



# Development of a solvometallurgical process for the separation of yttrium and europium by Cyanex 923 from ethylene glycol solutions



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## ABSTRACT

Recycling of critical raw materials such as rare-earth elements (REEs) is increasingly crucial in the development of a sustainable economy. Separation of individual REEs (mainly yttrium and europium) from lamp phosphor waste has become essential due to the substantial stockpiling of end-of-life fluorescent lamps. The mutual separation of Y(III) and Eu(III) from aqueous chloride solutions with solvating extractants by conventional extraction methods is highly inefficient. Hence, separation of Y(III) and Eu(III) was investigated using a novel technique called “non-aqueous solvent extraction”. Unlike conventional solvent extraction, the new approach uses two immiscible organic phases (more polar (MP) and less polar (LP)) instead of an aqueous and an organic phase. The present work describes a new solvometallurgical process for the separation of Y(III) and Eu(III) from ethylene glycol solutions using the solvating extractant Cyanex 923 in an aliphatic diluent. This extraction system exhibits improved separation compared to extraction from aqueous solutions. Following predictions based on a McCabe-Thiele diagram, a three-stage counter-current extraction simulation was carried out to extract Y(III) quantitatively, with 7% co-extraction of Eu(III) at a volume phase ratio of MP:LP of 1.5:1. The co-extracted Eu(III) was selectively scrubbed in two stages using an Y(III) scrub solution. Y(III) was recovered from the loaded less polar organic phase by precipitation stripping with an aqueous oxalic acid solution and a subsequent calcination step. Y<sub>2</sub>O<sub>3</sub> with a purity of more than 99.9% was obtained. A complete process flow sheet, comprising extraction, scrubbing and stripping steps for the separation of Y(III) and Eu(III) is reported. The feasibility of the developed process was successfully demonstrated in continuous mode using a battery of mixer-settlers.

## 1. Introduction

Rare-earth elements (REEs) play a key role in the development of green technologies. Due to the increasing demand and the supply risk of REEs, recovery of these valuable metals by urban mining has gained momentum [1,2]. Research efforts have been directed to reclaim REEs from end-of-life products such as fluorescent lamps, permanent magnets and NiMH batteries [1]. Lamp phosphor waste materials typically contain 20 wt% of REEs, including europium, yttrium, terbium, cerium and lanthanum [3]. There are different REE-containing phosphor materials present in fluorescent lamps: the red phosphor Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> (YOX), the blue phosphors BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> (BAM) and the green phosphors LaPO<sub>4</sub>:Ce<sup>3+</sup>,Tb<sup>3+</sup> (LAP), (Ce, Tb)MgAl<sub>11</sub>O<sub>19</sub> (CAT) or (Gd, Mg)B<sub>5</sub>O<sub>10</sub>:Ce<sup>3+</sup>,Tb<sup>3+</sup> (CBT). However, fluorescent lamps use is declining because of the increasing success of LED technology. It is estimated that around 25,000 tons of REEs will be available in the

stockpiled lamp phosphor waste by 2020 [1]. As a consequence, separating REEs from lamp phosphors is essential [4]. Investigating the separation of Y(III) and Eu(III) from the red lamp phosphor is interesting, since this phosphor has the highest intrinsic value.

The separation and recovery of REEs by hydrometallurgy involves leaching with aqueous solutions of acids and bases [5–10], solvent extraction with acidic, basic and solvating extractants [5,10–12] and precipitation with oxalic acid etc. process steps [5,8,13–15]. Unfortunately, the mutual separation of trivalent rare earths is difficult due to the fact that the separation factors between REEs are small because of their similar physical and chemical properties [10,16]. For instance, De Carolis et al. used the phosphonic acid extractant PC-88A to extract 91.6% of Y(III) and co-extracted 8.5% of Eu(III) [17]. Tunsu et al. developed a hydrometallurgical process for the recovery of REEs from fluorescent lamp phosphor waste fractions. A mixed REE oxide was obtained after extraction and stripping using 35 vol% Cyanex 923

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[18]. In a further study they achieved separation of yttrium and europium from aqueous chloride solutions in 10 stages, using a new organophosphorus chelating extractant, namely Cyanex 572, which is a mixture of phosphonic and phosphinic acids [19]. Innocenzi et al. showed that bis(2-ethylhexyl) phosphoric acid (D2EHPA) was superior for extraction and separation of yttrium over the other rare earths, compared to bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and Cyanex 572 from sulfate leach solutions at pH less than 1 [20].

However, hydrometallurgical separation processes for REEs usually require several tens of solvent extraction stages. Moreover, pH adjustment before solvent extraction and stripping of strongly complexed metals consumes substantial amounts of acids, generating large volumes of aqueous acidic waste streams that need to be treated [16,21]. To overcome these difficulties, research efforts have been directed to develop alternative technologies by replacing or modifying aqueous solutions with organic solvents in conventional solvent extraction, based on the different chemistry and behaviour of metal ions in non-aqueous solutions compared to aqueous solutions [22–25]. For instance, Hala carried out systematic studies on the extraction of metal ions from mixed organic-aqueous media using solvating extractants to evaluate the effect of water-miscible solvents on the extraction [26,27]. It was found that distribution ratios of yttrium were enhanced by the addition of alcohols to acidic aqueous solutions using the extractant tributyl phosphate (TBP) dissolved in benzene [26]. In another work, solvent extraction of Eu(III) with TBP, trioctylphosphine oxide (TOPO) and dioctylsulfoxide (DOSO) from mixed organic-aqueous media containing methanol, acetone, acetonitrile, ethylene glycol (EG), *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) was investigated [27]. These studies mainly focused on the water-miscible organic solvents with a maximum organic content of 40 to 50 vol%. In contrast, in non-aqueous solvent extraction, the feed phase contains (much) less than 50 vol% of water [23,24,28]. Hence, in non-aqueous solvent extraction, the traditionally used terms ‘aqueous’ and ‘organic’ phase are replaced by *more polar* (MP) and *less polar* (LP), respectively. There are few literature reports which make use of two immiscible organic phases for the solvent extraction studies of metal ions [28–30]. In our previous work, we described the potential of a non-aqueous solvent extraction system comprising EG and Cyanex 923 in *n*-dodecane as two immiscible organic phases that allowed to achieve higher separation factors than the corresponding aqueous systems. The extraction of heavy rare-earth elements (HREEs) was enhanced, while extraction of light rare-earth elements (LREEs) was suppressed by replacing water in the feed solution by EG [24,25]. EG is non-volatile, relatively inexpensive and has a low flammability. An additional advantage of EG is the possibility to produce it from renewable sources such as cellulose [31,32]. In the present work, application of the EG–Cyanex 923 non-aqueous solvent extraction system to the separation of trivalent yttrium and europium is reported. A feed solution simulating the fluorescent lamp waste composition was prepared by dissolving the respective chloride salts in EG solution. The feasibility of the non-aqueous solvent extraction process is demonstrated on a larger scale using a battery of mixer-settlers. This work shows that separation of rare earths is possible from chloride solutions by Cyanex 923, using non-aqueous media rather than aqueous ones. Moreover, for the first time, a process was developed for the separation of europium and yttrium using non-aqueous solvent extraction.

