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# Extraction of rare earth elements from waste products of phosphate industry

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## ABSTRACT

Rare earths are critical elements in our modern societies and the ever-increasing demand raises fears of supply risks in the coming years. This work dealt with the feasibility of extracting rare earth elements (REEs) from an industrial waste product from the exploitation of phosphate ores of "Djebel Onk" in Tébessa eastern region of Algeria. The solid residue was first leached at room temperature with three different inorganic acids (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) at various concentrations and leaching times. It was possible to recover almost 100 % of La, Ce, Eu, Gd and Y with HNO<sub>3</sub> 3 N in 24 h. However, only about 10 % of Yb were leached. The leachates were further treated with two organophosphorous extractants, trioctylphosphine oxide (TOPO) and di-(2-ethylhexyl) phosphoric acid (D2EHPA) at various concentrations in chloroform. A virtually total extraction of Eu, Gd, Y and Yb was achieved with TOPO at 0.3 M. The extraction efficiency of light rare earth elements (LREEs), La and Ce, was only 38 and 55 %, respectively. Very good selectivities between heavy rare earth elements (HREEs), and LREEs as well as between medium rare earth elements (MREEs) and LREEs were obtained but TOPO was unable to selectively separate HREEs from MREEs. Although D2EHPA led to lower REEs extraction efficiency than TOPO, it showed interesting performance for the selective separation of REEs into three fractions corresponding to LREEs (La and Ce), MREEs (Eu and Gd) and HREEs (Y and Yb).

## Keywords

Rare earths; liquid/liquid extraction; industrial waste product; Djebel Onk fluorapatite; valorization

## 1. Introduction

Rare earth elements (REEs), i.e. scandium, yttrium and the lanthanides, are considered as strategic metals for both civil and military applications. They have been increasingly used in the high-tech sector as they play a crucial role in the development of high-end smart materials [1–3]. Since the last two decades, a few producers (mainly from China) have conducted intensive extraction and commercialization of REEs [4,5]. The worldwide demand grows by about 10% per year in various applications such as permanent magnets, batteries for hybrid cars, wind turbine generators, luminophores, etc.[6,7]. Meanwhile, the European Union imports more than 90% of its needs in REEs [8].

REEs are relatively abundant on Earth but not in concentrated forms, which makes them economically challenging to obtain [9]. The main commercial sources of rare earth elements are monazite, xenotime and bastnasite [10,11]. Besides the historical mines Mountain Pass in California and Mount Weld in Australia, numerous new regions, such as in Tamtor (Russia), Strange lake (Canada), Araxà (Brazil), Ngualla (Tanzania), Zandkopsdrift (South Africa) and Norra Karr (Sweden), have begun exploration [12,13]. However, the continuous development of advanced technologies over the past decades has created increasing demand for REEs [9] and co-production is now considered as a promising alternative route allowing the valorization of REEs, especially for the heavy rare earth elements [14,15]. In contrast to end-of-life products [16], mining process residues typically contain low concentrations of REEs but they are produced in very large amount. Consequently, they are likely to become a significant source of REEs [17–19].

A large number of REE-bearing phosphate minerals have been found in nature, thus indicating that REEs have a strong affinity towards phosphates [16]. In this regard, apatite ores ( $\text{Ca}_{10}(\text{PO}_4)_6\text{A}_2$  with  $\text{A} = \text{F}, \text{OH}$  or  $\text{Cl}$ ), used for the production of phosphate fertilizers or phosphoric acid, have been treated for extraction of REEs as secondary products [20–22]. Apatite is an important host mineral for REEs in igneous and metamorphic rocks, with trivalent rare earth cations substituting calcium ions in the apatite lattice structure (with an REEs concentration that can exceed 1g per kg of ore) [23]. Furthermore, the huge amount of apatite ores on Earth (the world phosphate rock production is estimated to be more than 250 million tons per year [15]) makes this material a promising alternative source for extraction of REEs [24,25]. It is noteworthy, however, that extraction of REEs from apatite has not been extensively studied compared to other main minerals such as monazite, bastnasite and xenotime [9].

REEs are commonly subdivided into three categories: light (LREEs; La-Sm), medium (MREEs; Eu-Dy) and heavy (HREEs; Ho-Lu and Y) [26]. They are known to be difficult to separate from each other, due to their similar chemical and physical properties. Nevertheless, several processing routes have been developed to recover rare earths such as precipitation, filtration, adsorption, ion exchange and solvent extraction [10,11,27], the latter being currently considered as the most commercially-relevant technology [9,26,28]. Separation processes based on ion-exchange and solvent extraction techniques have been shown to allow separation between REEs [29]. With controlled experimental conditions, fair separations between LREEs and HREEs have been reported [9,30–32].

The aim of this work was to recover REEs from a sterile waste product of the phosphate industry exploiting phosphate ores of "Djebel Onk" in Tébessa eastern region of Algeria. The solid residue was first leached with three different inorganic acids (nitric, phosphoric and sulfuric acids) at different concentrations and leaching times. The leachates were further treated with two organophosphorous extractants (di-(2-ethylhexyl) phosphoric acid and trioctylphosphine oxide) at various concentrations in chloroform in order to assess the feasibility of extracting the various REEs.

## **2. Materials and methods**

### **2.1 Samples and reagents**

Sulfuric ( $\text{H}_2\text{SO}_4$ ), nitric ( $\text{HNO}_3$ ) and phosphoric ( $\text{H}_3\text{PO}_4$ ) acids (Reagent grade; Fluka) were used for apatite-ore leaching. Chloroform (Analytical grade; Fluka) was used as diluent for extractants. Organophosphorus extractants, di-(2-ethylhexyl) phosphoric acid (D2EHPA) and trioctylphosphine oxide (TOPO), were obtained from Sigma-Aldrich and used without further purification. The chemical structures of D2EHPA and TOPO are shown in Figure 1. REE nitrate standards (Sigma-Aldrich) were used for ICP-OES calibration. Deionized water was used for the preparation of all aqueous solutions.

