80 °C.

Table 4
Zn leaching efficiency after 120 min of oxidizing leaching at selected temperatures.

Conditions		Zn leaching efficiency (%)
Leaching media	Temperature (°C)	
(400 ml) 0.05 M H_2SO_4 + (60 ml 30 v/v %) H_2O_2 L/S = 23	40	22.31
	60	20.74
	80	23.06
(400 ml) 0.4 M H_2SO_4 + (60 ml 30 v/v %) H_2O_2 L/S = 23	40	24.63
	60	22.25
	80	19.24
(400 ml) 1 M H_2SO_4 + (60 ml 30 v/v %) H_2O_2 L/S = 23	40	13.10
	60	44.64
	80	39.15

Another possible phase detected in the leaching residue (0.05 M H_2SO_4 + H_2O_2, 60 °C) was TiO_2, which could be present in the input sample as well (but it was not visible due to its low content, below the detection limit of XRD qualitative phase analysis). CdS was partially leached and its diffractions are visible in XRD pattern of the leaching residue in Fig. 19. SiO_2 was also present in the residue and it was not leached under the given conditions.

Fig. 20 shows a comparison of XRD patterns of the leaching residues obtained after oxidizing leaching at the lowest (0.05 M H_2SO_4) and the highest (1 M H_2SO_4) initial concentrations of sulphuric acid at 60 °C. The XRD patterns suggest that leaching of oxysulphide phases from the phosphor was effective under both selected conditions. In the case of leaching solution (400 ml 1 M H_2SO_4 + 60 ml 30 v/v % H_2O_2), the leaching of ZnS was more significant than with leaching solution (400 ml 0.05 M H_2SO_4 + 60 ml 30 v/v % H_2O_2) according to Fig. 20. Moreover, under the same conditions a higher amount of solid product $PbSO_4$ (resp. other sulphates of Ba, Sr) was formed.

Fig. 21 presents a comparison of XRD patterns of the leaching residues obtained upon leaching in 0.4 M H_2SO_4, at 80 °C without H_2O_2 and 400 ml 0.4 M H_2SO_4 + 60 ml 30 v/v % H_2O_2, 80 °C. The comparison of patterns in Fig. 21 suggests that leaching of yttrium phases without hydrogen peroxide is not significant. When oxidizing leaching is applied the XRD pattern refers to increased leaching efficiency of Zn sulphide compared to non-oxidizing leaching. At the same time the XRD pattern indicates that addition of hydrogen peroxide has no significant influence on sulphates formation. $Y_4Al_2O_9$ phase leaching should be more effective under non-oxidizing conditions ($Y_4Al_2O_9$ phase was still present in leaching residues after oxidizing leaching compared to non-oxidizing conditions).

Fig. 22 shows a comparison of SEM microstructure and morphology of grains from the phosphor input sample (Fig. 22a) and the leaching residue (Fig. 22b and c) after leaching under optimal conditions (400 ml 0.4 M H_2SO_4 + 60 ml 30 v/v % H_2O_2, 80 °C). Grains of the input sample were more sharp-edged and smooth whereas the grains in the leaching residue were rough and rounded, indicating that the surface of particles was attacked by leaching. Square EDS analysis of the leaching residue (Fig. 23a) indicated that Si, Zn and Pb were present in