## 2. Experimental

### 2.1. Materials

Ethylene glycol (99.9%), propylene glycol (PG) ( $\geq 99\%$ ), poly (ethylene glycol) 200 (PEG 200) ( $> 99\%$ ) and methanol (99.99%) were purchased from Acros Organics NV (Geel, Belgium). 1-Decanol (99%) was supplied by Advocado Research Chemicals Ltd (Heysham, UK). Shell GTL solvent GS190 (GS190), a C10-C13 aliphatic diluent (normal

and *iso*-alkanes) with a boiling range of 187–218 °C, was provided by Shell (Rotterdam, The Netherlands). Cyanex 923 (93% trialkylphosphine oxides) was provided by Solvay (Toulouse, France).  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (99.9%),  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (99.8%) and oxalic acid were obtained from Sigma-Aldrich (Diegem, Belgium). Anhydrous lithium chloride (100%) was supplied by Fischer Scientific (Geel, Belgium). Hydrochloric acid (37%) and dimethyl sulfoxide (99.9%) were obtained from VWR Chemicals (Haasrode, Belgium). Methanesulfonic acid ( $\geq 99.5\%$ ) was purchased from Carl Roth GmbH Co. KG (Karlsruhe, Germany). Nitric acid (65%) and gallium standard ( $1000 \text{ mg L}^{-1}$ , in 2–5%  $\text{HNO}_3$ ) were supplied by Chem-Lab nv (Zedelgem, Belgium). The silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). The surfactant Triton X-100 was obtained from Merck KGaA (Darmstadt, Germany). All chemicals were used as received, without any further purification. For all dilutions, unless stated differently, Milli-Q water ( $0.055 \mu\text{S cm}^{-1}$ ) was used.

A feed solution of about  $11.1 \text{ g L}^{-1}$  Y(III),  $1.5 \text{ g L}^{-1}$  Eu(III) and  $2 \text{ mol L}^{-1}$  LiCl was prepared by dissolving the respective chloride salts in EG solution. The ratio of Y(III) and Eu(III) was representative to what is found in lamp phosphor waste. The viscosity of the feed solution at 25 °C was 76 mPa s and the water content was 1.54%. The LP solvent contained  $1 \text{ mol L}^{-1}$  Cyanex 923, and 10 vol% 1-decanol, diluted in GS190. 1-Decanol was added as phase modifier. Our previous results indicated that the addition of modifier is necessary to avoid third-phase formation [25]. The viscosity of the LP phase at 25 °C was 5.8 mPa s.

### 2.2. Instrumentation

The metal concentrations in the MP phase were measured in duplicate by total-reflection X-ray fluorescence (TXRF) on a Bruker S2 Picofox spectrometer, equipped with a molybdenum X-ray source and operated at a voltage of 50 kV. Mineralogical analysis of the precipitate and the rare-earth oxide was performed by a Bruker D2 PHASER XRD with Cu-K $\alpha$  X-ray radiation (30 kV; 10 mA). The step size increment was 0.02 (2 $\theta$ ) with 0.06 s/step. The raw data were processed both with the X'pert HighScore Plus PANalytical and EVA software with the ICDD database. Purity analysis of the oxalate and oxide fractions was done by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer Avio 500 spectrometer. The viscosity of the ethylene glycol feed solutions and the extractant phase was measured using an Anton Paar LOVIS 2000 M/ME rolling-ball viscometer. The determination of the water content of the feed solutions was performed using a C30S coulometric Karl Fischer titrator and HYDRANAL®-Coulomat AG analyte.

### 2.3. Batch-scale solvent extraction

The lab-scale, single-contact non-aqueous solvent extraction experiments were performed in 20 mL glass vials at room temperature, RT ( $20 \pm 2$  °C) with mechanical stirring (2mag MIX 15 eco model). Equal volumes of the two phases were mixed, i.e. either an aqueous solution as the MP and the LP containing Cyanex 923 for conventional solvent extraction or a non-aqueous MP and the LP containing Cyanex 923 for non-aqueous solvent extraction, except in the case variation of the phase ratio was needed. Once equilibrium was reached, phase separation was accelerated using an Eppendorf 5804 centrifuge, followed by separation of the two phases. The concentration of REEs in the raffinate was measured using TXRF after proper dilutions with diluted nitric acid and an aqueous solution of 5% Triton X100 surfactant. Addition of Triton X100 helps to form a homogeneous and flat sample layer on the quartz glass carrier [33]. A gallium standard solution was added to these samples as an internal standard. An aliquot of 2  $\mu\text{L}$  was placed on top of a quartz glass carrier, which was priorly pretreated with 30  $\mu\text{L}$  of a silicone solution in isopropanol and dried for 10 min at 60 °C. After drying for 30 min at 60 °C, each sample was subsequently analyzed for 300 s. Analysis was performed in duplicate. The concentration of the

metals in the LP phase were calculated using the mass balance.

The *distribution ratio* ( $D$ ) is expressed as the ratio of the concentration of the metal ion in the LP phase ( $C_{LP}$ ) to the concentration of the metal ion in the MP phase ( $C_{MP}$ ) at equilibrium:

$$D = \frac{C_{LP}}{C_{MP}} \quad (1)$$

The *percentage extraction* (% $E$ ) is the percentage of a certain metal ion extracted to the original metal amount in the feed. Using the definition of the distribution ratio, % $E$  can be defined as:

$$\%E = \frac{D}{D + V_{MP}/V_{LP}} \cdot 100 \quad (2)$$

With  $V_{MP}$  and  $V_{LP}$  the volume of the MP phase and LP phase (LP, i.e. Cyanex 923 in GS190), respectively. The separation factor ( $\alpha$ ) between Y(III) and Eu(III) can be defined as:

$$\alpha_{Y,Eu} = \frac{D_Y}{D_{Eu}} \quad (3)$$

#### 2.4. Counter-current extraction and scrubbing simulation

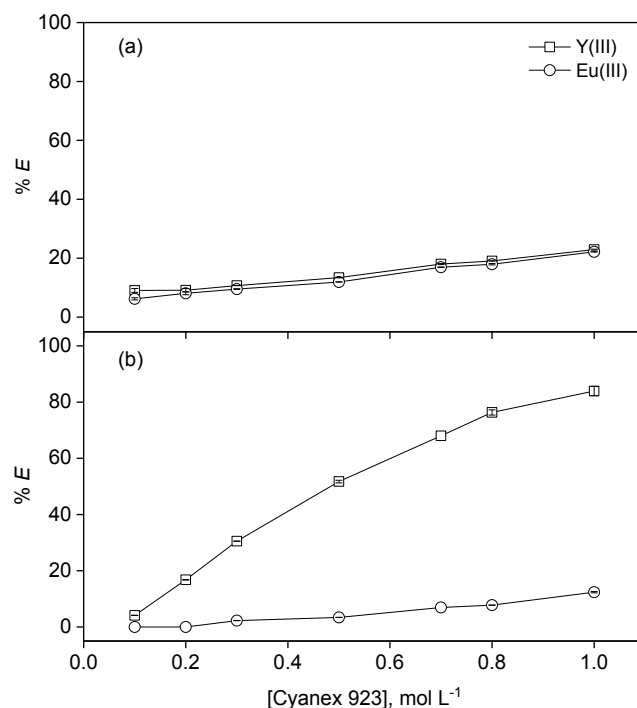
A batch simulation of a multistage solvent extraction experiment was performed to confirm the chosen parameters for this process [34]. A schematic overview of such a simulation for a three-stage counter-current extraction process, can be found in Fig. S1 (SI). A phase ratio MP:LP of 1 and 1.5:1 was tested. After three-stage contact, the loaded LP LO3 and LO4 and the MP raffinate R3 and R4 streams exiting the system were collected and analyzed for metal concentrations. An identical approach was chosen for the continuous counter-current scrubbing simulation [34]. Two different two-stage counter-current scrubbing experiments were simulated: 12.0 g L<sup>-1</sup> of Y(III) in EG scrub feed solution containing 1 and 2 mol L<sup>-1</sup> LiCl, MP:LP = 1:3.

#### 2.5. Continuous solvent extraction with mixer-settlers

Continuous experiments were performed in Rousselet PTFE lab-scale mixer-settler units of universal type (Model UX 1.1), having a mixer volume of 35 mL, a settler volume of 143 mL and a settler area of 49 cm<sup>2</sup>. In each settler, one baffle and two PTFE coalescence plates were present. Peristaltic pumps of the type Verderflex Vantage 3000P were used to pump the MP and LP phases. For the extraction, two extraction stages were used. The phase ratio was adjusted so that MP:LP = 1.5:1 in the settler. The flow rate of the MP phase was 2.4 mL min<sup>-1</sup>, while for the LP phase it was 1.6 mL min<sup>-1</sup>. For the continuous counter-current scrubbing experiment, two mixer-settler units were used with a fixed phase ratio of MP:LP = 1:3 in the settler. The flow rate of the MP phase was 1.5 mL min<sup>-1</sup>, while for the LP phase it was 4.5 mL min<sup>-1</sup>. Both the MP and LP phase were analyzed using TXRF. The loaded LP phase could be measured by diluting 20  $\mu$ L of the sample in ethanol.

#### 2.6. Recovery of yttrium(III) oxide

The scrubbed loaded LP phase was stripped with an aqueous oxalic acid solution, having a 1.2 times stoichiometric amount of oxalic acid with respect to Y(III) present in the LP phase. The MP:LP phase ratio was 1:1. Since a stable emulsion was formed at the liquid-liquid interphase after stirring for 0.5 h at RT, the experiment was repeated at 50 °C instead, resulting in better phase separation. The stripped LP phase was removed, following filtration of the REE oxalate precipitate. The precipitate was washed two times with 100 mL of ultrapure water and subsequently dried at 140 °C for 20 h. Calcination was carried out at 700 °C for 4 h in a muffle furnace.

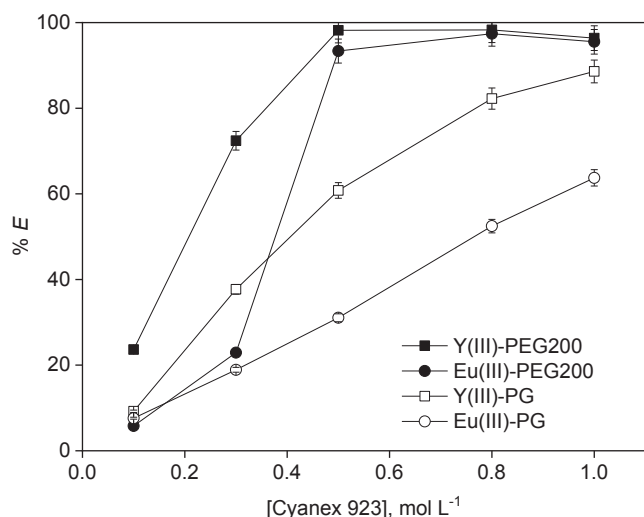


**Fig. 1.** Influence of the Cyanex 923 concentration on the separation of Y(III) and Eu(III) in (a) aqueous extraction and (b) non-aqueous extraction (EG). Conditions: volume MP:LP = 1:1, RT, 450 rpm, 1 h, [LiCl] = 2 mol L<sup>-1</sup>. Initial metal concentrations: [Y(III)]<sub>MP,H<sub>2</sub>O</sub> = 11.4 g L<sup>-1</sup>, [Eu(III)]<sub>MP,H<sub>2</sub>O</sub> = 1.4 g L<sup>-1</sup>, [Y(III)]<sub>MP,EG</sub> = 10.5 g L<sup>-1</sup>, [Eu(III)]<sub>MP,EG</sub> = 1.3 g L<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Comparison of aqueous and non-aqueous systems