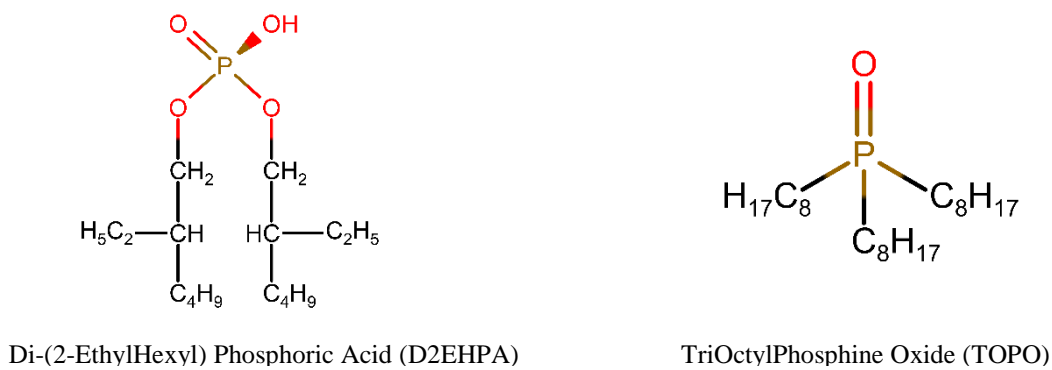


Figure 1. Chemical structures of the organophosphorus extractants.

Samples of apatite ore from Djebel Onk (Tébessa, Algeria) were provided by the Somiphos company. The flowsheet followed by the Somiphos company in its phosphate plant in Tébessa is shown in Figure 2. Among the various sterile wastes (i.e. products with a too low phosphate concentration for a profitable commercial exploitation) generated in the Somiphos' phosphate plant, sample T1 was selected in this study because it exhibited the highest REEs content (about 0.1 wt. %).

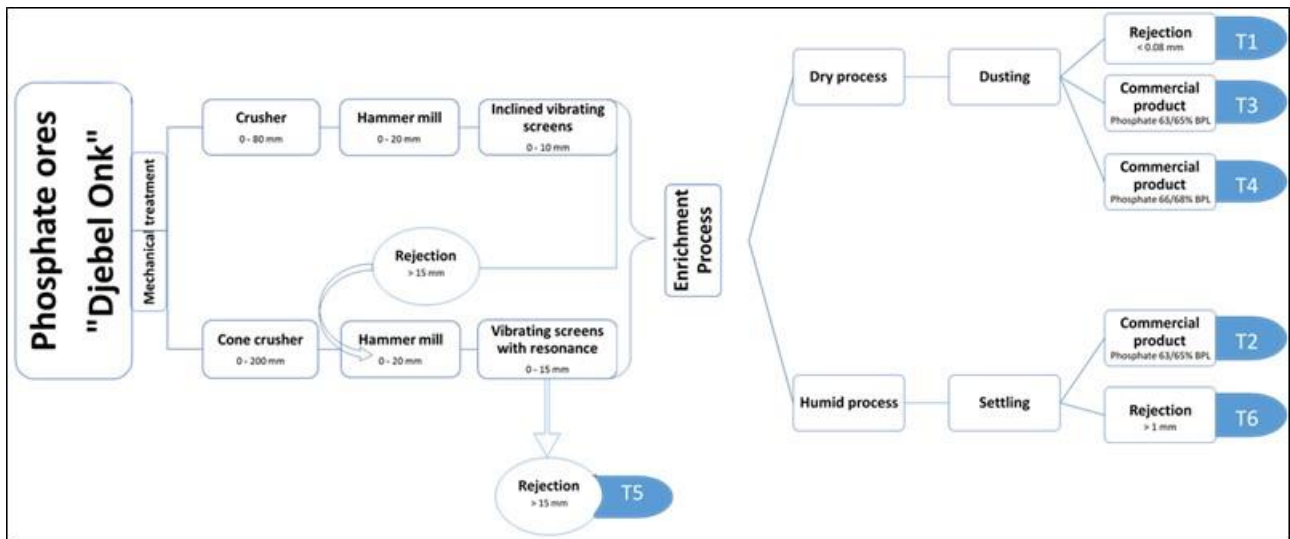


Figure 2. Different steps for the treatment of phosphate ores by the Somiphos company in Djebel Onk (Tébessa, Algeria). T2 – T4 are commercialized products whereas T1, T5 and T6 are waste products.

## 2.2 Characterization techniques

### 2.2.1 X-Ray Diffraction (XRD)

The mineralogical analysis of the phosphate ore residue T1 was carried out by X-ray diffraction (XRD). XRD data were collected using an X-ray diffractometer BRUKER-binary V3 (Raw) using Cu  $K\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), running at 40kV and 40mA, with detection in the  $2\theta$  range 10-90°.

### 2.2.2 X-Ray fluorescence (XRF)

The chemical composition of the phosphate ore residue was determined by X-ray fluorescence (XRF) with wavelength dispersive analysis (WD-XRF) by means of a PANalytical PW2400 Sequential WDXRF Spectrometer (X-ray tube anode material: Rh; power: 3 kW).

### 2.2.3 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) was used to determine the concentration of REEs in aqueous phases. Analyses were performed in emission mode with a 700 series Varian Vista Pro ICP-OES spectrometer with axial torch. The various standards used for ICP-OES and analysis conditions are given in Table 1.

Table 1. REE standards and wavelengths used for ICP-OES analyses.

<b>REEs standards properties</b>						
	Eu(NO <sub>3</sub> ) <sub>3</sub>	Gd(NO <sub>3</sub> ) <sub>3</sub>	Y(NO <sub>3</sub> ) <sub>3</sub>	Yb(NO <sub>3</sub> ) <sub>3</sub>	Ce(NO <sub>3</sub> ) <sub>3</sub>	La(NO <sub>3</sub> ) <sub>3</sub>
MW (g/mol)	337.98	343.26	274.92	359.06	326.12	324.92
Purity (%)	99.9	99.9	99.9	99.9	99.9	99.9
Wavelength (nm)	420.50	342.25	361.10	369.42	407.35	333.75
Intensity (a.u.)	241902.80	56269.00	121194.40	420567.90	10588.00	86890.70

### 2.3 Leaching procedure

The phosphate ore waste product T1 (Figure 2) was leached according to the protocol schematically shown in Figure 3. Briefly, 20 g of solid were soaked in 250 mL (S/L ratio = 80 mg / mL) of an acid aqueous solution at room temperature ( $T = 25 \pm 1 \text{ }^\circ\text{C}$ ).  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  were used at various concentrations ranging from 0.5 to 3 N. The system was stirred vigorously at 750 rpm for times ranging from 0.5 to 24 h. Eventually, the solid residues were separated from the leachates by means of a filter paper.