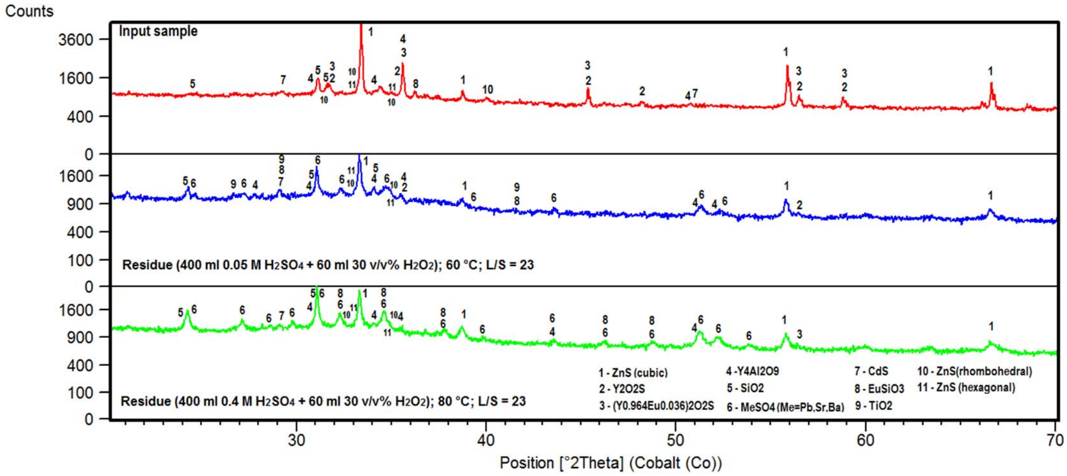

Fig. 19. XRD patterns comparison of input sample and leaching residues (400 ml 0.05 M H_2SO_4 + 60 ml 30 v/v % H_2O_2; 60 °C) and (400 ml 0.4 M H_2SO_4 + 60 ml 30 v/v % H_2O_2; 80 °C).

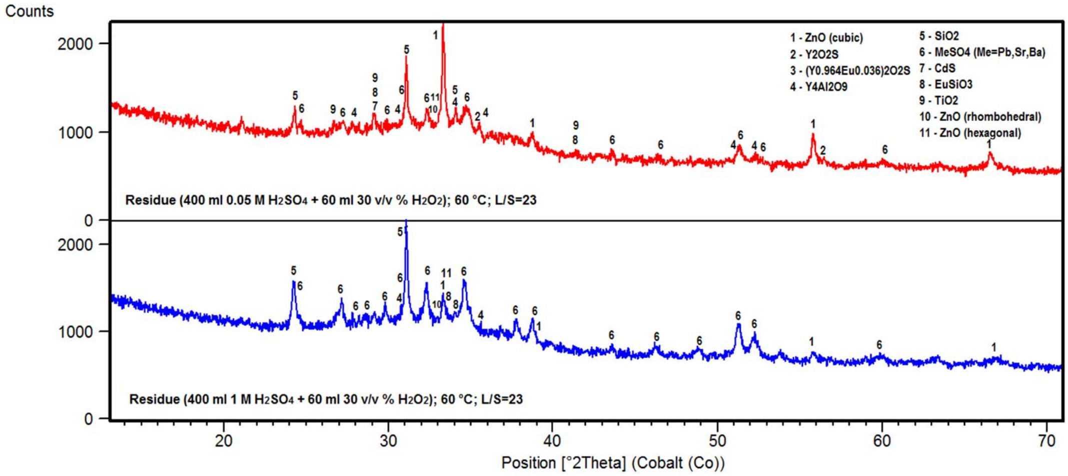

Fig. 20. XRD patterns of leaching residues (400 ml 0.05 M H_2SO_4 + 60 ml 30 v/v % H_2O_2) and (400 ml 1 M H_2SO_4 + 60 ml 30 v/v % H_2O_2); 60 °C.

