



**HAL**  
open science

# Leaching of rare earth elements (REEs) and impurities from phosphogypsum: A preliminary insight for further recovery of critical raw materials

C.R. Cánovas, S. Chapron, Guilhem Arrachart, S Pellet-Rostaing

## ► To cite this version:

C.R. Cánovas, S. Chapron, Guilhem Arrachart, S Pellet-Rostaing. Leaching of rare earth elements (REEs) and impurities from phosphogypsum: A preliminary insight for further recovery of critical raw materials. *Journal of Cleaner Production*, 2019, 219, pp.225-235. 10.1016/j.jclepro.2019.02.104 . hal-02062500

**HAL Id: hal-02062500**

**<https://hal.science/hal-02062500v1>**

Submitted on 22 Oct 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 **Leaching of rare earth elements (REEs) and impurities from phosphogypsum: a**  
2 **preliminary insight for further recovery of critical raw materials.**

3

4 *C.R Cánovas<sup>a,b\*</sup>, S. Chapron<sup>b</sup>, G. Arrachart<sup>b</sup>, S. Pellet-Rostaing<sup>b</sup>*

5 <sup>a</sup>*Department of Earth Sciences & Research Center on Natural Resources, Health and*  
6 *the Environment. University of Huelva, Campus "El Carmen", E-21071 Huelva, Spain.*

7 <sup>b</sup>*Institut de Chimie Séparative de Marcoule (ICSM) CEA, CNRS, ENSCM, Univ*  
8 *Montpellier, Marcoule, France.*

9

10 **Abstract**

11 Phosphogypsum is a pollutant waste generated by the fertilizer industry. Managing this  
12 pollutant is challenging due to the large volumes generated worldwide. A promising route  
13 is the valorization of phosphogypsum to recover rare earth elements. However,  
14 optimized recovery schemes are needed to create a cost-effective and environmentally  
15 friendly process. This paper studies the extraction efficiency of rare earth elements from  
16 phosphogypsum and the release of impurities during leaching in a variety of solutions  
17 and different working conditions. The best leaching performance was obtained using a 3  
18 M nitric acid (above 80%) solution that achieved a dissolution rate of 63% of the gypsum  
19 originally present. In contrast, using 0.5 M sulfuric acid extracted between 46% and 58%  
20 of the rare earth elements contained in phosphogypsum, dissolving less than 6% of the  
21 gypsum. This higher dissolution of gypsum led to a higher release of impurities by nitric  
22 acid. Increasing reaction times from 2h to 8h yielded an improvement of leaching  
23 efficiency of around 8% for both leaching solutions, while also promoting an increase of  
24 6% in the release of impurities. Adding DTPA resulted in poor leaching performance  
25 (from 13% to 22%). Pretreating phosphogypsum with water can remove a significant  
26 fraction of the impurities without scavenging rare earth elements. Mineralogical and  
27 chemical evidence suggests unreacted phosphate and fluoride are the most probable  
28 minerals hosting rare earth element minerals in phosphogypsum. The results of this

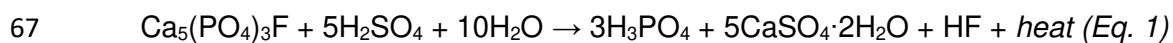
29 study could contribute to optimizing recovery methods to extract rare earth elements  
30 from phosphogypsum worldwide, thus helping achieve the goals of the circular economy.  
31 **Keywords:** recycling; metal recovery; hydrometallurgy; raw materials; secondary  
32 sources.

### 33 **1. Introduction**

34 Europe's mineral richness has been actively mined over many centuries, so accessible  
35 mineral deposits are mostly exhausted. Although raw materials are essential for the  
36 European Union's (EU) economy, their availability is increasingly under pressure.  
37 Experts in raw materials in the EU have identified a group of critical raw materials (e.g.  
38 rare earth elements (REEs), Sb, Be, Co, Ga, Ge, Mg, In, Platinum Group Elements  
39 (PGMs), Nb and Ta) that have high economic importance but are facing supply risks in  
40 the EU economy (EC, 2017). This is especially relevant for REEs, as at least 87% of the  
41 annual global supply in recent decades was provided by China (USGS 2016). This group  
42 of elements traditionally includes lanthanides (from La to Lu), but also other elements  
43 with similar geochemical behavior such as Sc and Y. In this sense, Sc is usually treated  
44 separately, as its production and applications are not strongly linked to other REEs. The  
45 remaining REEs can be split into light (LREEs, from La to Sm) and heavy rare earth  
46 elements (HREEs, Eu to Lu plus Y). This is the approach taken by several market  
47 reporters and mining companies based on chemical properties, geological availability,  
48 sources, supply demands, market values and end-markets. The importance of REEs to  
49 the economy comes from their wide range of uses, from energy production (e.g.  
50 petroleum cracking or magnets for wind turbines) to high-tech manufacturing (e.g.  
51 smartphones and lamps).

52 Europe's and other countries' strong dependence on external supply puts their  
53 economies at risk, which has encouraged them to seek alternative REE sources. This  
54 issue is especially important for countries without primary REE deposits. One of the most

55 promising secondary sources is End-of-Life products containing high concentrations of  
56 REEs, such as lamps or magnets. Thus, much research has recently been done on the  
57 urban mining of these products (e.g. Bandara et al., 2014; Binnemans and Jones, 2014;  
58 Binnemans et al. 2013; Innocenzi et al., 2014; Tunsu et al., 2015). However, much less  
59 attention has been paid to industrial landfilled stocks, which contain lower REE  
60 concentrations but have huge volume. One of the most significant examples is the  
61 unwanted by-products of fertilizer industries, such as phosphogypsum (PG). For this  
62 reason, these wastes are considered a promising source of REEs (e.g. Cánovas et al.,  
63 2017; Kulczycka et al., 2016; Rychkov et al., 2018). The fertilizer industry produces  
64 phosphoric acid ( $\text{H}_3\text{PO}_4$ ) from the wet chemical digestion of phosphate rock (fluorapatite,  
65  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) using sulfuric acid ( $\text{H}_2\text{SO}_4$ ), which generates large amounts of PG (gypsum,  
66  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The overall reaction is:



68 Although PG is mainly composed of gypsum, it may also contain small amounts of other  
69 solid phases as reaction products of the wet process (e.g. alkali fluorosilicates, fluorides),  
70 unreacted phosphate rock and gangue mineral particles (e.g. quartz, phosphates and  
71 feldspars). Moreover, PG also contains liquid inclusions and process waters trapped in  
72 the interstices of mineral particles. The term PG is, therefore, a collective term for a waste  
73 mixture comprising major solid and minor liquid waste components (Lottermoser, 2010).  
74 This waste is of environmental concern due to the high content of metals, metalloids and  
75 radionuclides (e.g. Bolívar et al., 2002; El Zrelli et al., 2016; Pérez-López et al., 2015;  
76 Tayibi et al., 2009). Some applications have been developed for this waste: in agriculture  
77 for soil amendment or as fertilizer; in the brick and cement industry; and in road  
78 construction (e.g. Cánovas et al., 2018a; Saadoui et al., 2017). However, the presence  
79 of metals of economic interest in these unwanted by-products can turn this potential  
80 waste into a commodity (Cánovas et al. 2017; Simandl, 2014). Around 70-85% of REEs  
81 originally present in phosphate rock end up in the PG (Habashi, 1985). Unlike metalloids

82 and radionuclides, REEs show low mobility under environmental conditions (Cánovas et  
83 al., 2018b). Although the REE content in PG varies notably depending on several factors,  
84 e.g. the nature of the phosphate rock used, the type of wet phosphoric acid process used  
85 and the efficiency of the plant operation, an average content of 0.4% has been estimated  
86 to be present in PG (Habashi, 1985), which is a very low value compared to those found  
87 in some common REE ore minerals such as bastnäsite, xenotime and monazite, which  
88 have average contents ranging from 2 to 20% (Simandl, 2014). However, the huge  
89 volume of PG landfilled near fertilizer industries may contain enough REEs to be mined  
90 if selective recovery methods are developed (Cánovas et al. 2017).

91 The extraction of valuable metals from metal-bearing materials is frequently performed  
92 using aqueous solutions. Some researchers have investigated the leaching of PG in  
93 different temperature conditions and with different concentrations of the acid. Habashi  
94 (1985) reported a recovery of around 50% of REEs contained in PG by leaching the un-  
95 wanted by-product at ambient temperature with a 0.1-0.5 M H<sub>2</sub>SO<sub>4</sub> at a solid-to-liquid  
96 ratio of 1:10. Preston et al. (1996) tested the leaching of REEs with sulfuric and nitric  
97 acid from PG derived from South-African phosphate rock. These authors reported higher  
98 efficiencies by leaching with HNO<sub>3</sub> instead of H<sub>2</sub>SO<sub>4</sub> and a maximum recovery of REEs  
99 with 3 M HNO<sub>3</sub>. Lokshin et al. (2002) found similar results in hemihydrates PG, which  
100 was attributed to the high solubility of REE-phosphates and REE alkali metal double  
101 sulfate in HNO<sub>3</sub>. More recently, Walawalkar et al. (2016) reported the leaching efficiency  
102 of REEs from PG using different acids (HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>). However, these  
103 researchers did not report the leaching of other impurities that could limit the efficiency  
104 of further selective extraction schemes. If these impurities are not identified and  
105 removed, they can cause emulsification of extraction systems and influence product  
106 purity (Ruan et al., 1995) However, there is still no evidence about the minerals hosting  
107 REEs in PG. Thus, the main aims of this work were: i) to study REE efficiency extraction  
108 (and other elements of economic interest, such as Sc, U and Th) from PG and the

109 release of impurities during leaching with commercial acids (HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>),  
110 especially considering the effect of leaching time on the release of target and unwanted  
111 metals; and ii) to provide some clues about the potential minerals controlling the mobility  
112 of REEs in PG. In addition, a comparative study was performed to determine the  
113 synergetic effect of acidic aqueous solutions containing diethylenetriaminepentaacetic  
114 acid (DTPA), a well-known water-soluble chelating agent (Chitry et al., 2005; Sorin et al.,  
115 2005). The results of this study may contribute to optimizing further hydrometallurgical  
116 steps, i.e. solution concentration and purification, and final metal recovery in order to  
117 achieve the sustainable valorization of PG and thus cleaner production in the fertilizer  
118 industry.

## 119 **2. Methods and materials**

### 120 **2.1. PG characterization**

121  
122 Samples of PG were collected from the Huelva PG stack deposited in the vicinity of  
123 Huelva town (SW Spain) during the manufacturing of phosphoric acid from 1968 to 2010.  
124 As a result, around 100 Mt of PG were stockpiled over approximately 1200 ha of  
125 marshland less than 300 m from the city. A composite sample of approximately 2 kg was  
126 collected from the PG stack using a polypropylene shovel, previously washed with  
127 distilled water, then transferred to polypropylene sterile bags. Due to the high  
128 compositional variability observed in the Huelva PG stack (Cánovas et al., 2017; 2018b),  
129 the composite sample may be not representative of the whole composition of the stack;  
130 however, it can be considered a representative PG material. The sample was then oven-  
131 dried (at 30 °C, to avoid mineral transformations), ground with an agate mortar until  
132 achieving the desired powder size (particle sizes ranged from 1 to 10 µm) and stored in  
133 sterile polypropylene containers until analysis. Subsamples were used for the different  
134 analytical procedures.