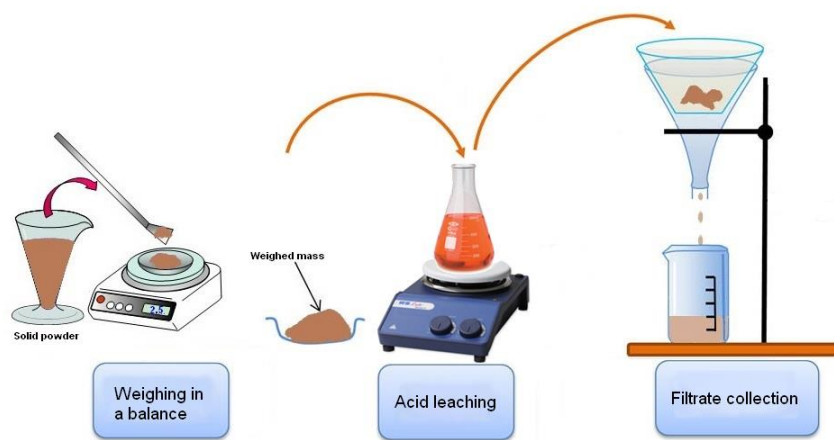


Figure 3. Leaching of the phosphate ore waste product.

The leachate composition was determined by ICP-OES after appropriate dilution. The leaching efficiency of REEs ( $E_{leach}$ ) was determined by the following equation:

$$E_{leach} = \frac{m_{leach}}{m_{0,T1}} \times 100 \quad (1)$$

where  $m_{leach}$  is the mass of the REE in the leachate and  $m_{0,T1}$  is the initial mass of the REE in the waste product T1.

## 2.4 Liquid / liquid extraction

After acidic leaching, solvent extraction was performed at room temperature. Two organophosphorous extractants were used, TOPO and D2EHPA (Figure 1), at various concentrations in chloroform. Chloroform is only weakly polar and therefore has a relatively low affinity for TOPO and D2EHPA (the P=O bond in TOPO and P=O, C-O-P and P-O-H bonds in D2EHPA bring them a polar character), which is beneficial for extraction. Indeed, diluent should not have a too high affinity towards the extractant because strong interactions between the extractant and the diluent would result in a lower concentration of “free” extractant available for reaction with metal at the liquid-liquid interface [33]. For instance, Smelov et al. reported a decrease in the extraction efficiency of zinc when increasing the solvent ability to solvate D2EHPA [34].

Solvent extraction was carried out by stirring equal volumes (5.0 mL) of aqueous organic phase and aqueous leachate (O/A volume ratio = 1) for 10 min using a mechanical stirrer (100 rpm), and by further separating the aqueous phase from the organic phase with a separating funnel. The concentrations of REEs in the aqueous phase before and after extraction were determined by ICP-OES. The distribution coefficient ( $D_{REE}$ ), extraction efficiency ( $E_{extr}$ ) and separation factor between two REEs  $i$  and  $j$  ( $SF_{i/j}$ ) were obtained from the following equations [31]:

$$D_{REE} = \frac{[REE]_{0,leach} - [REE]_{leach} \frac{V_{leach}}{V_{org}}}{[REE]_{leach}} \quad (2)$$

$$E_{extr} = 100 \left( 1 - \frac{[REE]_{leach}}{[REE]_{0,leach}} \right) \quad (3)$$

$$SF_{i/j} = \frac{D_{REE_i}}{D_{REE_j}} \quad (4)$$

where  $[REE]_{0,leach}$  and  $[REE]_{leach}$  are the REE concentration in the leachate before and after extraction, respectively, and  $V_{leach}$  and  $V_{org}$  are the volumes of the aqueous leachate and organic phase, respectively.



### 3 Results and discussion

#### 3.1. Characterization of the phosphate ore waste product

The XRD analysis (Figure 4) identified carbonate-fluorapatite as the main crystalline phase of the phosphate ore residue T1. Quartz was also found to be present in substantial amount, as already reported elsewhere [35].

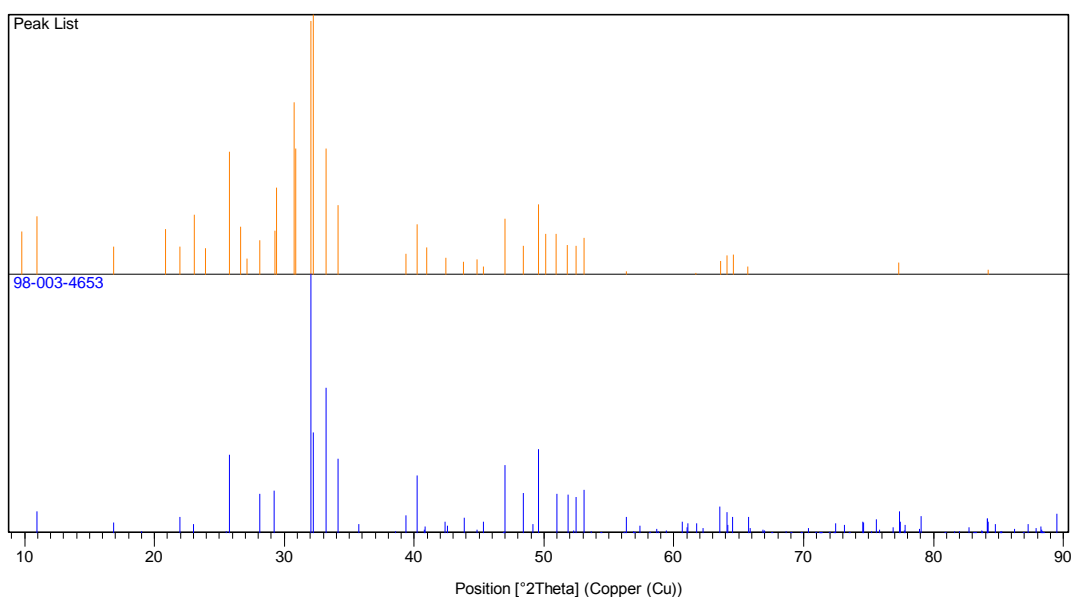


Figure 4. Comparison of the experimental XRD data (phosphate ore residue T1) with the ASTM XRD data reference 98-003-4653 (carbonate-fluorapatite:  $C_{1.483}Ca_{9.35}F_{1.98}O_{23.329}P_{4.72}$ ).