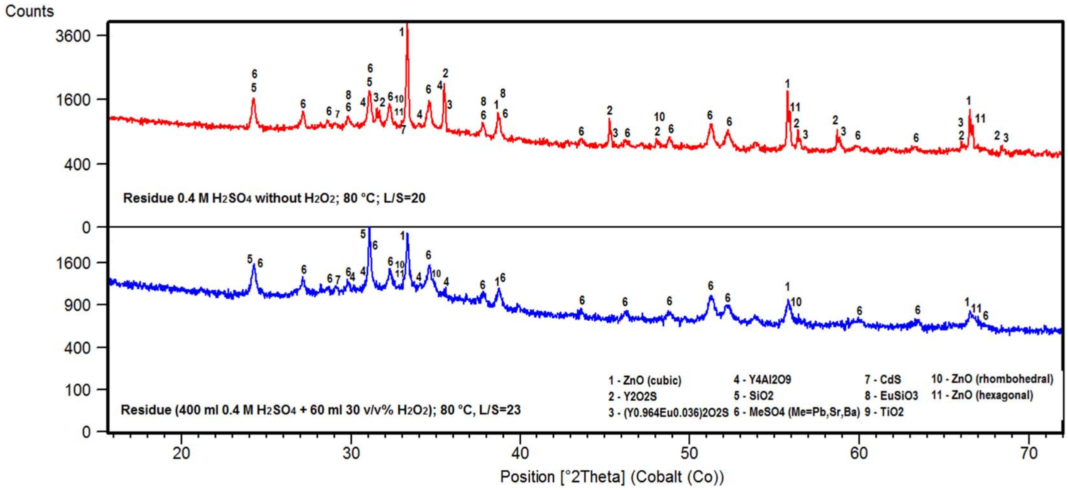

Fig. 21. XRD patterns of leaching residues leached in 0.4 M H_2SO_4 without H_2O_2 and with the H_2O_2 content (3.9 v/v %) at 80 °C.

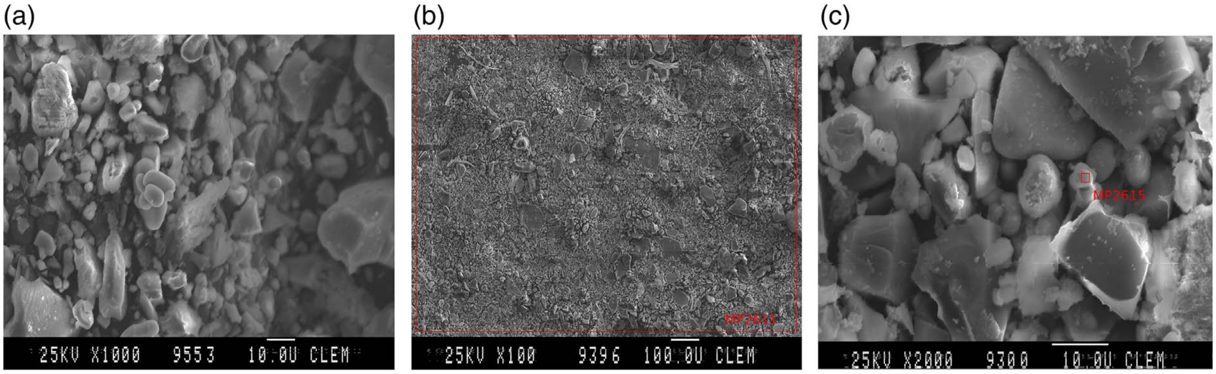

Fig. 22. SEM microstructure of samples: a) input; b) and c) leaching residue (400 ml 0.4 M H_2SO_4 + 60 ml 30 v/v % H_2O_2, 80 °C, L/S = 23, after 120 min).