135 The PG sample was chemically characterized using *aqua regia* extraction. This chemical  
136 extraction is commonly used to determine the pseudo-total metal content in

137 environmental samples, with good recovery percentages observed with respect to total  
138 content (Sastre et al., 2002). 10 mL of aqua regia (12 mol L<sup>-1</sup> HCl and 15.8 mol L<sup>-1</sup> HNO<sub>3</sub>  
139 in the ratio 3:1) were added to 1 g of PG in Teflon reactors, which were allowed to stand  
140 for 20 h in a fume cupboard and then simmered on a hot plate for 1 h at 100 °C. Finally,  
141 the concentrations of dissolved major and trace elements were determined using  
142 inductively coupled plasma atomic emission spectrometry (ICP-AES Jobin-Yvon  
143 Ultima2) and inductively coupled plasma mass spectrometry (ICP-MS Agilent 7700),  
144 respectively.

145 X-ray diffraction (XRD) patterns were obtained using a Bruker D5005 X-ray  
146 Diffractometer with Cu K $\alpha$  radiation. Diffractometer settings were: 40 kV, 30 mA, a scan  
147 range of 5-65° 2 $\Theta$ , a step size of 0.02 2 $\Theta$  and 2.4 s counted per step. Additional  
148 mineralogical information was obtained using a scanning electron microscope (Quanta  
149 200 ESEM FEG) coupled with an EDX analyzer (BRUKER XFlash® 5010 SDD) to  
150 perform qualitative and quantitative microanalyses.

## 151 **2.2. Leaching experiments**

152 Several leaching procedures were performed to study the release of target metals (i.e.  
153 REEs) and impurities from the PG. 3 M HNO<sub>3</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub> were selected as  
154 leaching solutions since previous researchers (Habashi, 1985; Preston et al. 1996) have  
155 reported optimal recoveries at these acid concentrations. All leaching experiments were  
156 performed using from high purity acids solutions Merck® at a solid-to-liquid ratio of 1:20  
157 with shaking at 500 rpm. The release of elements was studied at room temperature and  
158 different reaction times: 2, 4, 6 and 8 h. In addition, the synergistic effect of acids and  
159 chelating agents was assessed by the leaching of PG with dilute solutions of HNO<sub>3</sub> and  
160 H<sub>2</sub>SO<sub>4</sub> with 0.05 M DTPA (from Sigma-Aldrich, 99%) adjusted to pH 3-5 to determine the  
161 optimal value for REE extraction by DTPA. DTPA is an octadentate  
162 aminopolycarboxylate chelating agent, especially for REEs (Noack et al., 2016). The  
163 best performance was obtained by adjusting pH to 3; thus, acid solutions with 0.05 M

164 DTPA at this pH value were used in the leaching experiments. Liquid inclusions and  
165 process waters trapped in the interstices of PG mineral particles can form efflorescent  
166 salts during sample drying. To distinguish the metal contributions of these salts from  
167 those provided by the PG, leaching with distilled water (DW) was also performed at room  
168 temperature with an L/S ratio of 1:20 and identical reaction times as the acids. The effect  
169 of Al on the REE extraction was studied by adding known amounts of Al salts (1 M  
170 solution;  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , >99% from Sigma-Aldrich®) to the leaching  
171 solutions. The leaching solutions were removed from the residual solids by filtration (0.45  
172  $\mu\text{m}$ ) before analyses.

173 The concentrations of dissolved major and trace elements were determined by  
174 inductively coupled plasma atomic emission spectrometry (ICP-AES Jobin-Yvon  
175 Ultima2) and inductively coupled plasma mass spectrometry (ICP-MS Agilent 7700),  
176 respectively. Several blank samples were carried through the complete leaching  
177 experiments and all elements were below the equipment's detection limit. The detection  
178 limits were calculated by average and standard deviations from 10 blanks for each  
179 experimental procedure. The detection limits ranged from 0.5 to 0.02 mg/L for major  
180 elements and were 2  $\mu\text{g/L}$  for trace elements. All analyses were performed in triplicate  
181 to evaluate the analytical accuracy. Certified Reference Material SRM-1640 NIST fresh-  
182 water-type was also analyzed to assess the analytical precision. All measurements were  
183 within 5% of certified values.

### 184 **3. Results and discussion**

185

186

#### **3.1. Mineralogical and chemical composition of PG**

187 The XRD pattern (Fig. 1A) of the Huelva PG allowed identifying gypsum to be the main  
188 mineral present (above 90% of the mass; semi-quantitative analysis). The presence of  
189 quartz was also identified, although the secondary peaks were overlapped by gypsum's  
190 peaks. The low crystallinity or minor presence (below 10% of mass) of other minerals  
191 (e.g. fluorides, Fe hydroxides, phosphates, sulfides, etc.) precluded their identification



192 by XRD. However, a detailed examination by SEM revealed the presence of fluorite (Fig.  
193 1B) precipitated onto the gypsum surface. The spherical morphology of the fluorite  
194 crystals (Fig. 1C) suggests it formed as a reaction product of phosphate rock attacked  
195 with H<sub>2</sub>SO<sub>4</sub>. The chemical composition of PG can vary depending on the nature of the  
196 phosphate rock, the type of wet phosphoric acid process used, the efficiency of the plant  
197 operation and any contaminants transferred to the PG during manufacturing, leading to  
198 sharp differences in PG composition worldwide (Lottermoser, 2010; Macías et al., 2017).  
199 Tables 1 and 2 show the elemental abundance in the Huelva PG. Calcium and S are the  
200 main elements, as gypsum may account for up to 95% of the mineral mass. The  
201 phosphate rock used in the manufacturing of phosphoric acid in the Huelva fertilizer plant  
202 was sedimentary, composed mainly of carbonate fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>, CO<sub>3</sub>)<sub>3</sub>(F, O),  
203 which is also called francolite and may contain diverse impurities as crystallographic  
204 substitutions within the phosphate mineral (Lottermoser 2010). The main substitutes for  
205 Ca, F and P within the francolite lattice are Na, Sr, Mg and sulfate (Rutherford et al.,  
206 1994), which is reflected in the Huelva PG's high concentrations of Na (3190 mg/kg), Sr  
207 (542 mg/kg) and, to a lesser extent, Mg (52 mg/kg). However, these elements could also  
208 come from seawater, which was used as the carrier phase to transport the PG sludge  
209 from the fertilizer plant to the stacks.

210 Sedimentary phosphate rocks usually contain high concentrations of REE, U and Th  
211 (Jarvis et al. 1994); these may have been transferred to the PG, as evidenced by the  
212 high concentrations of HREEs (178 mg/kg), LREEs (167 mg/kg) and, to a lesser extent,  
213 U (45 mg/kg) and Th (1.6 mg/kg) found in the Huelva PG (Tables 1 and 2). The most  
214 abundant REE in the PG was Y (128 mg/kg), followed by the lighter La (62 mg/kg), Nd  
215 (48 mg/kg) and Ce (36 mg/kg; Table 1). The concentrations of other REEs were below  
216 20 mg/kg. However, francolite may also contain physical inclusions (e.g. quartz, clays,  
217 iron oxyhydroxides, halides, organic matter and sulfides) that can lead to a variety of  
218 crustal elements such as Si (2186 mg/kg), Al (1379 mg/kg) or K (50 mg/kg) and heavy

219 metals and metalloids such as Fe (52 mg/kg), Cu (41 mg/kg), Zn (11 mg/kg), Cr, V (5.1  
220 mg/kg), Ni (4.5 mg/kg), Cd (1.3 mg/kg), Nb (1.4 mg/kg), Mo and As (1.0 mg/kg; Table 2).

### 221 **3.2. Investigation of leaching methods applied to PG**

222 Figure 2A shows the leaching efficiency for REEs, Sc, Th and U related to the different  
223 aqueous solutions used. The highest leaching efficiency for both HREEs and LREEs  
224 was reached when leaching was performed in 3 M HNO<sub>3</sub> (86% and 82% of the total,  
225 respectively), while lower values were achieved using 0.5 M H<sub>2</sub>SO<sub>4</sub> (58% and 46%,  
226 respectively). However, these values are noticeably higher than those obtained by  
227 Rychkov et al. (2018) with the same H<sub>2</sub>SO<sub>4</sub> concentration, which is attributed to the  
228 preferential partitioning of REE in gypsum crystals over other minor phases in the studied  
229 PG samples. Proton concentration in the leaching solution may be one of the most  
230 important factors influencing REE efficiency, as it can lead to the dissolution of REE-  
231 hosting minerals. However, the REE extraction was not linear with H<sup>+</sup> concentration,  
232 which suggests that other factors (e.g. the different solubility of REE-hosting minerals,  
233 complexing, re-precipitation reactions, etc.) control the solubility of REE once dissolved  
234 in acid conditions. This accords with Rychkov et al. (2018), who reported an REE  
235 extraction efficiency of only around 10% using 3 M instead of 0.5 M H<sub>2</sub>SO<sub>4</sub> concentration.

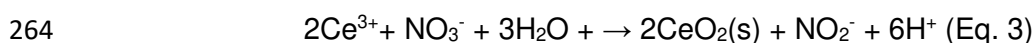
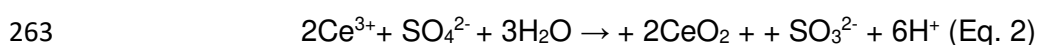
236 For other valuable metals such as Sc, which was almost entirely leached from PG using  
237 both acid solutions (around 99%; Fig. 2A), and Th (88% and 78% in HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>,  
238 respectively), good recovery rates were also achieved. However, U was barely extracted  
239 from PG using both dilute acids (21% for 3 M HNO<sub>3</sub> and 10% for 0.5 M H<sub>2</sub>SO<sub>4</sub>).

240 Lower REE recovery rates from PG were obtained by adding DTPA to both 5 mM HNO<sub>3</sub>  
241 (22% and 18%, respectively) and H<sub>2</sub>SO<sub>4</sub> (16% and 13%). Also, for Sc, the efficiency  
242 obtained by adding DTPA was considerably lower than that obtained with dilute  
243 solutions, irrespective of the acid used (43% and 36% with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>,  
244 respectively). However, the lowest rates using DTPA solutions were obtained for U

245 (<5%) and Th (<2%). The lower extraction rates obtained with DTPA may be related to  
246 the nature of element binding in PG minerals; elements are incorporated into the  
247 structure of minerals rather than attached to their surface by sorption or ion-exchange  
248 processes.

249 In the case of leaching with DW, the concentration of REE in DW was below the  
250 equipment's detection limit. Small amounts of Sc, U and Th (14%, 2.8% and 0.1%,  
251 respectively; Fig. 3A) were also released with DW, indicating the low occurrence of these  
252 elements in the easily-soluble fraction of the mineral assemblage.

253 Considering individual REEs (Fig. 2B-D), leaching with 3 M HNO<sub>3</sub> achieved efficiencies  
254 higher than 80% for all elements except Ce (67% of total), while lower values were  
255 recorded with 0.5 M H<sub>2</sub>SO<sub>4</sub> (from 62% to 38%). In the latter case, the lowest values were  
256 also observed for Ce, while the highest were obtained for the heavier elements (Yb, Lu  
257 and Y; Fig. 2D). The lower leaching performance of Ce could be attributed to the  
258 oxidation of Ce<sup>3+</sup> to Ce<sup>4+</sup>. The use of oxidizing acid solutions (i.e. 3 M HNO<sub>3</sub> and 0.5 M  
259 H<sub>2</sub>SO<sub>4</sub>) may enhance the oxidation and subsequent precipitation of the Ce<sup>4+</sup> oxide  
260 retained in the PG (Eqs. 2 and 3). The opposite trend was observed using DTPA diluted  
261 into the acids. These solutions not only caused the lowest values of REE release (from  
262 26% to 11%), but decreasing efficiency was also observed for the HREE group (Fig. 2D).