The REE content of the phosphate ore residue determined from XRF is shown in Table 2 (the full XRF results are provided in the Supporting Information).

Table 2. REE content of the phosphate ore residue.

Element	La	Ce	Eu	Gd	Y	Yb
wt. %	0.0280	0.0140	0.0004	0.0078	0.0363	0.0049

## 3.2. Leaching

### 3.2.1. Efficiency of the different acids

Three inorganic acids, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, were used for leaching the phosphate ore residue. The expected reactions between fluorapatite and these acids can be represented as follows [15,36,37]:

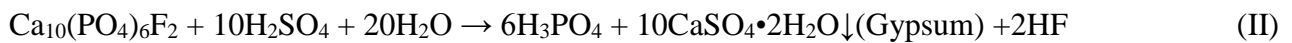
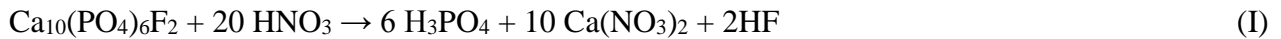


Figure 5a shows the REEs concentrations in the leachate after 3-hour leaching in 3N HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solutions. H<sub>3</sub>PO<sub>4</sub> has proven ineffective for leaching REEs. It is in qualitative agreement with Stone et al. who investigated the leachability of REEs from fluorapatite using HClO<sub>4</sub>, HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> and concluded that the dissolution of REEs in H<sub>3</sub>PO<sub>4</sub> was lower compared to the other three acids [24]. H<sub>2</sub>SO<sub>4</sub> allowed partial leaching of REEs from the phosphate ore residue. However, the leaching efficiency with H<sub>2</sub>SO<sub>4</sub> was found significantly lower than with HNO<sub>3</sub>, which is in line with reported literature [9,22,38–41]. The lower performance obtained with H<sub>2</sub>SO<sub>4</sub> results from the precipitation of gypsum (see reaction II) which tends to incorporate REEs. For instance, Ogata et al. reported that, at high H<sub>2</sub>SO<sub>4</sub> concentrations (up to 6 M), most of the REEs contained in apatite samples were lost due to co-precipitation with the formed gypsum [41]. We report in Figure 5b the leaching efficiency after 3-hour leaching in the various acids (concentration: 3 N). When leaching was carried out with HNO<sub>3</sub>, Eu was almost completely released from the phosphate ore residue while a moderate efficiency (~ 50 – 75 %) was obtained for La, Eu, Gd and Y. It is noteworthy that leaching efficiency was very weak for Yb (less than 5 %), whatever the acid used. It can thus be concluded that there is no correlation between the leaching efficiency and the category of REEs, i.e. LREEs, MREEs and HREEs.

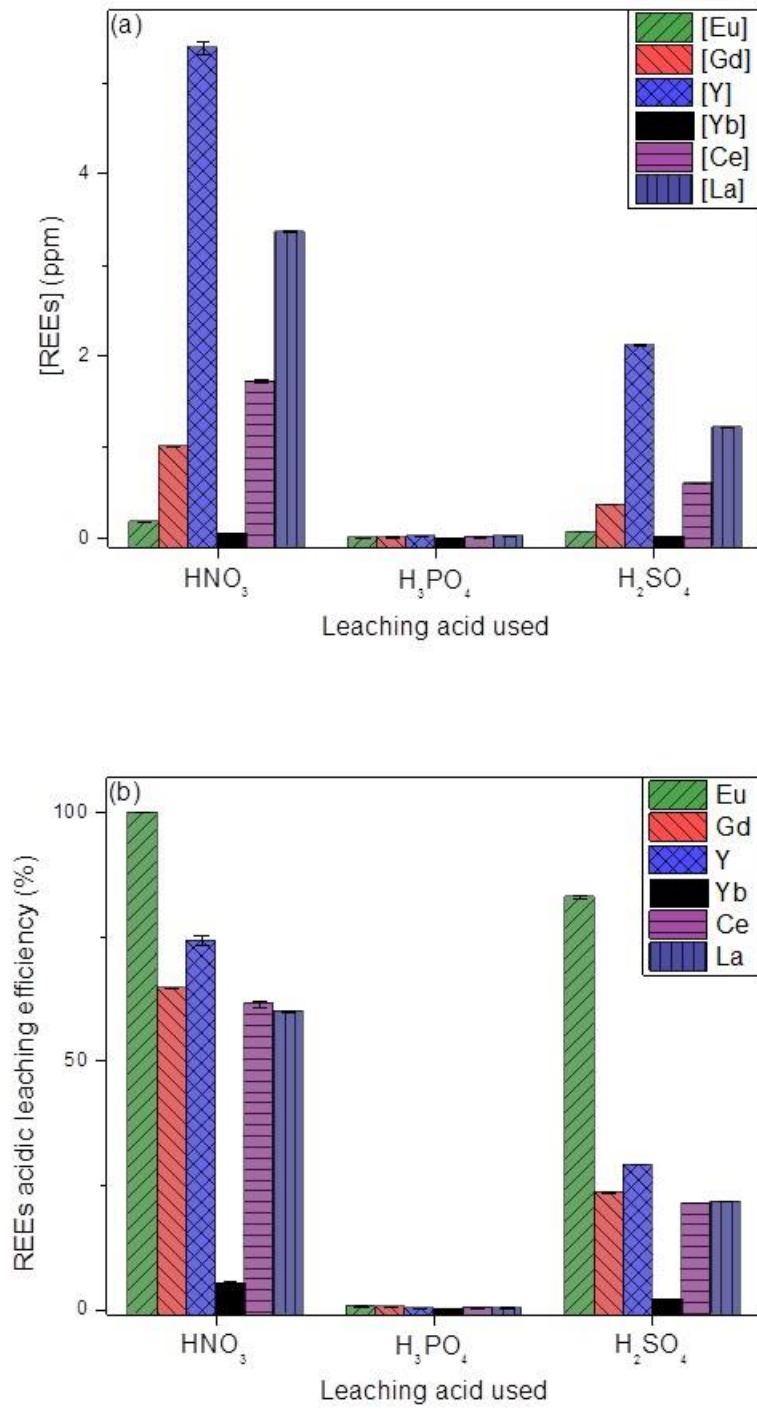


Figure 5. REEs concentrations in the leachate (a) and leaching efficiency (b) for various acids (acid concentration: 3 N; leaching time: 3 h).