The influence of the Cyanex 923 concentration on the extraction of Y and Eu was studied with EG feed solutions and aqueous feed solutions in order to assess the advantages of non-aqueous solvent extraction over conventional aqueous solvent extraction and the difference in extraction behaviour. The results are shown in Fig. 1. Two major differences between the aqueous and non-aqueous systems were observed. First, the percentage extraction of both Eu(III) and Y(III) is very low (< 25%) in the aqueous extraction system compared to the non-aqueous extraction system. Secondly, the extraction of europium is as efficient as the extraction of yttrium in aqueous environment. On the contrary, for non-aqueous extraction, the increase in extraction of yttrium is much higher than the increase in extraction of europium. These results show that the separation of Y from Eu is possible from EG solutions, while it is not possible from aqueous solutions. This is evident from the separation factors, presented in Table S1, i.e. 1.0 for aqueous systems, while it was 46 in EG systems extracted with 0.8 M of Cyanex 923. These data show that yttrium can be separated from europium from EG feed solutions, while it is not possible from aqueous feed solutions. These observations can be explained by the preference of the solvating extractant Cyanex 923 to extract the metals as metal cations coordinated to an anion (salt extraction). In aqueous solutions, the water molecules are strongly bonded to the REE and no chloride is present in the inner coordination sphere, which causes inefficient extraction from aqueous solutions. In addition, the solvent molecules coordinating to the REE have to be fully or partly replaced by Cyanex 923 molecules. This exchange is easier when using an ethylene glycol feed compared to the aqueous feed, since the energy required to remove the solvation sphere around the metal ion (solvation energy) is lower in the case of the ethylene glycol feed [35]. Secondly, Y(III) extracted more efficiently than Eu(III) from ethylene glycol feeds compared to aqueous feeds. This can be attributed



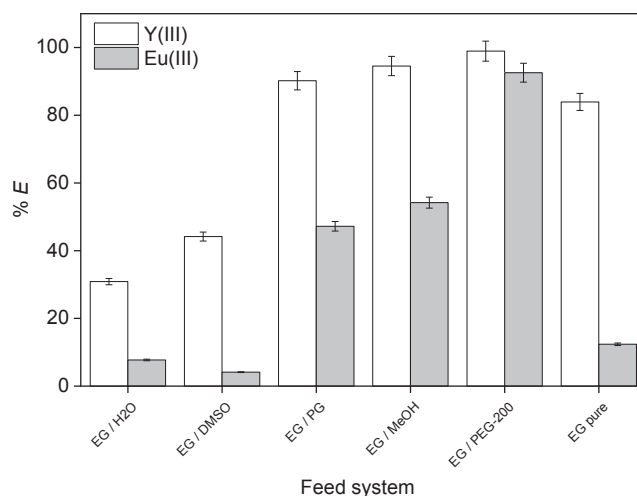
**Fig. 2.** Influence of the Cyanex 923 concentration on the separation of Y(III) and Eu(III) in PG and PEG200. Conditions: volume MP:LP = 1:1, room temperature, 450 rpm, 1 h, [LiCl] = 2 mol L<sup>-1</sup>. Initial metal concentrations: [Y(III)]<sub>MP,PG</sub> = 10.5 g L<sup>-1</sup>, [Eu(III)]<sub>MP,PG</sub> = 1.3 g L<sup>-1</sup>; [Y(III)]<sub>MP,PEG200</sub> = 11.6 g L<sup>-1</sup>, [Eu(III)]<sub>MP,PEG200</sub> = 1.6 g L<sup>-1</sup>.

the difference in charge density of REE ions: Y(III) have a smaller ionic radius and thus a higher charge density. Hence, the extractants bind Y(III) stronger, resulting in higher extraction efficiency. In the case of aqueous feed solution, this difference is less pronounced due to the poor extraction of both REEs from water with Cyanex 923.

The effect of Cyanex 923 on the extraction of Eu(III) and Y(III) was also studied from other polar phases, namely PG and PEG 200 (Fig. 2). For both the EG and PG systems, the percentage extraction of Y(III) increased with increasing Cyanex 923 concentration. Eventually, 88% of Y(III) was extracted in the case of the PG feed solution (84% for EG) at 1 mol L<sup>-1</sup> Cyanex 923. However, in the EG system, the co-extraction of Eu(III) was limited up to 0.8 mol L<sup>-1</sup> of Cyanex 923, whereas in the PG system already 50% of Eu(III) was co-extracted at the same concentration of Cyanex 923. This was also reflected in the separation factors, which were calculated to be 46 for EG and 4 for PG at a Cyanex 923 concentration of 0.8 mol L<sup>-1</sup> (Table S1). The extraction of LREEs from a PG solution is more efficient, eventually resulting in poor separation. In the case of PEG 200, a separation factor of only 1.4 was obtained at a Cyanex 923 concentration of 0.8 mol L<sup>-1</sup>. However, it is remarkable that at lower concentrations of Cyanex 923, the percentage extraction is already 72.4% for Y(III) and 22.9% for Eu(III), at 0.3 mol L<sup>-1</sup> of extractant. At this extractant concentration, the separation of both REEs from PEG 200 is optimal. Beyond 0.5 mol L<sup>-1</sup> of Cyanex 923, both Y(III) and Eu(III) are almost quantitatively extracted. The higher percentage extraction of both REEs from PEG 200 is possibly caused by the fact that PEG 200 can displace some water molecules in the primary sphere of the REE ion and wrap around the metal ion in a helical pattern [36].

### 3.2. Effect of polar co-solvents

The effect of polar co-solvents in the EG phase on the separation of Y(III) and Eu(III) was investigated for 1 mol L<sup>-1</sup> Cyanex 923. The addition of a co-solvent can influence the speciation and solvation of the REE ions, which might influence the separation factors and/or alter the extraction mechanism. In some cases, co-solvents can improve the mass transfer by lowering the viscosity. The following five co-solvents were tested, all in a 1:1 volume ratio with EG: (1) water, (2) methanol (MeOH), (3) PEG200, (4) dimethyl sulfoxide (DMSO) and (5) PG. The selected solvents were all fully miscible with the EG feed. As can be seen from Fig. 3, the addition of water and DMSO decreased the



**Fig. 3.** Influence of co-solvents in the EG feed system on the separation of Y(III) and Eu(III). Conditions: volume MP:LP = 1:1, EG:co-solvent = 1:1, room temperature, 600 rpm, 1 h, [Cyanex 923] = 1 mol L<sup>-1</sup>, [LiCl] = 2 mol L<sup>-1</sup>. Initial metal concentrations: [Y(III)]<sub>MP</sub> = 11.1 g L<sup>-1</sup>, [Eu(III)]<sub>MP</sub> = 1.5 g L<sup>-1</sup>.

percentage extraction of both Y(III) and Eu(III), while the addition of PG, MeOH and PEG200 increased the percentage extraction of both Y(III) and Eu(III).

It should be noted that the increase or decrease in the percentage extraction of both Y(III) and Eu(III) resulted in a decrease of the separation factors (Table S2). The difference in extraction among different mixed solvents can be correlated to different physical and chemical properties of the mixed feed solutions such as preferential solvation of the metal in one or the other solvent, Gutmann donor numbers, dielectric constants, the degree of salting-out effect and speciation. All these contribute to the extraction mechanism and thus to the percentage extraction of different REEs. Fundamental studies should be undertaken to gain more insight in the structure and speciation studies of rare-earth ion in mixed solvents, but this is beyond the scope of present study.