265 Regarding impurities, the use of HNO<sub>3</sub> promoted a higher gypsum dissolution rate  
266 compared to H<sub>2</sub>SO<sub>4</sub>. Around 63% of the Ca was leached with 3 M HNO<sub>3</sub>, while less than  
267 6% was released using 0.5 M H<sub>2</sub>SO<sub>4</sub> (Fig. 3A). The high concentration of the SO<sub>4</sub><sup>2-</sup> anion  
268 in the H<sub>2</sub>SO<sub>4</sub> leaching solution may limit the solubility of gypsum. However, adding  
269 chelating agents to H<sub>2</sub>SO<sub>4</sub> and a lower SO<sub>4</sub><sup>2-</sup> concentration (around 5 mM vs 0.5 M)  
270 caused a higher Ca release (15% of total) than that obtained with 0.5 M H<sub>2</sub>SO<sub>4</sub>.

271 A similar case was observed for Sr and Ba, which usually replace Ca in the gypsum  
272 lattice. Around 77% and 41% of both elements were released with 3 M HNO<sub>3</sub> and only  
273 18% and 1.0% were mobilized with 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (Fig. 4A). The high SO<sub>4</sub><sup>2-</sup>  
274 concentration in the leaching solution also limited the solubility of Pb. Thus, around 60%  
275 of Pb was released with 3 M HNO<sub>3</sub>, while less than 11% was extracted with 0.5 M H<sub>2</sub>SO<sub>4</sub>,  
276 a lower value than those obtained with DTPA solutions (27% and 15%, respectively).  
277 Appreciable differences in the rate of P release were also observed depending on the  
278 acid used. Around 84% of P was dissolved using 3 M HNO<sub>3</sub>, but only 25% was dissolved  
279 with 0.5 M H<sub>2</sub>SO<sub>4</sub>. These differences may be related to the increasing dissolution rates  
280 from the acidity of phosphate present in the PG as minor minerals (although this was not  
281 observed by SEM).

282 The addition of DTPA to dilute acids provided similar leaching efficiencies (or even  
283 higher) than those obtained with more concentrated acids for different metals such as  
284 Mg, Mn, Cu and Zn, although with different leaching percentages (Fig. 3B). More than  
285 80% of Mg, around 60% of Mn and lower values for Zn (32-42%) and Cu (less than 10%)  
286 were observed. However, the high values obtained with DW suggest the efflorescent  
287 salts originated from liquid inclusions trapped in the lattice interstice as the main  
288 contributor of these metals. Arsenic also seems to be linked to efflorescent salts; around  
289 75% was leached with DW and around 90% using other leaching solutions (Fig. 3B). The  
290 presence of these elements (i.e. Cu, Zn, As and Mn) in PG as liquid inclusions could be  
291 related to the sulfuric acid used during phosphoric acid manufacturing in Huelva, which  
292 was mainly obtained by pyrite roasting and SO<sub>2</sub> recovery, which may lead to the  
293 accumulation of these elements as impurities (Macías et al., 2017)

294 Although considerable amounts of Fe and, to a lesser extent, Se and Al were released  
295 from the water-soluble fraction, the leaching of these elements may be governed by acid  
296 concentration: the greater the acidity, the higher the release into the liquor solution (Fig.  
297 3C). Higher releases were observed for Co and V using 3 M HNO<sub>3</sub> (33% and 20%,

298 respectively) than with the rest of leaching solutions. In contrast, adding DTPA to dilute  
299 acid solutions yielded higher release rates than those obtained with 0.5 M H<sub>2</sub>SO<sub>4</sub> (and  
300 in some cases with 3 M HNO<sub>3</sub>) for Cd, Cr, Ni, Mo and Nb (Fig. 3D).

### 301 **3.3. Effect of time on acid leaching efficiency**

302 Table 1 shows the effect of time on REE leaching efficiency using 0.5 M H<sub>2</sub>SO<sub>4</sub> and 3 M  
303 HNO<sub>3</sub>. Note the progressive improvement in leaching performance with time for both  
304 acids. Average increases of 4.0%, 6.9% and 7.4% in REE leaching rates were obtained  
305 at 4, 6 and 8h for 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively. The REE leaching rates with 3 M HNO<sub>3</sub>  
306 were slightly higher than those obtained when 0.5 M H<sub>2</sub>SO<sub>4</sub> was used at 4 and 8h (5.4%  
307 and 8.1%, respectively), but lower at 6h (5.9%; Table 1). Nevertheless, a prolonged  
308 reaction time also enhanced the release of impurities from PG (Table 2). Average  
309 increases of 1.0%, 3.0% and 6.1% were obtained by raising the reaction time of PG with  
310 0.5 M H<sub>2</sub>SO<sub>4</sub> from 2 to 4, 6 and 8h, respectively. In contrast, respective increases of  
311 3.2%, 2.6% and 6.4% were obtained for the same time increases with 3 M HNO<sub>3</sub>.

312 The different leaching efficiencies for Ca obtained with 0.5 M H<sub>2</sub>SO<sub>4</sub> and 3 M HNO<sub>3</sub>  
313 reflects the different solubilities of gypsum with both acidic solutions. However, the  
314 maximum values were not recorded at the end of the experiment, especially for of 3 M  
315 HNO<sub>3</sub>; the maximum value (71%; Table 2) was obtained at 2h, and it decreased  
316 afterwards. This is attributed to a possible re-precipitation of gypsum during the leaching  
317 experiment. This is supported by the images obtained by SEM, in which particles of re-  
318 precipitated gypsum can be observed at the end of the reaction (Fig. 4).

319 The most striking case was observed for Fe. Around 30% and 46% more Fe were  
320 extracted at 8h than at 2h using 0.5 M H<sub>2</sub>SO<sub>4</sub> and 3 M HNO<sub>3</sub>, respectively. Although  
321 around 40% of Fe is water soluble (Fig. 3C), the progressive dissolution of Fe oxides  
322 contained as minor phases in PG may control the release of Fe upon acid attack. A  
323 similar case was observed for As, which was also present mainly in the water-soluble

324 fraction (around 70%). This element is commonly retained in Fe oxides by sorption (Gault  
325 et al., 2005); thus, the progressive dissolution of these phases with increasing reaction  
326 times increased the leaching efficiency (around 18% for both acids; Table 2). Other  
327 elements whose releases increased with increasing reaction times were Sc (32% and  
328 14%, respectively), Mg (15% and 10%), Th (13% and 10%), Na and Cr (10% and 12%).  
329 This may have been caused by the progressive dissolution of other minor minerals  
330 present in PG such as clays, feldspars or halides. In contrast, other elements such as  
331 Ba, Sr, Cu, Zn, Ni and U did not show significant changes with increasing reaction times.

### 332 **3.4. Minerals hosting rare earth elements (REE) in PGs**

333 The siting of trace elements, metals and metalloids in PG is variable and has been  
334 previously discussed. For instance, the presence of Cd and Sr has been linked to  
335 gypsum by Ca substitutions in the crystal lattice (Rutherford et al., 1994), while U and  
336 Se may be adsorbed onto the surfaces of gypsum and Fe oxyhydroxides, respectively  
337 (Arocena et al., 1995). However, there is controversy as to which minerals host REE in  
338 PG. Some authors, e.g. Borges et al. (2016), have pointed to different minerals, such as  
339 sulfates, carbonates, fluorides and phosphates, as the main carriers of REE. However,  
340 other authors have suggested a single mineral phase as the REE carrier in PG. Gypsum,  
341 the main mineral phase in PG, is commonly considered to be the principal REE carrier  
342 in PG. Habashi (1985) observed the impossibility of recovering all REEs contained in PG  
343 without destroying the PG lattice. However, Walawalkar et al. (2016) did not find REEs  
344 in the surface gypsum using spectroscopy techniques. Lokshin et al. (2002) arrived at  
345 the same result; based on PG leaching with 96% HNO<sub>3</sub>, they concluded that the REEs  
346 are not incorporated in gypsum, but rather exist as separate phases. The results  
347 obtained in this work agree well with these findings: high REE extraction was observed  
348 during H<sub>2</sub>SO<sub>4</sub> leaching despite the low gypsum dissolution (5.7%).

349

350 Shivaramaiah et al. (2016) reported that Eu is not incorporated into the gypsum lattice,  
351 but rather exists as a separate secondary phase, a metastable

352 amorphous/nanocrystalline precipitate of phosphate and sulfate. This finding fits well  
353 with the high phosphate extraction with HNO<sub>3</sub> (84%; Fig. 3) obtained in this study, but  
354 not with H<sub>2</sub>SO<sub>4</sub> (25%; Fig. 3), thus suggesting the presence of other mineral phases  
355 hosting REE. In this context, the presence of F has been scarcely considered in previous  
356 works on REE extraction, despite being abundant in PG and being known to be a strong  
357 REE scavenger in geological matrices (e.g. Ayora et al. 2016; Cánovas et al. 2018b).  
358 During the manufacturing of phosphoric acid, high concentrations of Ca and F are  
359 released, which could precipitate as fluorite, as evidenced by the presence of this mineral  
360 in the raw PG sample (Fig. 1). A detailed examination of leached PG samples under  
361 SEM showed that fluorite originally present in raw PG (Fig. 4) remains in samples after  
362 treatment with both DTPA and water solutions, while in all acid-treated samples (i.e.  
363 HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>), fluorite was absent. Unfortunately, F concentration was not  
364 determined in solution. In order to test the influence of fluoride on REE solubility, we  
365 studied the addition of aluminum, which is commonly used to remove fluoride from  
366 drinking water (George et al., 2010), to leaching solutions. Figure 5 shows the REE  
367 leaching performance by adding different amounts of Al salts (0, 0.25, 0.50 and 0.75  
368 millimoles) to the leaching solutions. As can be seen, far from increasing the REE  
369 leaching efficiency after adding Al salts, the extraction of these elements decreases  
370 progressively during the addition of Al salts. The addition of high concentrations of sulfate  
371 and nitrate ions (the counter-ions of Al cation in salts) into the solution could have limited  
372 the REE solubility. Rare earth double sulfates exhibited poor solubility, even in acidic  
373 aqueous solution (Kul et al., 2008), thus the precipitation of these phases may have  
374 limited the REE solubility. In contrast, REE nitrate salts exhibit a high solubility; therefore,  
375 other factors may have limited the REE solubility after Al salts addition. The precipitation  
376 of other Al minerals from solution may have been responsible for such a decrease.  
377 However, this hypothesis must be tested in detail in further studies.