### 3.2.2. Impact of nitric acid concentration

HNO<sub>3</sub> was considered for the subsequent parts of this study as it was shown to yield the best results (section 3.2.1). Figure 6 shows the leaching efficiency in HNO<sub>3</sub> solutions of various concentrations ranging from 0.5 to 3 N for a leaching time of 0.5 h. The leaching of the phosphate ore residue increased with increasing nitric acid concentration, in good agreement with the literature [15]. It should be stressed, however, that increasing too much the acid concentration would be detrimental for REEs extraction by cation-exchanger extractant such as D2EHPA [11]. Eu was more efficiently leached than the other REEs, whatever the acid concentration, and was completely released from the solid from a nitric acid concentration of 2 N. The acid concentration did not impact the overall sequence of leaching efficiency.

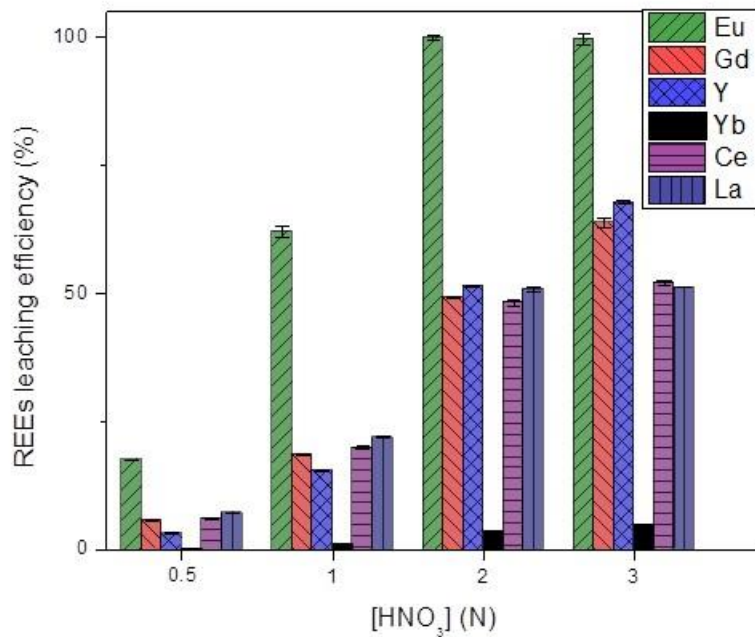


Figure 6. Leaching efficiency for various HNO<sub>3</sub> concentrations (leaching time: 0.5 h).

### 3.2.3 Leaching time

Figure 7 reports the impact of the leaching time on REEs release. All experiments were carried out in HNO<sub>3</sub> 3 N at room temperature. Eu was totally released from the solid after 0.5 h. On the other hand, only ~ 50-70 % of La, Ce, Gd and Y were released under these operating conditions. Walawlakar et al. reported similar leaching efficiencies for La, Ce and Y contained in phosphogypsum samples leached with HNO<sub>3</sub> 3 N in only 20 min but by working at temperatures in the range 50 - 80°C [42].

Besides, Banihashemi et al. used 65 wt. % HNO<sub>3</sub> at 90°C to leach iron-rich phosphate ores and reported leaching efficiencies not exceeding 40 % for La, Ce and Y after 1.5 h [43]. We observed only a slight improvement of leaching efficiency for La, Ce, Gd and Y after 3 h. However, extending the leaching time up to 24 h resulted in an almost total leaching of La, Ce, Gd and Y. Finally, HNO<sub>3</sub> acid was found to be relatively ineffective for the leaching of Yb from the phosphate ore residue as leaching efficiency did not exceed 10 % after 24 h.

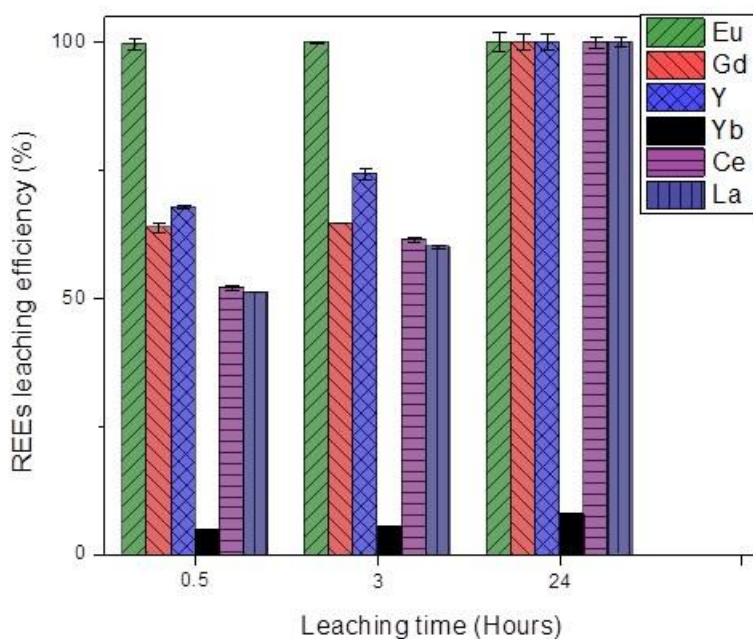
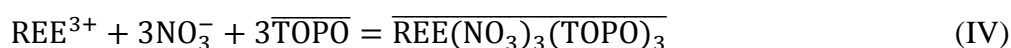


Figure 7. Leaching efficiency for various leaching times (leaching agent: 3N HNO<sub>3</sub>).