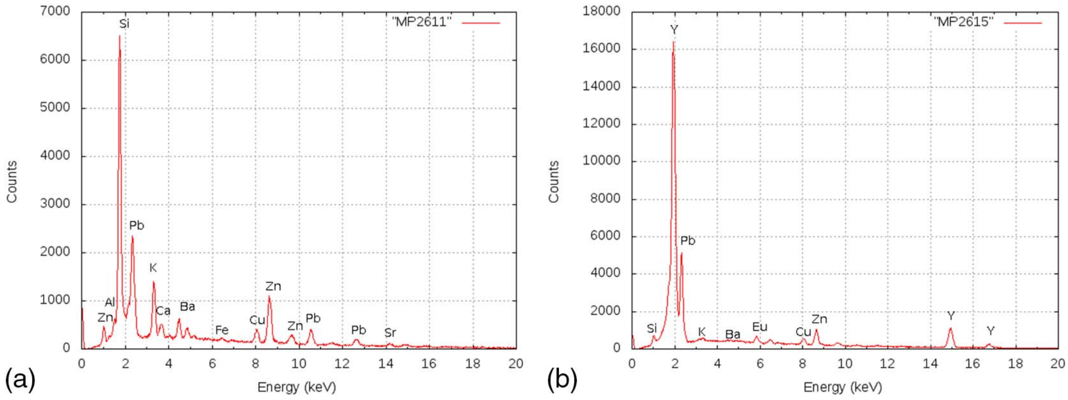

Fig. 23. EDS spectra of the leaching residue (400 ml 0.4 M H_2SO_4 + 60 ml 30 v/v % H_2O_2, 80 °C, L/S = 23, after 120 min): a) selected area of the leaching residue in Fig. 22b (area MP2611) b) selected particle of the leaching residue in Fig. 22c (MP2615).

the residue but Y and Eu were not identified. More detailed spot analysis of single phosphor particles (Fig. 23b) confirmed the presence of residual Y (MP2615). This was also confirmed by the leaching efficiencies, which were lower than 100% (Figs. 14a and 16a). Although EDS analysis (Fig. 23) did not verify the presence of sulphur in the leaching residue, from the XRD patterns (in Fig. 19) and the thermodynamic study it was evident that sulphate phases could be formed (reactions 6, 11, 16, 20–21, 23–26). In addition, part of Y (and Eu) could also precipitate in sulphate form after a longer period of leaching, especially at the lower L/S ratios.

5. Conclusion

The main aim of this work was to study and define the thermodynamic aspects and optimal conditions for Y, Eu and accompanying elements (namely Zn, Cd) leaching from phosphor coatings from obsolete screens in sulphuric acid media under non-oxidizing and oxidizing conditions. The results showed the following:

- XRD analysis of the input phosphor sample indicated the possible presence of three structures of ZnS, i.e. cubic, rhombohedral and hexagonal;

- Thermodynamic study showed that phosphor leaching in sulphuric acid without an oxidant led to elemental sulphur, $H_2(g)$ and subsequently $H_2S(g)$ formation, even though the formation of elemental sulphur and water was also probable;
- Thermodynamic calculations indicated that in the presence of H_2O_2 in the system $SO_2(g)$ could be formed. On the other hand, formation of H_2SO_4 as a semi-product was possible if elemental sulphur was created during leaching at the same time;
- Non-oxidizing leaching results showed very low extraction of Y and Eu after 2 h (up to 9% at 80 °C in 0.4 M H_2SO_4). Zn and Cd leaching efficiency after leaching in 1 M H_2SO_4 at 80 °C for 1 h was around 10% and 50% respectively;
- The high leaching efficiency of Y and Eu (~95%) is possible to achieve even at low acid concentration in the leaching solution (400 ml 0.4 M H_2SO_4 with 60 ml 30 v/v % H_2O_2 dosage) at 80 °C and L/S ratio 23 after 20 min. Zn leaching efficiency under these conditions was relatively low (20%). Cd achieved a higher leaching efficiency (80%), but the concentration in the leaching liquor represented only 0.12 g/l.
- The comparable leaching efficiency of Y and Eu (around 90%) was obtained in the leaching solution (400 ml 0.05 M H_2SO_4 and 60 ml 30 v/v % H_2O_2) at 60 °C under the same conditions. Zn and Cd leaching efficiency reached 20% and 55% respectively;
- Apparent activation energy values for Y and Eu leaching in the leaching solutions (400 ml 0.4 M H_2SO_4 with 60 ml 30 v/v % H_2O_2) in the temperature range 40–80 °C indicated diffusion as the rate controlling step. In contrast, at the higher initial acid concentration (1 M H_2SO_4) activation energy values suggested a leaching mechanism change (chemical reaction) for Y as well as Eu at temperatures above 40 °C.

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