### 3.3. Influence of the LiCl concentration

A salting-out agent is an electrolyte containing the anion of the extractable species and a non-extractable cation, which aids in extraction by improving phase separation and/or the distribution ratio. In this case, LiCl was used because of its good solubility in EG [25]. The effect of the LiCl concentration on the extraction of Y(III) and Eu(III) was studied with a LiCl concentration varying between 0 and 4 mol L<sup>-1</sup> using 1 mol L<sup>-1</sup> Cyanex 923 (Fig. 4). As expected, the extraction of Y(III) and Eu(III) increased with increasing chloride concentration. The co-extraction of Eu(III) was negligible up to [LiCl] = 1 mol L<sup>-1</sup>, while the percentage extraction for Y(III) increased rapidly with increasing LiCl concentrations. Between [LiCl] = 2 mol L<sup>-1</sup> and 4 mol L<sup>-1</sup>, the Eu(III) percentage extraction increased at similar pace as it did for Y(III) between 0 and 2 mol L<sup>-1</sup>. Meanwhile, the percentage extraction approached 100% for Y(III) and 80% for Eu(III) at [LiCl] = 4 mol L<sup>-1</sup>. A LiCl concentration of 2 mol L<sup>-1</sup> was chosen as the optimal concentration for the further development of the process.

### 3.4. Influence of the MP:LP phase ratio

The effect of the more-polar-to-less-polar volume phase ratio on the extraction of Y(III) and Eu(III) from an EG feed solution containing 2 mol L<sup>-1</sup> LiCl was investigated with 1 mol L<sup>-1</sup> Cyanex 923 (Fig. 5). The MP:LP phase ratio was varied from 1:7 to 7:1. A McCabe-Thiele plot was constructed to determine the number of theoretical stages required

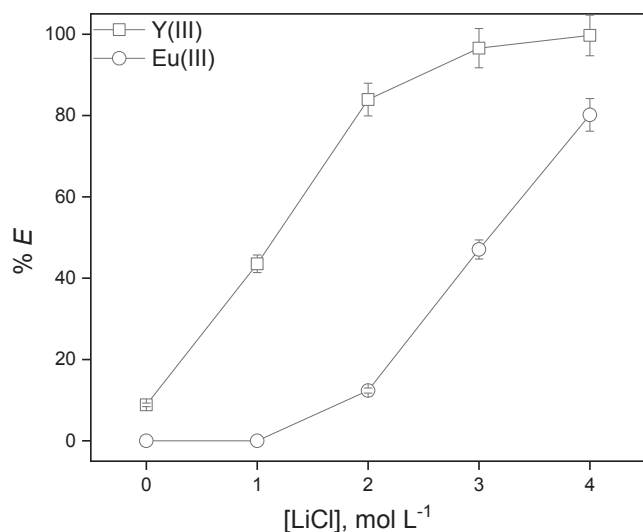


Fig. 4. Influence of the LiCl concentration on the separation of Y(III) and Eu(III) from EG feed. Conditions: volume MP:LP = 1:1, room temperature, 450 rpm, 1 h, [Cyanex 923] = 1 mol L<sup>-1</sup>. Initial metal concentrations: [Y(III)]<sub>MP</sub> = 11.1 g L<sup>-1</sup>, [Eu(III)]<sub>MP</sub> = 1.5 g L<sup>-1</sup>.

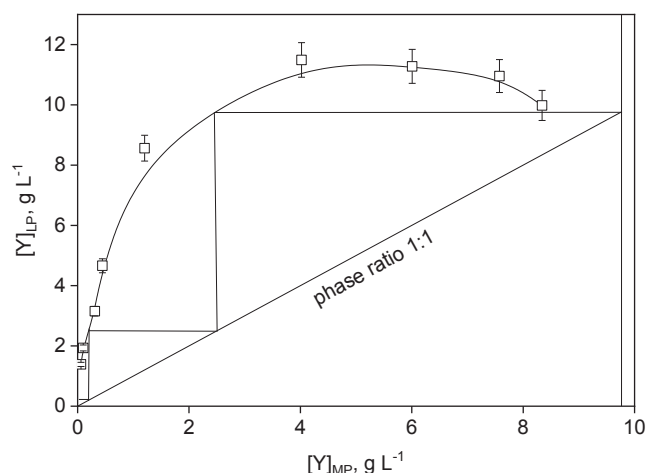


Fig. 5. McCabe-Thiele diagram for the extraction of Y(III) from EG (+LiCl) using Cyanex 923 diluted in GS190 Shell solvent. Conditions: room temperature, 600 rpm, 1 h, [Cyanex 923] = 1 mol L<sup>-1</sup>, [LiCl] = 2 mol L<sup>-1</sup>. Initial metal concentrations: [Y(III)]<sub>MP</sub> = 11.1 g L<sup>-1</sup>, [Eu(III)]<sub>MP</sub> = 1.5 g L<sup>-1</sup>.

for quantitative extraction of Y(III) at a selected MP:LP phase ratio. It was found that three counter-current stages are required to achieve quantitative extraction of Y(III) at a volume phase ratio of 1:1. There is still some co-extraction of Eu(III), indicating the necessity of scrubbing to remove the co-extracted Eu(III). A MP:LP phase ratio of 1:2 would result in two theoretical stages. However, two times the amount of LP phase is needed in this case, which is economically less interesting. Moreover, it would result in a less concentrated loaded LP phase. Finally, co-extraction of Eu(III) would increase, since more extractant would be available. Consequently, a volume phase ratio of 1:1 is considered to be optimal.

### 3.5. Counter-current extraction simulation studies

Based on the McCabe-Thiele diagram predictions, a three-stage counter-current extraction simulation (CCES) was carried out at a volume phase ratio of 1:1 with 1 mol L<sup>-1</sup> Cyanex 923 diluted in the aliphatic diluent GS190, containing 10 vol% 1-decanol. The EG feed solution contained 10.4 g L<sup>-1</sup> of Y(III), 1.3 g L<sup>-1</sup> of Eu(III) and 2 mol L<sup>-1</sup>

**Table 1**  
Results of the combined raffinate after the three-stage CCES.<sup>a</sup>

Phase ratio (MP:LP)	Raffinate (g L <sup>-1</sup> )		Loaded LP phase (g L <sup>-1</sup> )		%E	
	Y(III)	Eu(III)	Y(III)	Eu(III)	Y(III)	Eu(III)
1:1	0.0	0.5	10.4	0.9	100	63.3
1.5:1	0.07	1.3	17.3	0.1	99.4	7.0

<sup>a</sup> Conditions: room temperature, 450 rpm, 15 min, [Cyanex 923] = 1 mol L<sup>-1</sup>, [LiCl] = 2 mol L<sup>-1</sup>. Initial metal concentrations: [Y(III)]<sub>MP</sub> = 11.1 g L<sup>-1</sup>, [Eu(III)]<sub>MP</sub> = 1.5 g L<sup>-1</sup>.