### 3.3. Extraction of REEs

Based on the results reported in section 3.2, extraction of REEs was carried out after the leaching of the phosphate ore residue with HNO<sub>3</sub> 3 N for 24 h at room temperature. Figure 8 shows the extraction efficiency of the various REEs by TOPO in chloroform. TOPO is a neutral solvation extractant. In highly concentrated nitric systems as those considered in this study, REEs are coordinated around the phosphoryl group of TOPO (the electron donor character of the oxygen atom of the phosphoryl group is strengthened by the three long alkyl chains), yielding an extractable neutral amino complex. The overall reaction can be represented as [11,29]:



where  $\overline{\text{TOPO}}$  and  $\overline{\text{REE}(\text{NO}_3)_3(\text{TOPO})_3}$  denote TOPO and the complex in the organic phase, respectively.

As expected from reaction IV, the extraction efficiency was found to increase with the concentration of TOPO and a virtually total extraction of Eu, Gd, Y and Yb was achieved with 0.3 M of extractant. These results are of great practical interest for valorizing waste products of the phosphate industry as Y and Eu have been designated as critical REEs that are expected to be in short supply in the coming years [44]. La and Ce were much less extracted, with performance not exceeding 38 and 55 %, respectively. Qualitatively similar results were reported for tributylphosphate, another neutral solvation extractant with which only REEs lighter than Sm were effectively extracted from nitric systems [11]. It is noteworthy that much lower extraction efficiencies were reported for both LREEs and HREEs (~ 10 and 20 %, respectively) when TOPO diluted in kerosene was used to extract REEs from apatite ores leached with sulfuric acid [9]. It confirms the major impact of (i) the nature of the acid used in the leaching step and (ii) the type of diluent, on the liquid/liquid extraction.

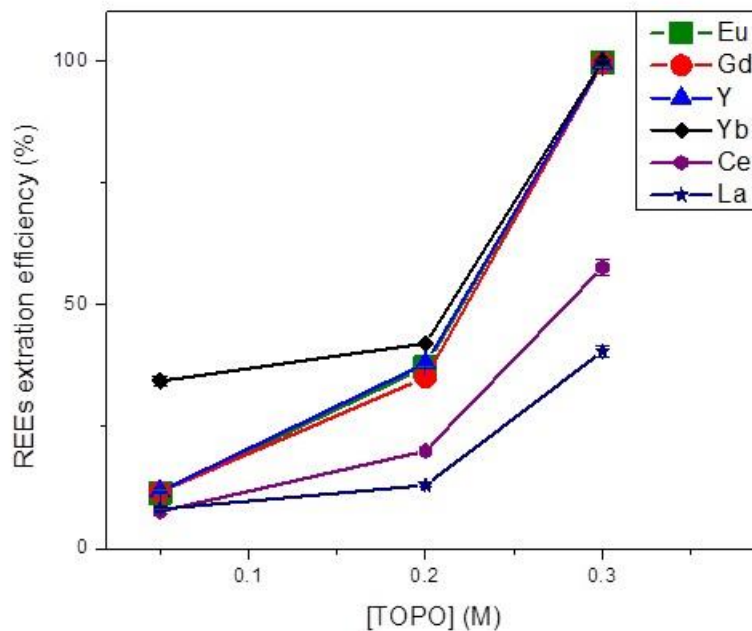


Figure 8. REEs extraction efficiency as a function of TOPO concentration.

Figure 9 shows the separation factors (computed from Equation 4) between the three categories of REEs (HREEs, MREEs and LREEs) as a function of the TOPO concentration. The selectivity between HREEs and LREEs was found to increase with the TOPO concentration (Figure 9a). It reached values in the range 150 – 750 for 0.3 M, thus offering excellent capabilities for selective separation of HREEs

and LREEs. It can be noted, however, that much smaller selectivities (not exceeding 6) were obtained when using lower TOPO concentrations (0.05 and 0.2 M). The selectivity between HREEs and MREEs was very low, irrespective of the TOPO concentration (Figure 9b), while the selectivity between MREEs and LREEs increased with the TOPO concentration and exceeded 100 for the highest TOPO concentration (Figure 9c). Finally, as shown in Figure 9d, TOPO was unable to separate selectively REEs belonging to the same category (HREEs, MREEs or LREEs).