378

### 379 **3.5. Hydrometallurgical implications**

380 The first stage in REE recovery from waste materials is the leaching of elements from  
381 the solids. To optimize further steps during the hydrometallurgical process (i.e.  
382 concentration, purification and recovery), the choice of the leaching solution should  
383 reflect a balance between the release of target metals and impurities. Among the  
384 leaching solutions tested, acids showed the best REE extraction rates, suggesting that  
385 REE extraction is controlled by acidity. However, although the best REE-leaching  
386 performance was obtained using a 3 M HNO<sub>3</sub> solution (above 80%); a high concentration  
387 of impurities (i.e. Ca, SO<sub>4</sub>, Sr, Cd and Ba) was also obtained in the resulting acid liquor  
388 due to the high dissolution rate of gypsum (around 63%; Table 3). The dissolution of  
389 other minor minerals (i.e. Fe oxides, clays, feldspars, halides and phosphates) present  
390 in PG also yielded high release rates for elements such as Na, Fe, P, Mg, K, Cr, Th and  
391 Sc. However, the use of 0.5 M H<sub>2</sub>SO<sub>4</sub> extracted between 46% and 58% of the REEs  
392 contained in PG, while dissolving less than 6% of the gypsum. Thus, this acid liquor  
393 contained lower concentrations of Ca, Na, Ba, Cd and other impurities than those found  
394 in the 3 M HNO<sub>3</sub> liquor (Table 3). As a result, the extraction with 0.5 M H<sub>2</sub>SO<sub>4</sub> provided  
395 an enriched solution of REEs and other metals of economic interest, while leaving a  
396 relatively clean phosphogypsum (Table 3) that could be used in other applications. For  
397 instance, the Cd content in the original PG was 1.3 mg/kg, which exceeds the threshold  
398 value of 0.7 mg/kg for fertilizers according to Spanish Rules (BOE, 2013). After acid  
399 leaching, the Cd content in the residues was 0.30 mg/kg and 0.87 mg/kg, using 3 M  
400 HNO<sub>3</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively (Table 3). This Cd reduction in PG residues is of  
401 paramount importance due to the high translocation observed in PG-amended soils  
402 (Enamorado et al., 2014).

403 An important parameter in hydrometallurgical processes is the kinetics (contact time) of  
404 leaching solutions. The increase of reaction time from 2h to 8h yielded an improvement  
405 of REE-leaching efficiency of around 8% for both leaching solutions, while promoting an  
406 increase of 6% in the release of impurities. Considering the similar ratio of target-to-



407 unwanted elements, the question to be answered is if this increase of leaching efficiency  
408 is worth the energy and time consumption. Still, further steps are needed to concentrate  
409 and separate REEs. The results obtained in this study show that the washing of PG with  
410 water considerably reduces the contents of impurities in the solid: around 80% of the  
411 total content of Mg, Mn and As, 40% of Fe, and 30% of Cd and Zn. Another possibility,  
412 not tested in this study, is the leaching of the residual PG (containing both target metals  
413 and impurities; Table 3) with recycled acid solutions from subsequent recovery steps. In  
414 light of these results, a potential leaching process could be proposed (Fig. 6). The PG  
415 samples should be initially washed with freshwater to reduce impurities. Then, the  
416 washed PG would be leached with 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions for 2h (Fig. 6). The resulting  
417 acid liquor would be used in further selective recovery schemes for REEs (and other  
418 elements of economic interest). After this step, the acid liquor could be recycled to  
419 improve the REE extraction rates and the removal of impurities. As a result, an REE-rich  
420 acid liquor solution and a clean PG could be obtained (Fig. 6).

### 421 **3.6. Technical and economic limitations of the recovery process**

422 The current policy of PG stacking has been recently questioned due to the cost, safety  
423 and environmental impacts associated with this waste management practice. Therefore,  
424 industry and policymakers must be involved in the search for technological solutions to  
425 recover raw materials from PG.

426 The results obtained in this work only address bench scale leaching tests to extract REE  
427 from PG samples at different reaction times. Thus, improved schemes are needed for  
428 successful upscaling need to fulfill certain technical and economic conditions. In this  
429 sense, the substitution of primary raw material for a secondary one within a circular  
430 economy implies that both the economy and sustainability of the recovery process must  
431 be competitive compared to primary processes. In this sense, as evidenced by this study,  
432 the extraction of REE and other metals of economic interest from PG is technically  
433 feasible; however, difficulties are commonly found during the selective separation of

434 target metals from impurities to obtain a pure product that fulfills market requirements  
435 (Cánovas et al., 2017). From a circular economy perspective, residues after metal  
436 recovery should have improved qualities so that they either can be reutilized as a new  
437 product/material or stored more safely than the original material. In this case, the  
438 leaching of PG with  $H_2SO_4$  generates waste cleaner than the original material (Table 3),  
439 which could lead to its reutilization in agriculture or building.

440 Additionally, the proposed extraction scheme could be competitive in price compared to  
441 primary processes. A rough economic estimation of the proposed process (Fig. 6) can  
442 be done based on the price and quantities of materials used. Around  $1000 \text{ Mm}^3$  of water  
443 and  $13.86 \text{ Mm}^3$  of  $H_2SO_4$  would be needed to treat around  $100 \text{ Mm}^3$  of PG. Considering  
444 unitary values of  $90 \text{ €/m}^3$  of  $H_2SO_4$  and  $0.94 \text{ €/m}^3$  of  $H_2O$ , a total cost of 2187 M € may  
445 be feasible for the whole process. Considering the total value of 6438 M € estimated by  
446 Cánovas et al. (2017) for Sc, Y and REE contained in the Huelva PG deposit (based on  
447 London Metal Market prices and market corrections), the proposed method could be  
448 considered technically and economically effective.

## 449 **Conclusions**

450 This paper provides information about leaching of PG with acids and chelating agents in  
451 order to study the release of target metals (i.e. REEs) and impurities. This information is  
452 of paramount importance in further hydrometallurgical processing steps in order to  
453 recover REEs contained in these wastes. The possibility of exploitation of a secondary  
454 source of REEs may have a great impact on the economies of countries where primary  
455 sources of REEs is lacking.

456 The best REE leaching performance was obtained using a solution 3 M  $HNO_3$  (above  
457 80%) which caused a dissolution rate of 63% of gypsum originally present. The use of  
458 0.5 M  $H_2SO_4$  extracted between 46 and 58% of REE contained in PG, dissolving less  
459 than 6% of gypsum. The higher mineral dissolution rate obtained with 3 M  $HNO_3$  caused

460 not only a greater release of target elements but also of impurities such as Ca, SO<sub>4</sub>, Sr,  
461 Cd, P and Ba into the resulting liquor. The increase of reaction time from 2h to 8h yielded  
462 an improvement of REE leaching efficiency of around 8% for both leaching solutions  
463 while promoting an increase of 6% in the release of impurities. The lower leaching  
464 performance for REE with both acids was observed for Ce, which could be attributed to  
465 the oxidation of Ce<sup>3+</sup> and subsequent precipitation of Ce<sup>4+</sup> oxide. On the other hand, the  
466 addition of chelating agents provided poor REE leaching performances (from 13 to 22%)  
467 suggesting that sorption processes may play a minor role in REE mobility.

468 The pretreatment of PG with water would remove a significant fraction of impurities  
469 without depletion of REEs; around 80% of Mg, Mn and As, 40% of Fe, and 30% of Cd  
470 and Zn of the total content. These elements may be mainly contained in highly-soluble  
471 minerals such as sulfate or chloride, however other impurities remain in the PG due to  
472 their presence in less soluble minerals such as Fe and Mn oxide, fluoride or phosphate.  
473 Mineralogical and chemical evidences point at phosphate and fluoride minerals as the  
474 main REE carriers phase in PG. However, the role of F in the mobility of REE needs to  
475 be addressed in detail in further studies. Optimized leaching methods of PG to selectively  
476 dissolve both minerals are needed to overcome the technical and economic barriers of  
477 REE recovery from PG.

478

#### 479 **Acknowledgements**

480 This study was funded by the European Union's Seventh Framework Program, Marie  
481 Skłodowska-Curie actions and the Ministry of Economy, Innovation, Science and  
482 Employment of the Junta de Andalucía by the program TalentHub (COFUND - Grant  
483 Agreement 291780). C.R Cánovas was funded by the Talent Consolidation Program of  
484 the University of Huelva. The authors are also very grateful to the funding support for the  
485 Committee of Experts on "The environmental diagnosis and the proposal of measures

486 of restoration of the phosphogypsum stacks of Huelva”, appointed by the City Hall of  
487 Huelva. We would also thank to Dra Cecília Maria Villas Bôas de Almeida (co-Editor in  
488 chief), Dra Maria Teresa Moreira (Associate Editor) and five anonymous reviewers that  
489 notably improved the quality of the original manuscript.

490

#### 491 **Conflict of Interest Statement**

492 Conflict of Interest – None

493

#### 494 **References**

495 Arocena, J.M., Rutherford, P.M., Dudas, M.J., 1995. Heterogeneous distribution of trace  
496 elements and fluorine in phosphogypsum by-product. *Sci. Total Environ.* 162(2-3),  
497 149-160.

498 Ayora, C., Macias, F., Torres, E., Lozano, A., Carrero, S., Nieto, J.M., Perez-Lopez, R.,  
499 Fernandez-Martinez, A., Castillo-Michel, H., 2016. Recovery of rare earth elements  
500 and yttrium from passive-remediation systems of acid mine drainage. *Environ. Sci.*  
501 *Technol.* 50, 8255–8262. <https://doi.org/10.1021/acs.est.6b02084>.

502 Bandara H.M.D., Darcy J.W., Apelian D., Emmert M.H., 2014. Value analysis of  
503 neodymium content in shredder feed: toward enabling the feasibility of rare earth  
504 magnet recycling. *Environ. Sci. Technol.* 48, 6553–6560. doi: 10.1021/es405104k.

505 Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Yang, Y. Walton, A., Buchert,  
506 M., 2013. Recycling of rare earths: a critical review. *J Clean. Prod.* 51, 1-22.  
507 <http://dx.doi.org/10.1016/j.jclepro.2012.12.037>.

508 Binnemans, K., Jones P.T., 2014. Perspectives for the recovery of rare earths from end-  
509 of-life fluorescent lamps. *J. Rare Earths* 32, 195-200. [https://doi.org/10.1016/S1002-](https://doi.org/10.1016/S1002-0721(14)60051-X)  
510 [0721\(14\)60051-X](https://doi.org/10.1016/S1002-0721(14)60051-X).

511 BOE, 2013. Real Decreto 506/2013, de 28 de junio, sobre productos fertilizantes. BOE  
512 164, de 10 de julio de 2013. BOE-A-2013-7540.  
513 <https://www.boe.es/eli/es/rd/2013/06/28/506/con>.

514 Bolívar J.P., García-Tenorio R., Más J.L., Vaca F., 2002. Radioactive impact in  
515 sediments from an estuarine system affected by industrial waste releases. *Environ.*  
516 *Int.* 27, 639–645. [https://doi.org/10.1016/S0160-4120\(01\)00123-4](https://doi.org/10.1016/S0160-4120(01)00123-4).