LiCl. The results are presented in Table 1. As expected, when a volume phase ratio of 1:1 was used, the extraction percentage for Y(III) reached 100%. However, the co-extraction of Eu(III) was significant, attaining a value of 63%. The availability of an excess of Cyanex 923 extractant is most likely the reason for the significant co-extraction of Eu(III). Therefore, to minimize the co-extraction of Eu(III), the process was fine-tuned by increasing the MP:LP volume phase ratio to 1.5:1, which was tested in a second three-stage CCES. The analysis of the combined raffinate showed the presence of 0.07 g L<sup>-1</sup> of Y(III) and 1.3 g L<sup>-1</sup> of Eu(III), corresponding to a percentage extraction of 99.4% for Y(III) and 7% for Eu(III). Although the fine-tuning of the volume phase ratio already greatly reduced the co-extraction of Eu(III) from 63% to 7%, subsequent removal of Eu(III) by scrubbing is still necessary.

### 3.6. Scrubbing studies

Sufficient amount of loaded LP was generated (by mixing equal volumes of MP and LP in a single contact) to carry out the scrubbing studies in order to find the suitable scrubbing agent solution and to understand the scrubbing behaviour of Eu(III). Different EG-based scrubbing solutions were tested (Table 2). The volume phase ratio of these batch-scale scrubbing experiments was MP:LP = 1:3. Pure EG without added LiCl resulted in 100% scrubbing efficiency of Eu(III), but there was a significant loss of Y(III) (~46%), which is unacceptable. Increasing the LiCl concentration in the scrubbing solution decreased the scrubbing efficiency of Eu(III) and the loss of Y(III), due to the shift of the solvent extraction equilibrium towards the extracted metal complexes. In order to suppress the loss of Y(III) and to increase the scrubbing efficiency of Eu(III), the principle of the *crowding effect* of the LP was exploited by adding Y(III) to the scrubbing solution [37]. In this case, the loss of Y(III) was minimized, while it can be seen that the scrubbing efficiency of Eu(III) decreased with increasing LiCl concentration.

The use of Y(III) in the scrubbing solution over pure salt or acid solution had two advantages. First, the Eu(III) was selectively removed without any loss of loaded Y(III). Secondly, the scrub raffinate

**Table 2**  
Scrubbing of Eu(III) from loaded solvent ([Cyanex 923] = 1 mol L<sup>-1</sup>) using EG solutions.<sup>a</sup>

EG scrub solution	Scrub raffinate (g L <sup>-1</sup> )		Scrubbed LP phase (g L <sup>-1</sup> )		%Scrubbing	
	Y(III)	Eu(III)	Y(III)	Eu(III)	Y(III)	Eu(III)
0 M LiCl, Y	21.2	1.06	6.8	0.00	32.7	100
1 M LiCl, Y	9.2	0.73	10.6	0.00	–	99.2
2 M LiCl, Y	3.2	0.49	12.5	0.08	–	63.7
0 M LiCl, no Y	14.0	0.86	5.4	0.00	46.4	100
1 M LiCl, no Y	4.2	0.69	8.7	0.04	13.1	90.7
2 M LiCl, no Y	1.2	0.36	9.7	0.38	3.98	46.7

<sup>a</sup> Conditions: MP:LP = 1:3, room temperature, 600 rpm, 1 h. Initial metal concentrations: [Y(III)]<sub>MP</sub> = 10.5 – 11.3 g L<sup>-1</sup>, [Y(III)]<sub>LP</sub> = 10.1 g L<sup>-1</sup>, [Eu(III)]<sub>LP</sub> = 0.24 g L<sup>-1</sup>.

**Table 3**  
Analysis results of the combined raffinates after the two-stage CCSS.<sup>a</sup>

[LiCl]	Scrub raffinate (g L <sup>-1</sup> )		Scrubbed LP phase (g L <sup>-1</sup> )		%Scrubbing	
	Y(III)	Eu(III)	Y(III)	Eu(III)	Y(III)	Eu(III)
1 M	21.1	0.5	14.3	0.00	25.0	100
2 M	12.7	0.3	17.1	0.00	1.4	100

<sup>a</sup> Conditions: room temperature, 450 rpm, 15 min. Initial metal concentrations: [Y(III)]<sub>MP</sub> = 12.0 g L<sup>-1</sup>; [Y(III)]<sub>LP</sub> = 17.3 g L<sup>-1</sup>; [Eu(III)]<sub>LP</sub>, 1 M LiCl = 0.2 g L<sup>-1</sup>; [Eu(III)]<sub>LP</sub>, 2 M LiCl = 0.1 g L<sup>-1</sup>.

containing Eu(III) and Y(III) could be recycled back to the extraction feed. A two-stage counter-current scrubbing simulation (CCSS) was conducted using an EG feed solution containing 12 g L<sup>-1</sup> Y(III) and LiCl. The results indicated that 100% scrubbing of Eu(III) was achieved with a loss of 1% of Y(III) when using a Y(III)-scrub feed solution with 2 M LiCl (Table 3).

### 3.7. Stripping studies

Stripping studies were conducted to recover the loaded metal ions using different stripping agents. Aqueous hydrochloric acid (HCl<sub>aq</sub>), methanesulfonic acid (MSA) and oxalic acid solutions were tested (Table 4). A loaded LP phase containing 9.5 g L<sup>-1</sup> of Y(III) and 0.24 g L<sup>-1</sup> of Eu(III) was generated by single contact and used for this purpose. It was observed that stripping of Eu(III) was quantitative with HCl<sub>aq</sub> for all tested concentrations, while the stripping of Y(III) seemed to be difficult and reached a maximum of 84%. MSA efficiently stripped both Eu(III) (100%) and Y(III) (~97%) from the loaded organic phase. 100% precipitation stripping of both Y(III) and Eu(III) was achieved with a 1 mol L<sup>-1</sup> solution of oxalic acid in water. Oxalic acid dissolved in EG also efficiently stripped both REEs, but the REE oxalates were found to be soluble in the EG solution under the applied experimental conditions. Therefore, the precipitation stripping with an aqueous oxalic acid solution of 1 mol L<sup>-1</sup> was selected, since it is straightforward to subsequently obtain REE oxides by calcination of the corresponding REE oxalates.