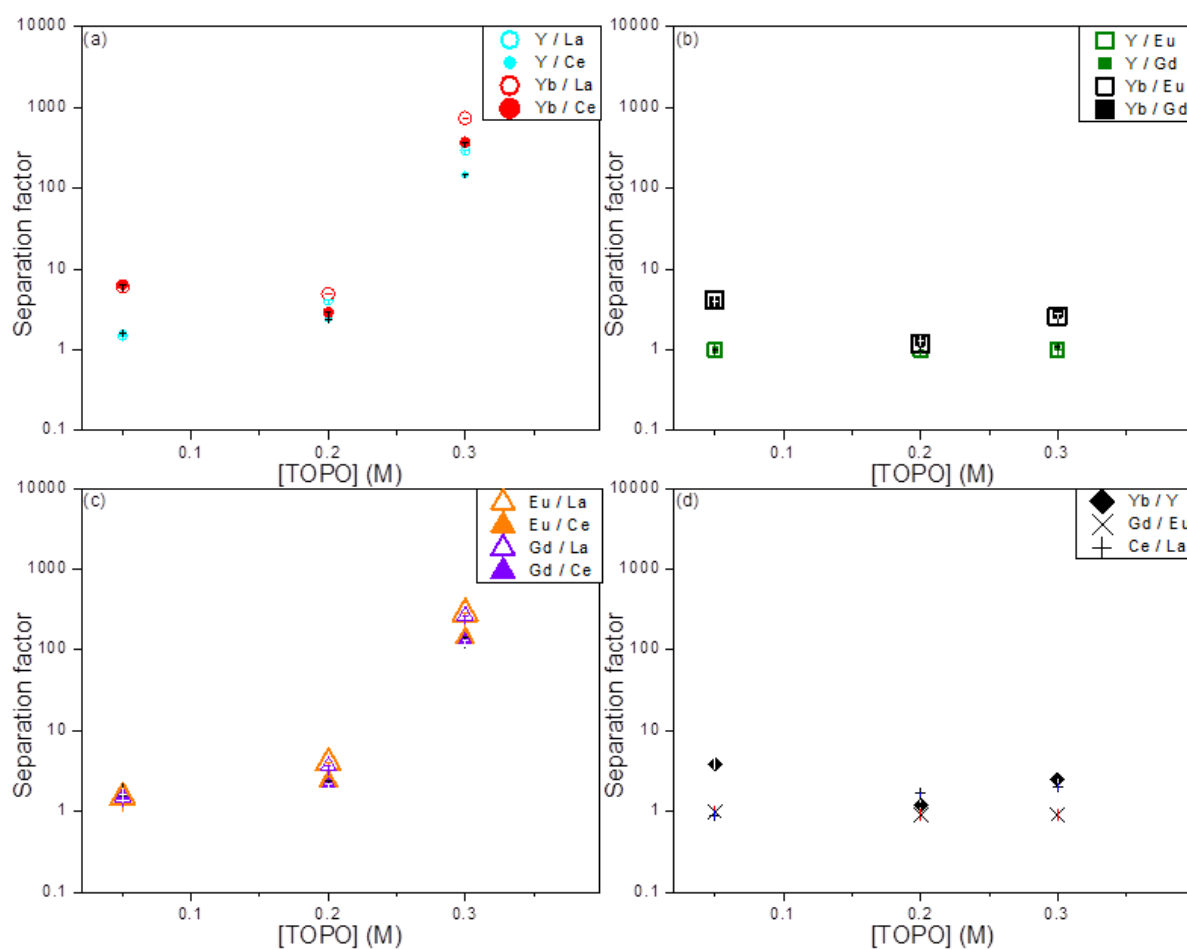


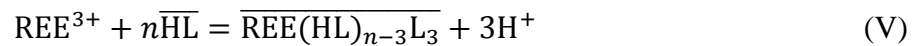
Figure 9. Separation factors between REEs as a function of TOPO concentration. (a) selectivity between HREEs and LREEs; (b) selectivity between HREEs and MREEs; (c) selectivity between MREEs and LREEs; (d) selectivity among REEs belonging to the same category.

Figure 10 shows the extraction efficiency of the various REEs by D2EHPA in chloroform. Similarly to TOPO, the REEs extraction efficiency was found to increase with increasing the D2EHPA

concentration in the organic phase. It is worth mentioning, however, that increasing the extractant concentration leads to an increase in the organic-phase viscosity, and thus a too high extractant concentration may result in difficulty of phase separation [31].

From the results shown in Figure 10 it can be concluded that the extraction efficiency of D2EHPA increased with decreasing the ionic radius of REEs [45]. Similar results were reported elsewhere [9–11,30]. It can be understood thanks to the HSAB theory [46] since D2EHPA can be considered as a hard (Lewis) base due to its chemical structure with localized partial charges. The hardness of REEs (Lewis acids) increases as their ionic radius decreases, which results in stronger interactions with D2EHPA and thus better extraction efficiency.

Extraction efficiencies were typically lower with D2EHPA than with TOPO with a maximum efficiency of 88 % for Yb (the hardest acid among the various REEs under consideration) and less than 3 and 4 % for La and Ce, respectively. The lower performance of D2EHPA is partly due to the high acidity of the nitric-phosphoric acid solution obtained by leaching fluorapatite with nitric acid (reaction I). Indeed, D2EHPA belongs to the category of cation-exchanger extractants whose action can be represented in the following general and simplified form (organophosphoric acids tend to form dimers in low polar media) [47]:



where  $\overline{\text{HL}}$  and  $\overline{\text{REE}(\text{HL})_{n-3}\text{L}_3}$  denote D2EHPA and the metal-extractant complex in the organic phase, respectively.

D2EHPA therefore mainly operates by ion exchange (proton vs. metal), which is thermodynamically less favorable in a strongly acidic medium as shown by reaction V [11,48]. That is also why much higher concentrations of D2EHPA were required (up to 1.8 M) compared to TOPO (not above 0.3 M).



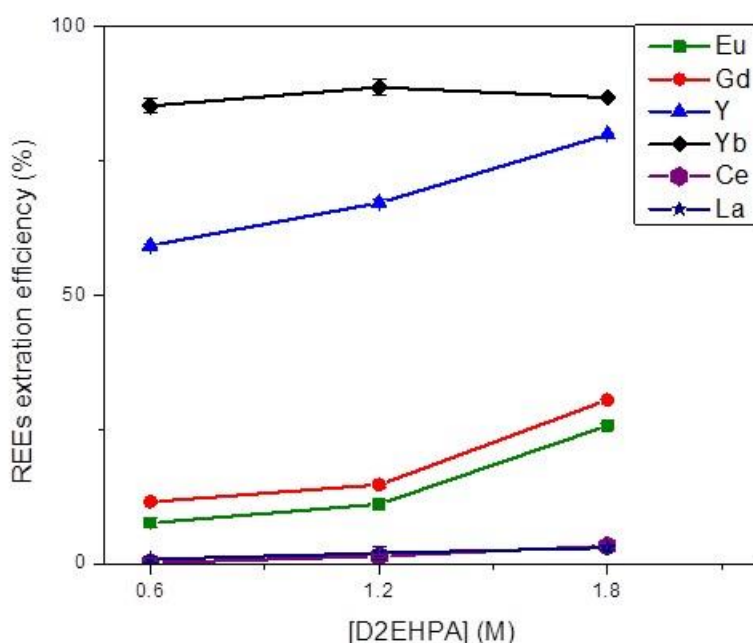


Figure 10. REEs extraction efficiency as a function of D2EHPA concentration.