- 517 Borges, R.C., Fávaro, D.I.T., Caldas, V.G., Lauria, D.C., Bernedo, A.V.B., 2016.  
518 Instrumental neutron activation analysis, gamma spectrometry and geographic  
519 information system techniques in the determination and mapping of rare earth  
520 element in phosphogypsum stacks. *Environ. Earth Sci.* 75, 705.  
521 <https://doi.org/10.1007/s12665-016-5468-x>.
- 522 Cánovas, C.R., Pérez-López, R., Macías, F., Chapron, S., Nieto, J.M., Pellet-Rostaing,  
523 S., 2017. Exploration of fertilizer industry wastes as potential source of critical raw  
524 materials. *J. Clean. Prod.* 143, 497–505.  
525 <https://doi.org/10.1016/j.jclepro.2016.12.083>.
- 526 Cánovas, C.R., Macías, F., Pérez-López, R., Basallote, M.D., Millán-Becerro, R., 2018a.  
527 Valorization of wastes from the fertilizer industry: Current status and future trends. *J.*  
528 *Clean. Prod.* 174, 678-690. <https://doi.org/10.1016/j.jclepro.2017.10.293>.
- 529 Cánovas C.R., Macías F., Pérez-López, R., Nieto, J.M. (2018b). Mobility of rare earth  
530 elements, yttrium and scandium from a phosphogypsum stack: Environmental and  
531 economic implications. *Sci. Total Environ.* 618, 847-857.  
532 <https://doi.org/10.1016/j.scitotenv.2017.08.220>.
- 533 Chitry, F., Pellet-Rostaing, S., Gozzi, C., Lemaire, M., 2001. Separation of  
534 lanthanides(III) by nanofiltration-complexation in aqueous medium. *Separ. Sci.*  
535 *Technol.* 36, 605-618. <https://doi.org/10.1081/SS-100102949>.
- 536 El Zrelli, R., Courjault-Radé, P., Rabaoui, L., Castet, S., Michel, S., Bejaoui, N., 2016.  
537 Heavy metal contamination and ecological risk assessment in the surface sediments  
538 of the coastal area surrounding the industrial complex of Gabes city, Gulf of Gabes.  
539 *SE Tunisia. Mar. Pollut. Bull.* 101, 922-929.  
540 <http://dx.doi.org/10.1016/j.marpolbul.2015.10.047>.
- 541 Enamorado, S., Abril, J.M., Delgado, A., Más, J.L., Polvillo, O., Quintero, J.M., 2014.  
542 Implications for food safety of the uptake by tomato of 25 trace-elements from  
543 phosphogypsum amended soil from SW Spain. *J. Hazard. Mater.* 266, 122-131.  
544 <https://doi.org/10.1016/j.jhazmat.2013.10.12.1019>.
- 545 European Commission, 2017. Study on the review of the list of Critical Raw Materials:  
546 executive summary. European Commission, Directorate-General for Internal Market,  
547 Industry, Entrepreneurship and SMEs ([https://publications.europa.eu/en/publication-](https://publications.europa.eu/en/publication-detail/-/publication/08fdab5f-9766-11e7-b92d-01aa75ed71a1/language-en)  
548 [detail/-/publication/08fdab5f-9766-11e7-b92d-01aa75ed71a1/language-en](https://publications.europa.eu/en/publication-detail/-/publication/08fdab5f-9766-11e7-b92d-01aa75ed71a1/language-en);  
549 accessed July 25<sup>th</sup> 2018).
- 550 Gault, A.G., Cooke, D.R., Townsend, A.T., Charnock, J.M., Polya, D.A., 2005.  
551 Mechanisms of arsenic attenuation in acid mine drainage from Mount Bischoff,  
552 Western Tasmania. *Sci. Total Environ.* 345, 219–228.  
553 <http://dx.doi.org/10.1016/j.scitotenv.2004.10.030>.

- 554 George, S., Pandit, P., Gupta, A.B., 2010. Residual aluminium in water defluoridated  
555 using activated alumina adsorption—modeling and simulation studies. *Water Res.* 44  
556 (10), 3055–3064. <https://doi.org/10.1016/j.watres.2010.02.028>.
- 557 Habashi F., 1985. The recovery of the lanthanides from phosphate rock. *J. Chem.*  
558 *Technol. Biotechnol. A* 35, 5-14.
- 559 Innocenzi V., De Michelis I., Kopacek B., Veglio, F., 2014. Yttrium recovery from primary  
560 and secondary sources: a review of main hydrometallurgical processes. *Waste*  
561 *Manag.* 34, 1237-1250. <http://dx.doi.org/10.1016/j.wasman.2014.02.010>.
- 562 Jarvis, I., Burnett, W.C., Nathan, Y., Almbaydin, F.S.M., Attia, A.K.M, Castro, L.N.,  
563 Flicoteaux, R., Hilmy, M.E., Husain, V., Qutawnah, A.A., Serjani, A., Zanin, Y.N.,  
564 1994. Phosphorite geochemistry: state-of-the-art and environmental concerns. *Ecl*  
565 *Geol Helv* 87, 643–700.
- 566 Kul, M., Topkaya, Y., Karakaya, İ. (2008). Rare earth double sulfates from pre-  
567 concentrated bastnasite. *Hydrometallurgy* 93(3–4), 129-135.  
568 <https://doi.org/10.1016/j.hydromet.2007.11.008>.
- 569 Kulczycka, J., Kowalski, Z., Smol, M., Wirth, H., 2016. Evaluation of the recovery of rare  
570 earth elements (REE) from phosphogypsum waste case study of the WIZOW  
571 chemical plant (Poland). *J. Clean. Prod.* 113, 345-354.  
572 <https://doi.org/310.1016/j.jclepro.2015.1011.1039>.
- 573 Lokshin, E.P, Vershkova, Y.A, Vershkov, B.V, Tareeva, O.A, 2002. Leaching of  
574 Lanthanides from Phosphohemihydrate with Nitric Acid. *Russian Journal of Applied*  
575 *Chemistry* 75 (11), 1753-1759
- 576 Lottermoser, B.G., 2010. *Mine wastes: Characterization, treatment, environmental*  
577 *impacts*. Springer Berlin Heidelberg. Second Edition, 1-301 p.
- 578 Macías, F., Cánovas, C.R., Cruz-Hernández, P., Carrero, S., Asta, M.P., Nieto, J.M.,  
579 Pérez-López, R., 2017. An anomalous metal-rich phosphogypsum: characterization  
580 and classification according to international regulations. *J. Hazard. Mater.* 331, 99–  
581 108. <https://doi.org/10.1016/j.jhazmat.2017.02.015>.
- 582 Noack, C.W., Perkins, K.M., Callura, J.C., Washburn, N.R., Dzombak, D.A., Karamalidis,  
583 A.K. (2016). Effects of ligand chemistry and geometry on rare earth  
584 elementpartitioning from saline solutions to functionalized adsorbents, *ACS Sustain.*  
585 *Chem. Eng.* 4 (2016) 6115–6124,  
586 <http://dx.doi.org/10.1021/acssuschemeng.6b01549>.
- 587 Pérez-López, R., Nieto, J.M., de la Rosa, J.D., Bolívar, J.P., 2015. Environmental tracers  
588 for elucidating the weathering process in a phosphogypsum disposal site: implications  
589 for restoration. *J. Hydrol.* 529, 1313–1323.

- 590 Preston, J.S., Cole, P.M., Craig, W.M., Feather, A.M., 1996. The recovery of rare earth  
591 oxides from a phosphoric acid by-product.1. Leaching of rare earth values and  
592 recovery of a mixed rare earth oxide by solvent extraction. *Hydrometallurgy* 41, 1-19.
- 593 Rychkov, V.N., Kirillov, E.V., Kirillov, S.V., Semenishchev, V.S., Bunkov, G.M., Botalov,  
594 M.S., Smyshlyayev, D.V., Malyshev, A.S., 2018. Recovery of rare earth elements from  
595 phosphogypsum. *J. Clean. Prod.* 196, 674-681.  
596 <https://doi.org/10.1016/j.jclepro.2018.06.114>.
- 597 Ruan, C., Jingming, X., Peijiong, H., Yongjun, Z., 1995. Recovering RE from leaching  
598 liquor of rare earth ore by extraction. *Transactions of Nonferrous Metals Society of*  
599 *China* 5 (4), 36–40.
- 600 Rutherford, P.M., Dudas, M.J., Samek, R.A., 1994. Environmental impacts of  
601 phosphogypsum. *Sci. Total Environ.* 149, 1-38.
- 602 Saadaoui, E., Ghazel, N., Ben Romdhane, C., Massoudi, N., 2017. Phosphogypsum:  
603 potential uses and problems -a review. *Int. J. Environ. Stud.* 207-233.  
604 <https://doi.org/10.1080/00207233.2017.1330582>
- 605 Sastre, J., Sahuquillo, A., Vidal, M., Rauret, G., 2002. Determination of Cd, Cu, Pb and  
606 Zn in environmental samples: microwave-assisted total digestion versus aqua regia  
607 and nitric acid extraction. *Anal. Chim. Acta* 462, 59–72.  
608 [https://doi.org/10.1016/S0003-2670\(02\)00307-0](https://doi.org/10.1016/S0003-2670(02)00307-0)
- 609 Shivaramaiah, R., Lee, W., Navrotsky, A., Yu, D., Kim, P., Wu, H., Hu, Z., Riman, R.,  
610 Anderko, A., 2016. Location and stability of europium in calcium sulfate and its  
611 relevance to rare earth recovery from phosphogypsum waste. *Am Mineral* 101, Issue  
612 8, 1854-1861. DOI: 10.2138/am-2016-5684.
- 613 Simandl, G.J., 2014. Geology and market-dependent significance of rare earth element  
614 resources. *Miner Deposita* 49, 889-904. DOI 10.1007/s00126-014-0546-z.
- 615 Sorin, A., Favre-Réguillon, A., Pellet-Rostaing, S., Sbaï, M., Szymczyk, A., Fievet, P.,  
616 Lemaire, M., 2005. Rejection of Gd(III) by nanofiltration assisted by complexation on  
617 charged organic membrane: influence of pH, pressure, flux, ionic strength and  
618 temperature. *J. Membrane Sci.*, 267, 41-49.  
619 <https://doi.org/10.1016/j.memsci.2005.05.022>.
- 620 Tayibi, H., Choura, M., López, F.A., Alguacil, F.J., López-Delgado, A., 2009.  
621 Environmental impact and management of phosphogypsum. *J. Environ. Manag.* 90,  
622 2377–2386. <https://doi.org/10.1016/j.jenvman.2009.03.007>.
- 623 Tunsu C., Petranikova, M., Gergorić, M., Ekberg, C., Retegan, T., 2015. Reclaiming rare  
624 earth elements from end-of-life products: a review of the perspectives for urban  
625 mining using hydrometallurgical unit operations. *Hydrometallurgy* 156, 239-258.  
626 <http://dx.doi.org/10.1016/j.hydromet.2015.06.007>.

627 USGS, 2016. Mineral Commodity Summaries 2016. U.S. Geological Survey, 2016,  
628 Mineral commodity summaries 2016: U.S. Geological Survey, 202 p.,  
629 <http://dx.doi.org/10.3133/70140094>.

630 Walawalkar, M., Nichol, C.K., Azimi, G., 2016. Process investigation of the acid leaching  
631 of rare earth elements from phosphogypsum using HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>.  
632 Hydrometallurgy 166, 195–204. <http://dx.doi.org/10.1016/j.hydromet.2016.06.008>.

633

634

### 635 **FIGURE CAPTIONS**

636 **Figure 1.** XRD pattern (A) and SEM images of the PG raw sample (B). Gy: gypsum; Ft:  
637 fluorite.

638 **Figure 2.** Leaching efficiency (with error bars) for REE, Sc, Th and U using different  
639 aqueous solutions: 3 M HNO<sub>3</sub> (red bars), 0.5 M H<sub>2</sub>SO<sub>4</sub> (blue bars), HNO<sub>3</sub> + 0.5 M DTPA  
640 (green bars), H<sub>2</sub>SO<sub>4</sub> + 0.5 M DTPA (black bars) and distilled water (DW, white bars).  
641 Leaching time: 8 h.