### 3.8. Process flow sheet

A flow sheet for the process based on the counter-current solvent

**Table 4**  
Stripping of Y(III) from the loaded solvent ([Cyanex 923] = 1 mol L<sup>-1</sup>).<sup>a</sup>

Stripping agent	Concentration (mol L <sup>-1</sup> )	Strip raffinate (g L <sup>-1</sup> )		Stripped LP phase (g L <sup>-1</sup> )		%Stripping	
		Y(III)	Eu(III)	Y(III)	Eu(III)	Y(III)	Eu(III)
HCl	0.1	7.8	0.25	2.3	0.00	77.7	100
	0.5	8.4	0.26	1.7	0.00	83.7	100
	1	8.5	0.26	1.6	0.00	84.1	100
	2	8.4	0.27	1.7	0.00	82.9	100
	3	8.4	0.25	1.7	0.00	83.0	100
Oxalic acid in H <sub>2</sub> O	1	Ppt. <sup>b</sup>	Ppt. <sup>b</sup>	0.0	0.00	100.0	100
Oxalic acid in EG	0.1	7.2	0.24	2.3	0.01	76.3	97.9
MSA	0.5	7.5	0.29	2.0	0.00	79.2	100
	1	9.0	0.29	0.5	0.00	94.7	100
	1	9.1	0.29	0.2	0.00	96.5	100
	2	9.2	0.29	0.3	0.00	97.5	100

<sup>a</sup> Conditions: MP:LP = 1:1, room temperature, 600 rpm, 1 h. Initial metal concentrations: [Y(III)]<sub>LP</sub> = 9.5 g L<sup>-1</sup>, [Eu(III)]<sub>LP</sub> = 0.24 g L<sup>-1</sup>.

<sup>b</sup> Ppt. = REE oxalate precipitate.

extraction simulations is presented in Fig. 6. Y(III) could be extracted in a three-stage counter-current process using a LP phase containing 1 mol L<sup>-1</sup> Cyanex 923 + 10 vol% 1-decanol in GS190 diluent. The volume phase ratio was MP:LP = 1.5:1. The limited amount of co-extracted Eu(III) was removed by a two-stage counter-current scrubbing procedure, using an EG solution containing Y(III) and LiCl. The scrub raffinate could be recycled back to the extraction feed. The feasibility of both non-aqueous extraction and scrubbing (both two stages) was demonstrated by lab-scale mixer-settlers. Y(III) was stripped from the loaded LP phase by an aqueous solution of oxalic acid (1.2 times stoichiometric amount) to recover Y<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>, followed by 4 h of calcination at 700 °C to ensure complete conversion to Y<sub>2</sub>O<sub>3</sub>. Subsequently, the regenerated LP phase can be reused in the extraction stages. Previous studies already demonstrated the recyclability and good stability of this system [25]. McCabe-Thiele analysis showed that Eu(III) can be recovered in four stages from the raffinate (Fig. S2). The metal-depleted extraction raffinate (EG + 2 mol L<sup>-1</sup> LiCl) can be reused to prepare the extraction feed in the next cycle. It should be noted here that the distribution of EG and LiCl to the less-polar phase and the distribution of Cyanex 923 to the more-polar phase should be taken into account for the reuse in the next cycles. However, the mutual solubilities of EG and Cyanex 923 are very limited and comparable with aqueous solvent extraction conditions [25].

### 3.9. Mixer-settler experiments

In order to test the feasibility of working in continuous mode, the extraction process was tested in lab-scale mixer-settlers. The recycle of scrub raffinate was not considered here. The composition of the MP and LP phase, the scrubbing agent, the volume phase ratio and the theoretical number of stages were determined. In a scope test, two extraction units were used. During the experiment, the extraction behavior of Y(III) and Eu(III) was tracked by taking a sample of the MP and LP phase every 30 min from each extraction chamber. After about two hours of operation, equilibrium was reached, after which the system remained stable over time, with only minor variations in the metal concentrations. No precipitation or third-phase formation was observed during the entire operation. As a result, Fig. 7 shows the concentration profile of Y(III) and Eu(III) across the mixer-settler battery. Although only a two-stage extraction was performed, already 97.3% of Y(III) was extracted. Co-extraction of Eu(III) was limited to 13.1%, which was subsequently completely removed from the loaded LP phase after the two scrubbing stages. A small amount of Y(III) (0.1 g L<sup>-1</sup>) was extracted from the scrub feed to the loaded LP phase. The final loaded LP phase exiting the mixer-settlers had a purity of Y(III) of 99.9%.

### 3.10. Recovery of yttrium(III) oxide

After the continuous scrubbing experiment, the loaded LP phase contained 17.7 g L<sup>-1</sup> of Y(III). Precipitation stripping was performed using 1.2 times stoichiometric amount of oxalic acid with respect to Y(III) by addition of a 0.364 mol L<sup>-1</sup> aqueous solution in a 1:1 vol phase ratio. TXRF analysis of the LP phase confirmed complete stripping. After the recovered oxalate residue was filtrated and dried, it was calcined at 700 °C for 4 h. The oxalate residue was determined to be fully converted into Y<sub>2</sub>O<sub>3</sub>, based on the XRD diffractogram (Fig. 8). The purity was determined by ICP and corresponded to 99.92% Y(III) (RSD = 3.5%) and 0.08% Eu(III) (RSD = 2.9%).

## 4. Conclusions

A solvometallurgical process for the separation of Y(III) and Eu(III) from EG solutions using the extractant Cyanex 923 was developed. This separation is relevant to the recycling of rare earths from fluorescent phosphor powder waste. Y(III) was selectively extracted with minimum co-extraction of Eu(III) using 1 mol L<sup>-1</sup> Cyanex 923 from EG + LiCl