Although TOPO led to higher REEs extraction efficiencies than D2EHPA, the latter enabled more selective separations between the different REEs categories as shown in Figure 11 which reports the various separation factors as a function of the D2EHPA concentration. Overall, it was observed that the selectivity factors decreased as the D2EHPA concentration increased, in contrast to TOPO. Selectivity factors in the range 100 – 5600 were obtained between HREEs and LREEs (Figure 11a), thus highlighting the excellent ability of D2EHPA to separate these two categories of REEs. The selectivity between HREEs and MREEs was lower but still interesting with values in the range 9 – 71 (Figure 11b), i.e. much better than with TOPO. A fair separation was obtained between MREEs and LREEs, with separation factors around 10 (reaching up to ~ 100 for Eu / Ce and Gd / Ce with 0.6 M D2EHPA) (Figure 11c). Finally, as shown in Figure 11d, D2EHPA did not allow efficient separation between REEs belonging to the same category (just like TOPO).

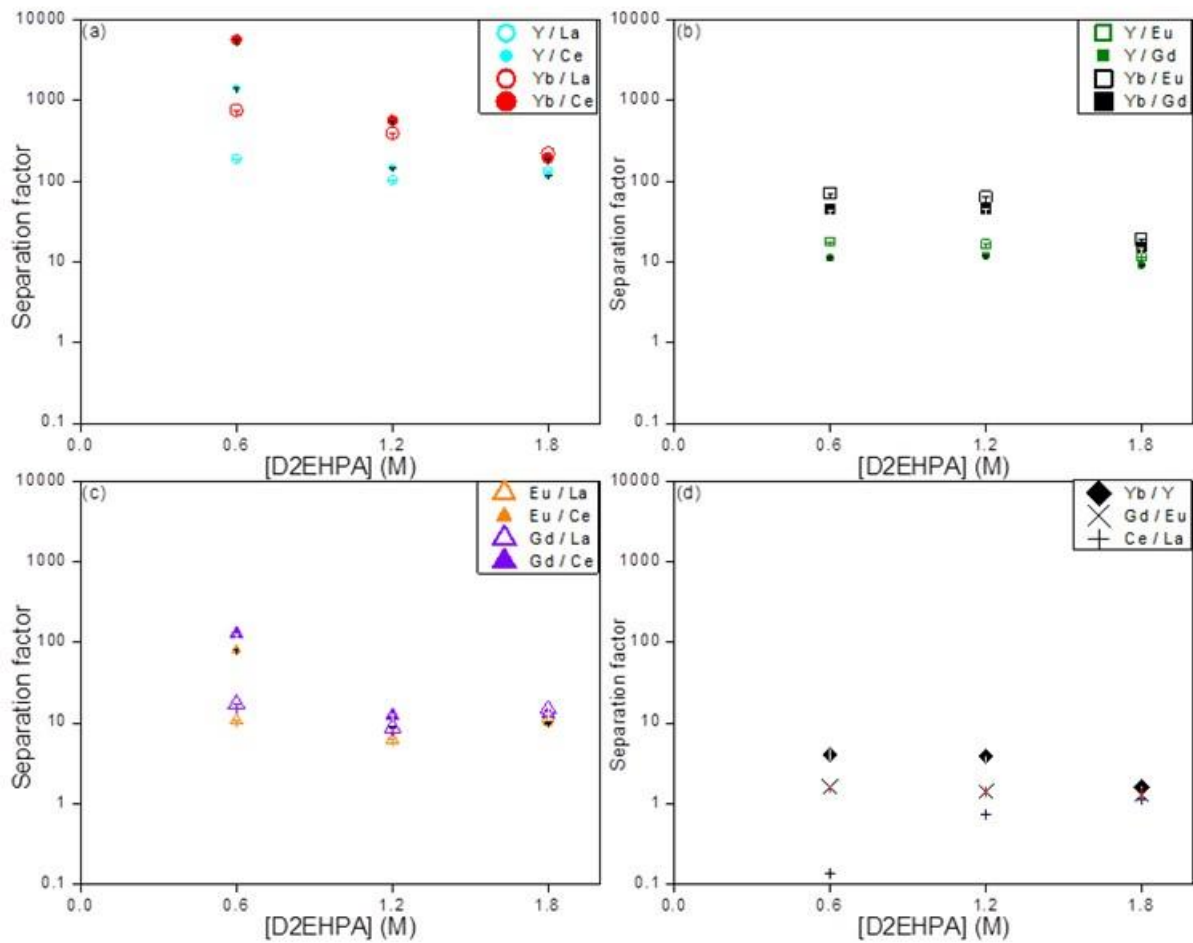


Figure 11. Separation factors between REEs as a function of D2EHPA concentration. (a) selectivity between HREEs and LREEs; (b) selectivity between HREEs and MREEs; (c) selectivity between MREEs and LREEs; (d) selectivity among REEs belonging to the same category.

#### 4. Conclusion

In this study, the feasibility of extracting REEs contained in an industrial waste product from phosphate ores of "Djebel Onk" (Tébessa, Algeria) was investigated. The phosphate ore residue, mainly composed of carbonate-fluorapatite and quartz, was first leached by considering three inorganic acids (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) at room temperature. The best results were obtained with HNO<sub>3</sub> 3 N. After 24 h, it was indeed possible to recover almost 100 % of all REEs from the solid residue (La, Ce, Eu,

Gd and Y) with the exception of Yb for which leaching efficiency did not exceed 10 %. Liquid / liquid extraction was further applied with various concentrations of organophosphorous extractants (TOPO and D2EHPA) in chloroform at room temperature. TOPO at 0.3 M enabled a virtually total extraction of Eu, Gd, Y and Yb while La and Ce were much less extracted (38 and 55 %, respectively). TOPO at 0.3 M also showed excellent selectivities between HREEs (Y, Yb) and LREEs (La, Ce) and between MREEs (Eu, Gd) and LREEs with separation factors up to ~ 750 and 100, respectively. However, it failed to selectively separate HREEs from MREEs. D2EHPA exhibited lower extraction efficiencies (max. 88 % for Yb) than TOPO but it has proven to be more efficient in terms of selectivity, thus potentially allowing the separation of REEs into three fractions corresponding to LREEs, MREEs and HREEs. Overall, the selectivity between REEs belonging to different categories increased with the TOPO concentration whereas the opposite was observed with D2EHPA. None of these organophosphorous extractants was able to yield a satisfying separation between REEs belonging to the same category (HREEs, MREEs or LREEs).

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