642 **Figure 3.** Leaching efficiency (with error bars) for main impurities using different aqueous  
643 solutions: 3 M HNO<sub>3</sub> (red bars), 0.5 M H<sub>2</sub>SO<sub>4</sub> (blue bars), HNO<sub>3</sub> + 0.5 M DTPA (green  
644 bars), H<sub>2</sub>SO<sub>4</sub> + 0.5M DTPA (black bars) and distilled water (DW, white bars). Leaching  
645 time: 8 h.

646 **Figure 4.** SEM images of raw and HNO<sub>3</sub> treated PG samples. Gy: gypsum; Ft: fluorite;  
647 Gy rep: reprecipitated gypsum.

648 **Figure 5.** Effect of the addition of Al salts to the acid leaching solutions (0.5 M H<sub>2</sub>SO<sub>4</sub>  
649 and 3 M HNO<sub>3</sub>) on the REE extraction efficiency.

650 **Figure 6.** Flowsheet of the leaching process proposed based on results obtained in this  
651 study.

652

### 653 **TABLE CAPTIONS**

654 **Table 1.** Effect of leaching time on the release of rare earth elements (REE) and yttrium  
655 in the acid liquor (0.5 M H<sub>2</sub>SO<sub>4</sub> and 3 M HNO<sub>3</sub>).

656 **Table 2.** Effect of leaching time on the release of unwanted elements in the acid liquor  
657 (0.5 M H<sub>2</sub>SO<sub>4</sub> and 3 M HNO<sub>3</sub>).

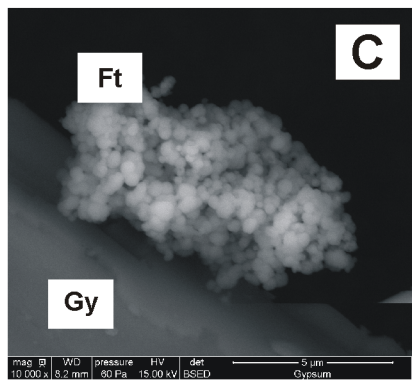
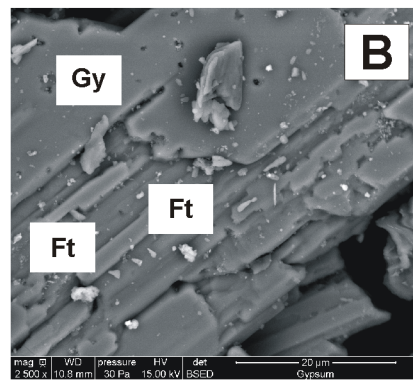
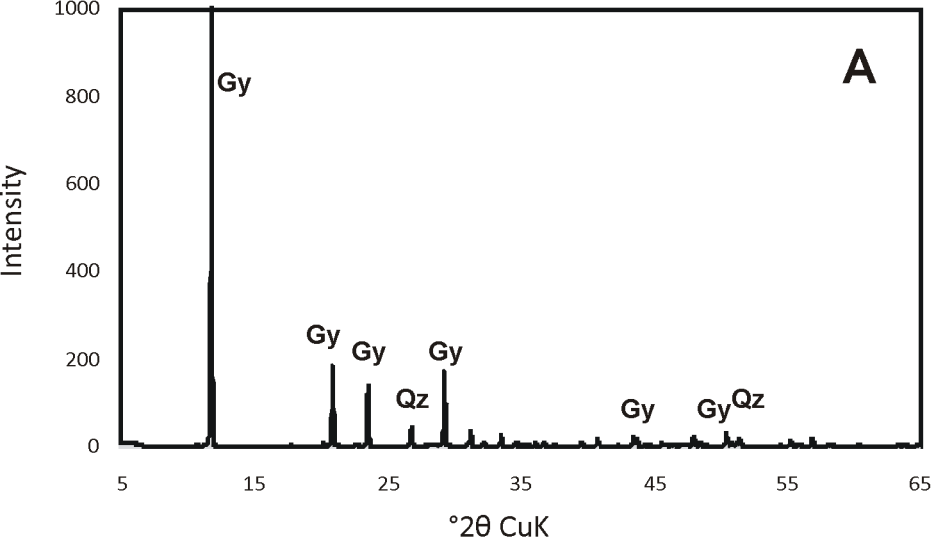
658 **Table 3.** Mass balance of the elements originally present in phosphogypsum during the  
659 leaching process. Elements in mg/kg.

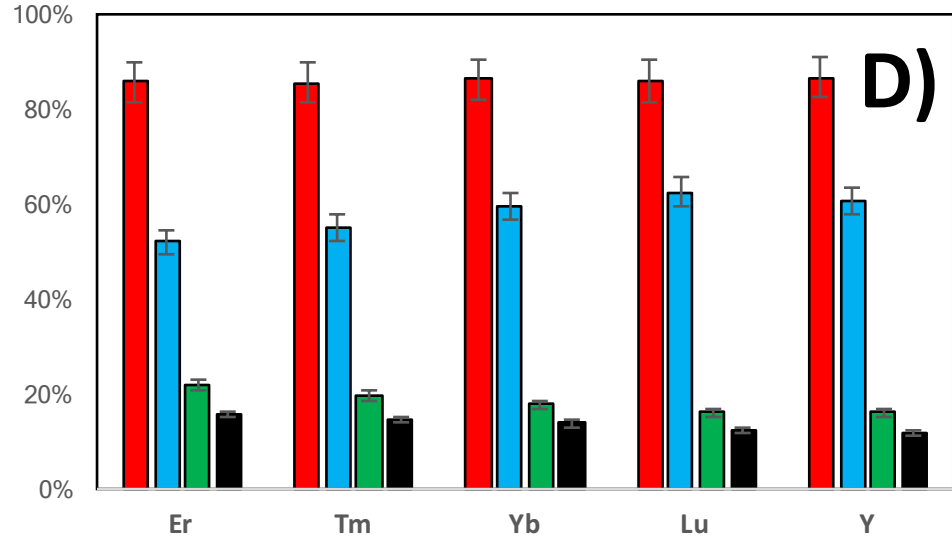
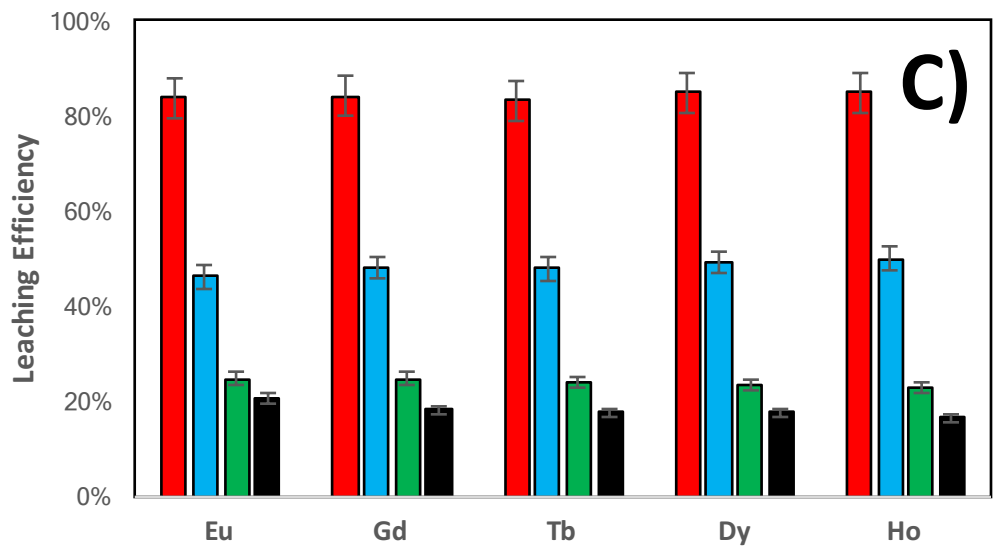
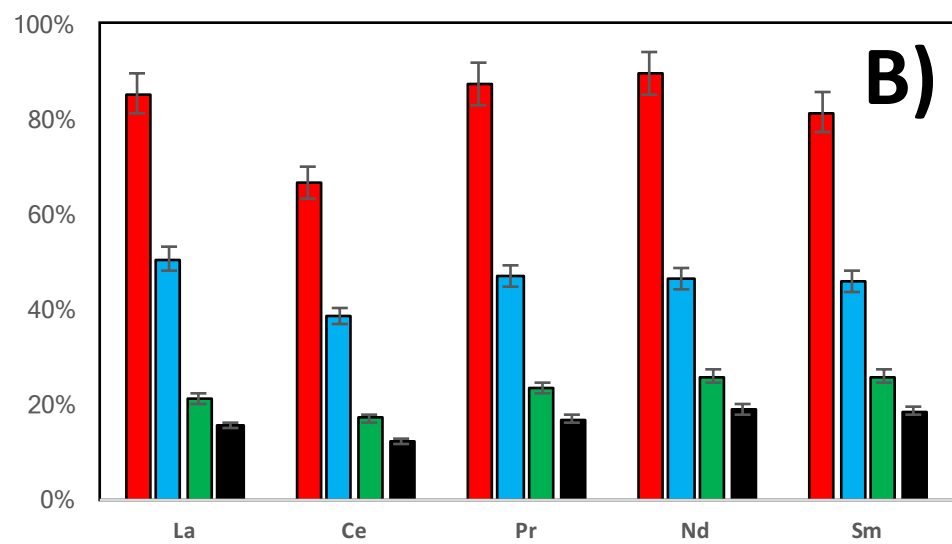
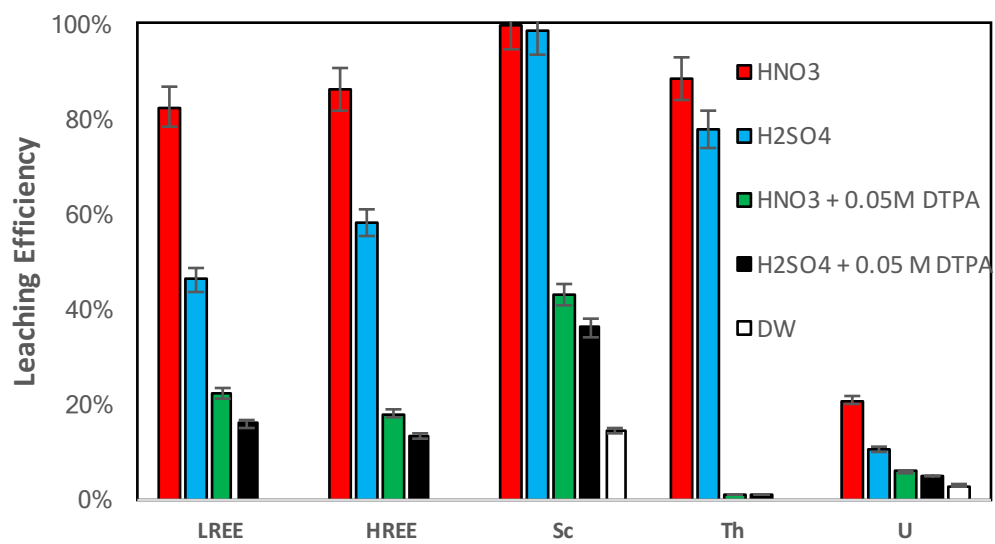
660