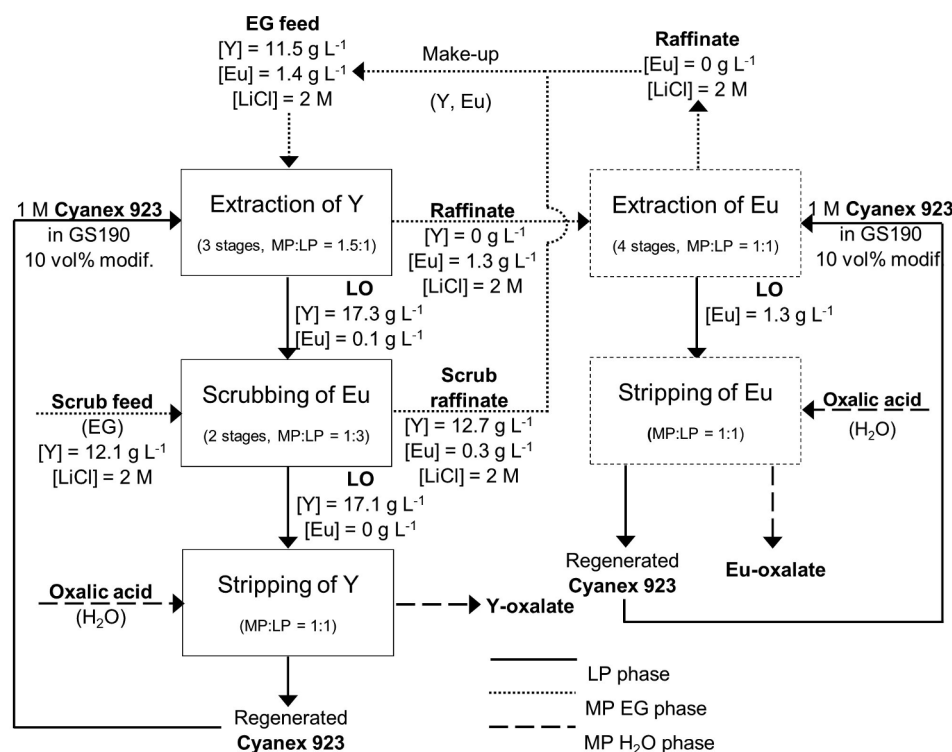


Fig. 6. Flow sheet for a non-aqueous process for the separation of Y(III) and Eu(III). MP phase is EG + 2 M LiCl, LP phase is 1 mol L<sup>-1</sup> Cyanex 923 in GS190 diluent + 10 vol% of 1-decanol (modif.). LO = loaded LP phase. The concentrations presented correspond to the first cycle (not considering the recycle conditions). The dashed boxes indicate theoretical operations, the full boxes have been tested on larger scale.

solutions, whereas the extraction was inefficient from aqueous chloride solutions. Based on the McCabe-Thiele plot predictions, three-stage counter-current extraction simulations were conducted to fully extract Y(III). The co-extracted Eu(III) was removed by a two-stage counter-current scrubbing with an Y(III)-containing scrub feed solution. The loaded Y(III) was recovered as an oxalate by precipitation stripping with an aqueous oxalic acid solution, which was subsequently calcined to Y<sub>2</sub>O<sub>3</sub> with a purity of more than 99.9%. As a result, a complete

process flow sheet comprising extraction, scrubbing and stripping steps was proposed. For the first time, a non-aqueous extraction process has been performed in continuous mode in a lab-scale mixer-settler set-up, which confirmed the feasibility of the developed process. This solvo-metallurgical process has several advantages over aqueous processes, among which a limited number of stages and a reduced consumption of acids and bases are important improvements.

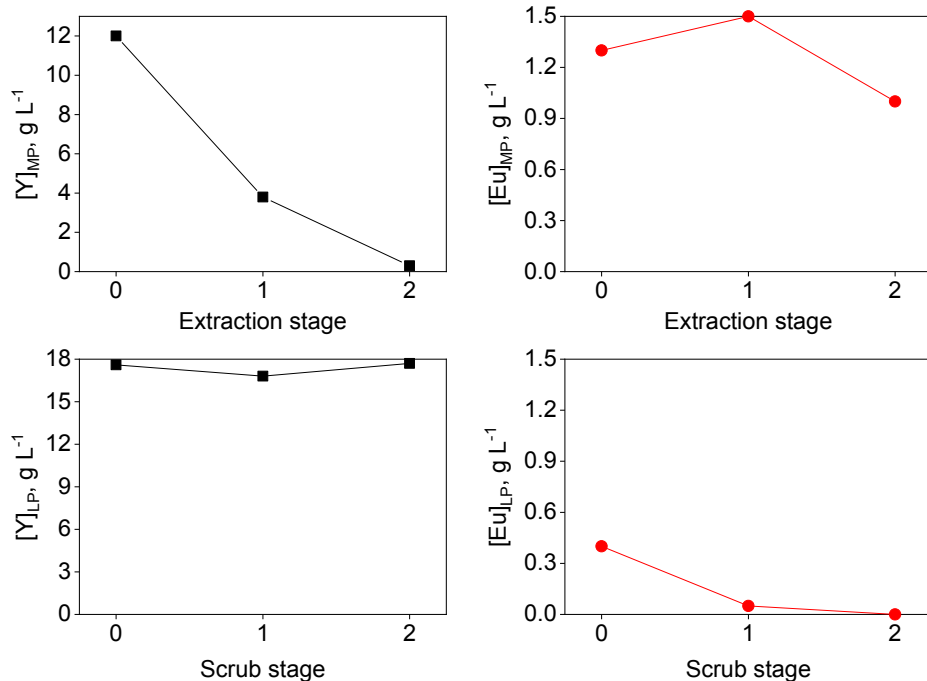


Fig. 7. Concentration profile of Y(III) (left) and Eu (III) (right) in the extraction (top, MP) and scrubbing (bottom, LP) mixer-settler experiment. Conditions: volume MP:LP = 1.5:1, room temperature, 900 rpm. Initial metal concentrations for extraction experiment: [Y(III)]<sub>MP</sub> = 12.0 g L<sup>-1</sup>, [Eu (III)]<sub>MP</sub> = 1.2 g L<sup>-1</sup>; initial scrub feed concentration: [Y(III)]<sub>MP</sub> = 11.6 g L<sup>-1</sup>.

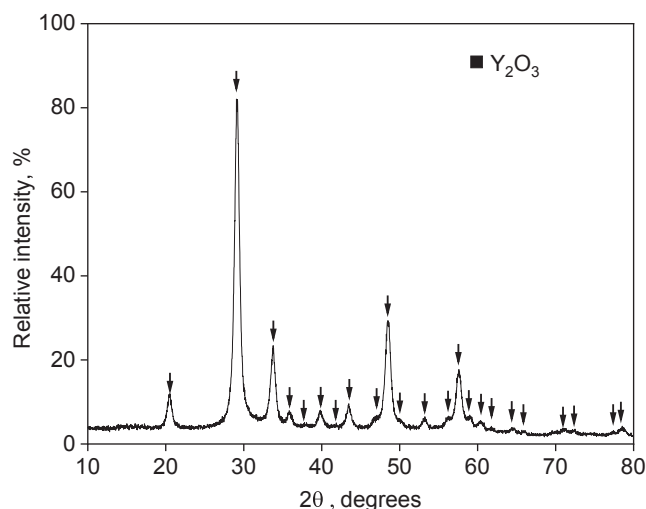


Fig. 8. XRD diffractogram of  $Y_2O_3$ , obtained after calcination of the corresponding yttrium(III) oxalate.

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### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.116193>.

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