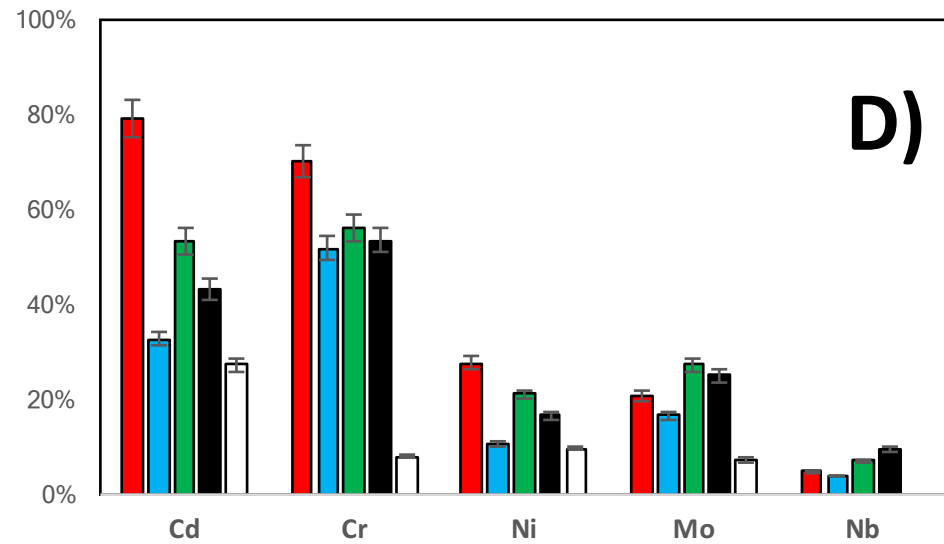
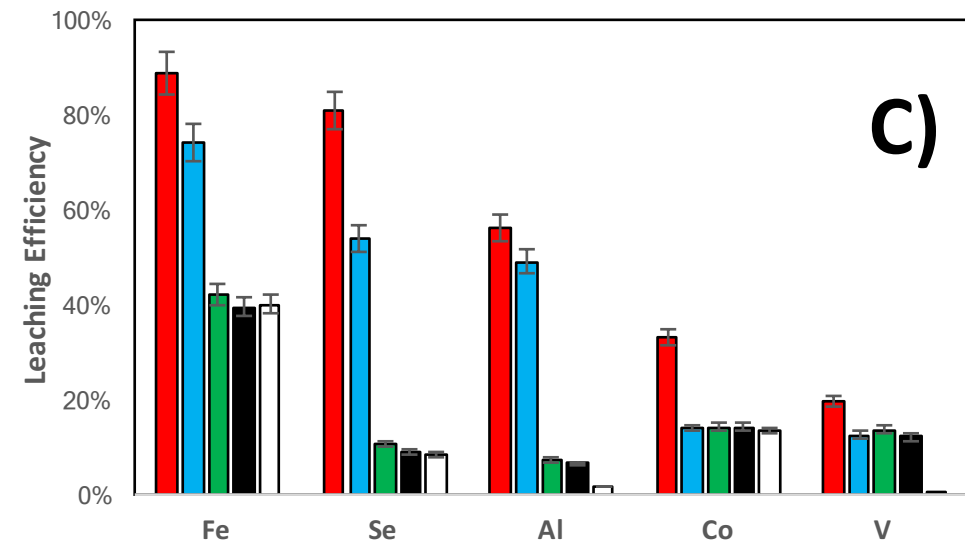
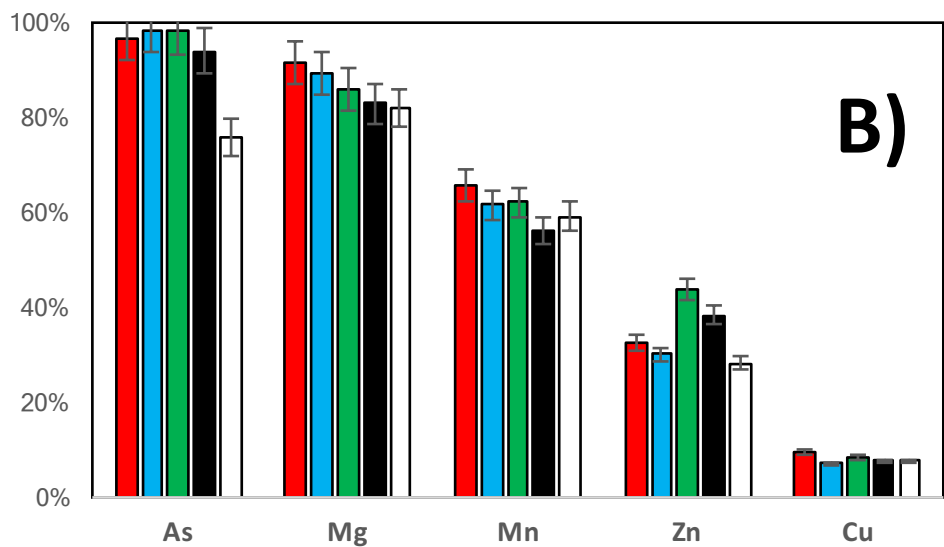
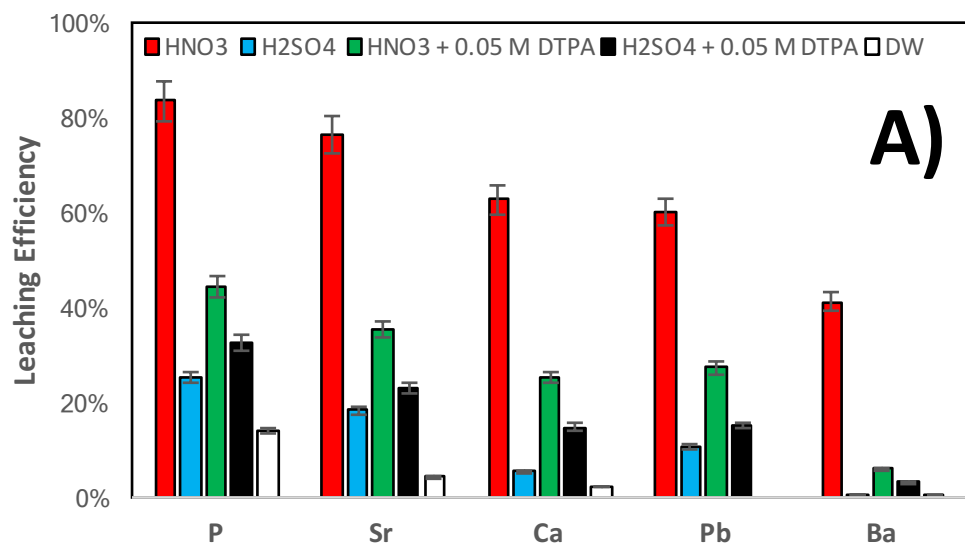
661

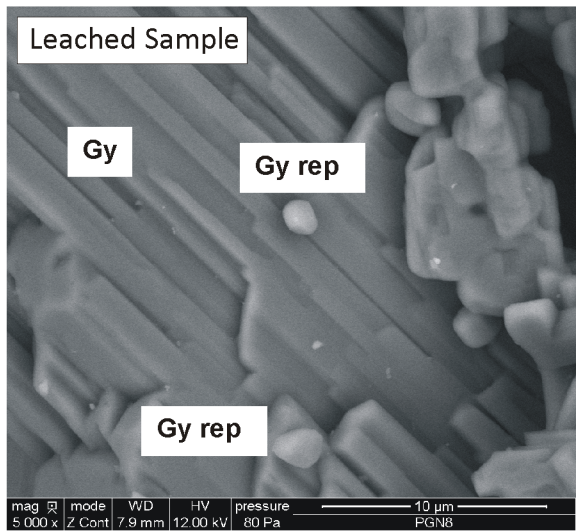
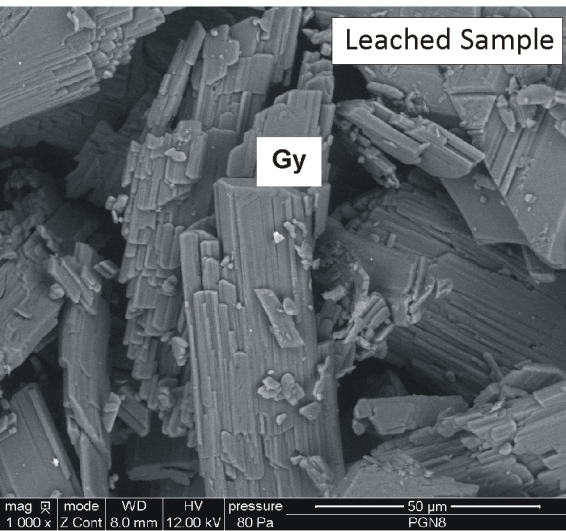
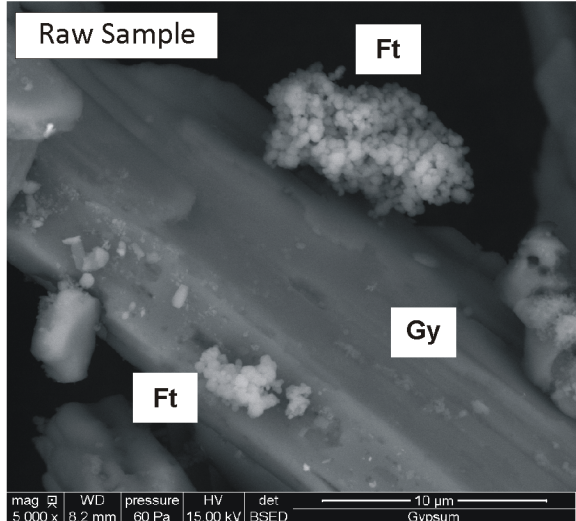
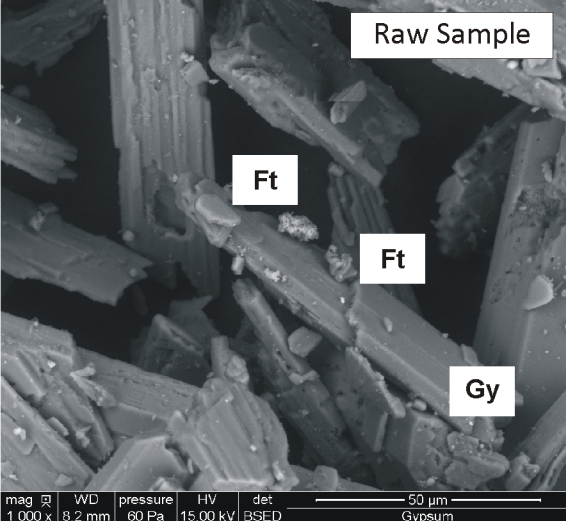
662

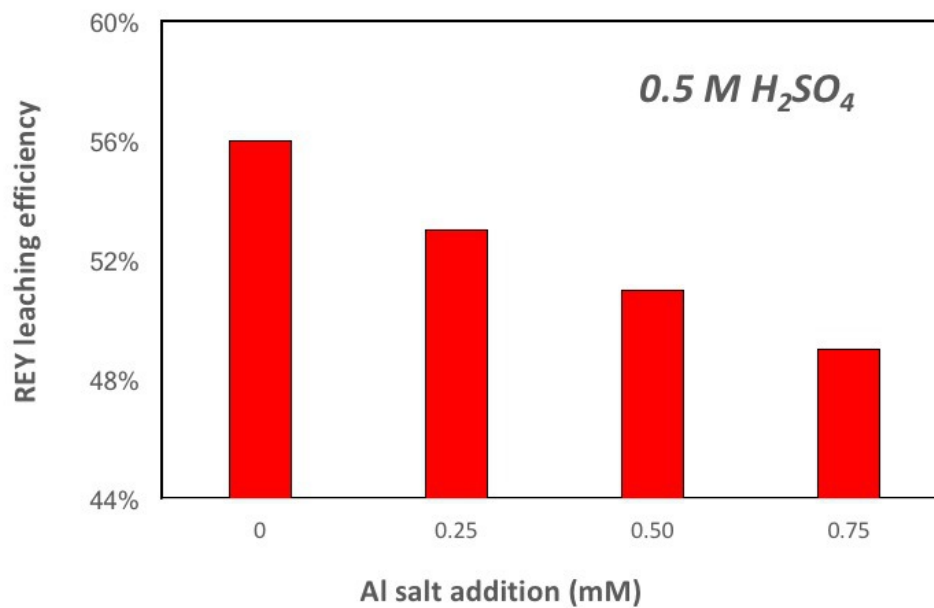
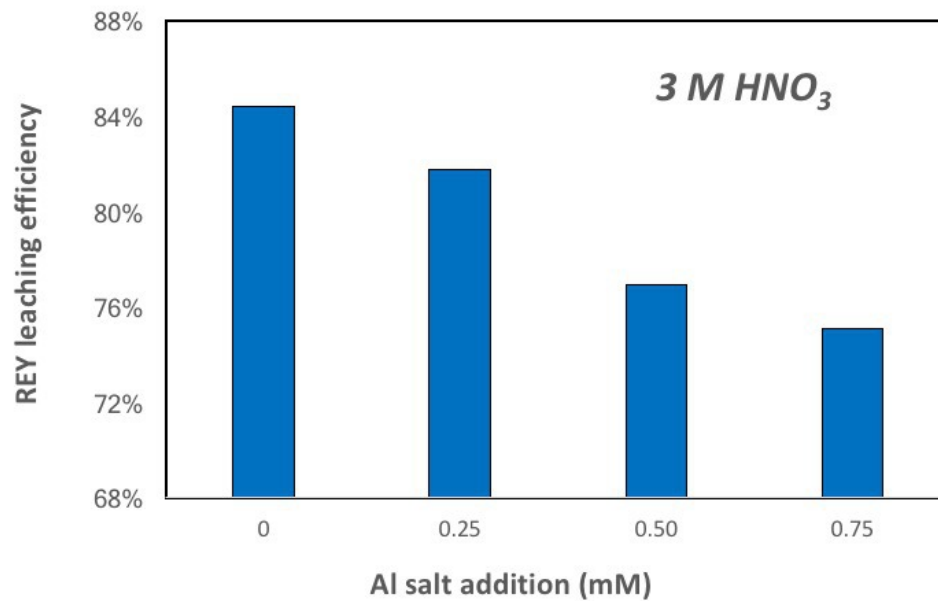


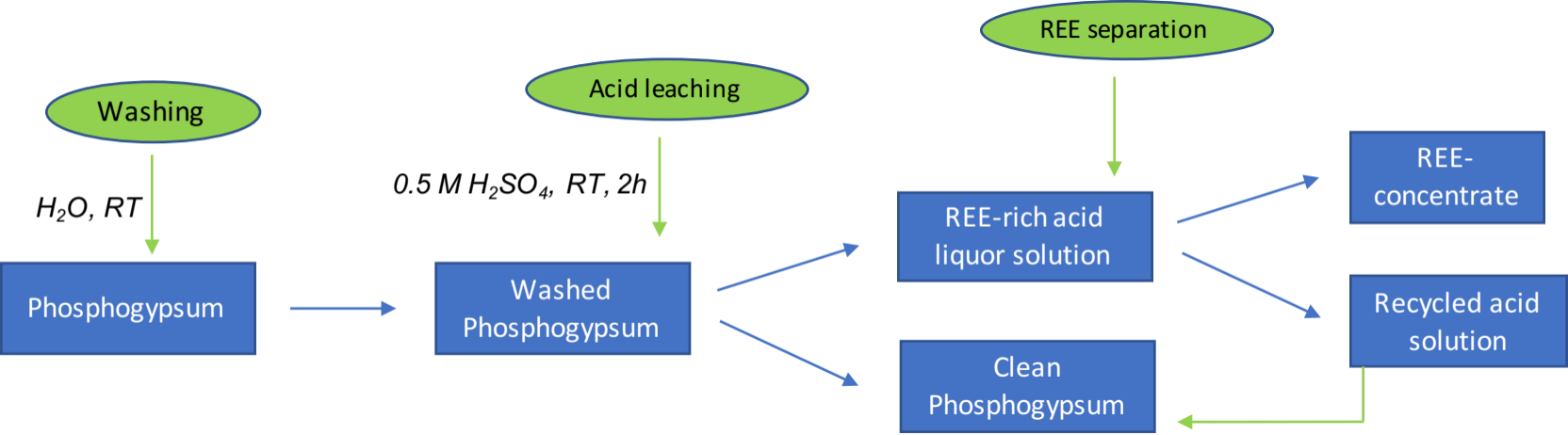












Leaching solution		0.5 M H <sub>2</sub> SO <sub>4</sub>				3 M HNO <sub>3</sub>			
		2h	4h	6h	8h	2h	4h	6h	8h
<i>Element</i>	<i>Total (mg/kg)</i>								
La	62	43%	47%	50%	50%	78%	83%	83%	85%
Ce	36	33%	36%	38%	38%	61%	65%	65%	67%
Pr	11	41%	45%	47%	47%	80%	85%	85%	87%
Nd	48	44%	43%	46%	46%	82%	87%	88%	90%
Sm	9.2	39%	43%	45%	46%	75%	79%	79%	81%
Eu	1.8	39%	43%	46%	46%	75%	81%	81%	84%
Gd	12	41%	45%	48%	48%	77%	81%	82%	84%
Tb	1.8	41%	45%	48%	48%	75%	81%	82%	83%
Dy	13	41%	46%	49%	49%	76%	81%	83%	85%
Ho	3.0	42%	47%	50%	50%	75%	82%	82%	85%
Er	8.9	43%	48%	51%	52%	76%	82%	83%	86%
Tm	1.1	46%	52%	55%	55%	76%	82%	83%	85%
Yb	7.2	50%	56%	59%	60%	78%	84%	84%	86%
Lu	1.0	52%	58%	62%	62%	77%	83%	84%	86%
Y	129	52%	56%	60%	61%	79%	83%	84%	87%
LREE	167	41%	43%	45%	46%	75%	80%	81%	82%
HREE	178	49%	54%	57%	58%	78%	83%	83%	86%
<i>Average Increase</i>		-	4.0%	6.9%	7.4%	-	5.4%	5.9%	8.1%

Leaching solution	Time	0.5 M H <sub>2</sub> SO <sub>4</sub>				3 M HNO <sub>3</sub>			
		2h	4h	6h	8h	2h	4h	6h	8h
<i>Element</i>	<i>Total (mg/kg)</i>								
Ca	264305	5.6%	5.5%	5.7%	5.6%	71%	66%	59%	63%
S	177302	-	-	-	-	63%	55%	51%	55%
Na	3189	90%	92%	100%	100%	84%	87%	88%	96%
P	2660	21%	25%	26%	25%	71%	77%	78%	84%
Al	1379	42%	43%	49%	49%	52%	54%	52%	56%
Sr	542	16%	18%	20%	20%	71%	72%	71%	76%
Ba	95	0.76%	0.77%	0.78%	0.79%	40%	35%	38%	41%
Fe	52	45%	44%	53%	74%	43%	57%	67%	89%
K	50	57%	63%	71%	85%	72%	82%	79%	79%
U	45	8.8%	10%	10%	10%	18%	20%	20%	21%
Mg	43	74%	80%	81%	89%	81%	84%	82%	91%
Cu	41	3.9%	4.7%	5.1%	5.8%	4.0%	4.1%	4.1%	4.5%
Zn	11	25%	29%	28%	29%	25%	31%	30%	24%
Cr	5.1	42%	47%	49%	52%	58%	62%	65%	70%
V	5.0	10%	12%	12%	13%	16%	18%	19%	20%
Ni	4.5	10%	10%	10%	11%	26%	28%	26%	27%
Pb	2.1	8.0%	9.0%	9.6%	11%	51%	56%	58%	60%
Th	1.6	65%	71%	77%	78%	78%	85%	85%	88%
Nb	1.4	2.8%	2.8%	3.4%	3.8%	3.7%	3.4%	4.5%	4.7%
Cd	1.3	28%	32%	31%	33%	69%	75%	77%	79%
Sc	1.0	67%	78%	89%	99%	85%	94%	94%	99%
As	1.0	80%	89%	90%	98%	79%	86%	85%	97%
Mo	0.91	12%	14%	15%	17%	18%	19%	20%	21%
Se	0.90	42%	48%	53%	54%	78%	82%	76%	81%
W	0.46	13%	16%	17%	16%	36%	39%	45%	41%
Sn	0.46	8.6%	8.6%	8.6%	8.6%	10%	10%	11%	12%
Mn	0.29	61%	54%	50%	65%	57%	53%	53%	51%
Co	0.28	14%	14%	14%	14%	31%	33%	29%	33%
Ga	0.26	37%	35%	37%	40%	51%	55%	55%	59%
Be	0.18	22%	22%	22%	22%	64%	78%	75%	79%
Sb	0.12	50%	55%	58%	64%	51%	55%	55%	72%
<i>Average Increase</i>		-	1.0%	3.0%	6.1%	-	3.2%	2.6%	6.4%



---

	<u>Phosphogypsum</u>	<u>0.5 M H<sub>2</sub>SO<sub>4</sub></u>		<u>3 M HNO<sub>3</sub></u>		<u>Fertilizer</u>
		<u>Liquor solution</u>	<u>Residue</u>	<u>Liquor solution</u>	<u>Residue</u>	<u>Limit value</u>
<i>Weight (g)</i>	1000	-	943	-	370	
Ca	264305	14881	249423	165719	98586	
Na	3189	3189	0	3074	115	
P	2660	674	1986	2226	434	
Al	1379	677	703	776	604	
Sr	542	110	432	410	132	
Ba	95	0.97	94	39	56	
Fe	52	38	14	46	6.0	
K	50	42	8.0	40	10	
U	45	5.0	40	9	36	
Mg	43	38	5.0	39	4.0	
Cu	41	3.0	38	2.0	39	70
Zn	11	3.3	7.7	2.7	8.3	200
Cr	5.1	2.6	2.5	3.6	1.5	70
V	5.0	0.60	4.4	1.0	4.0	
Ni	4.5	0.50	4.0	1.2	3.3	25
Pb	2.1	0.20	1.9	1.3	0.80	45
Th	1.6	1.2	0.40	1.4	0.20	
Nb	1.4	0.10	1.3	0.10	1.3	
Cd	1.3	0.43	0.87	1.0	0.30	0.7
Sc	1.0	0.99	0.01	0.99	0.01	
As	1.0	0.98	0.02	0.96	0.04	
Mo	0.91	0.15	0.76	0.19	0.72	
Se	0.90	0.49	0.41	0.73	0.17	
W	0.46	0.07	0.39	0.19	0.27	
Sn	0.46	0.04	0.42	0.05	0.41	
Mn	0.29	0.19	0.10	0.15	0.14	
Co	0.28	0.04	0.24	0.09	0.19	
Ga	0.26	0.10	0.16	0.15	0.11	
Be	0.18	0.04	0.14	0.14	0.04	
Sb	0.12	0.08	0.04	0.09	0.03	

---