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

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Abstract

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

study could contribute to optimizing recovery methods to extract rare earth elements from phosphogypsum worldwide, thus helping achieve the goals of the circular economy.

Keywords: recycling; metal recovery; hydrometallurgy; raw materials; secondary sources.

1. Introduction

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

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

promising secondary sources is End-of-Life products containing high concentrations of REEs, such as lamps or magnets. Thus, much research has recently been done on the urban mining of these products (e.g. Bandara et al., 2014; Binnemans and Jones, 2014; Binnemans et al. 2013; Innocenzi et al., 2014; Tunsu et al., 2015). However, much less attention has been paid to industrial landfilled stocks, which contain lower REE concentrations but have huge volume. One of the most significant examples is the unwanted by-products of fertilizer industries, such as phosphogypsum (PG). For this reason, these wastes are considered a promising source of REEs (e.g. Cánovas et al., 2017; Kulczycka et al., 2016; Rychkov et al., 2018). The fertilizer industry produces phosphoric acid (H_3PO_4) from the wet chemical digestion of phosphate rock (fluorapatite, $Ca_5(PO_4)_3F$) using sulfuric acid (H_2SO_4), which generates large amounts of PG (gypsum, $CaSO_4 \cdot 2H_2O$). The overall reaction is:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF + \textit{heat (Eq. 1)}$$

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

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

The extraction of valuable metals from metal-bearing materials is frequently performed using aqueous solutions. Some researchers have investigated the leaching of PG in different temperature conditions and with different concentrations of the acid. Habashi (1985) reported a recovery of around 50% of REEs contained in PG by leaching the un-wanted by-product at ambient temperature with a 0.1-0.5 M H_2SO_4 at a solid-to-liquid ratio of 1:10. Preston et al. (1996) tested the leaching of REEs with sulfuric and nitric acid from PG derived from South-African phosphate rock. These authors reported higher efficiencies by leaching with HNO_3 instead of H_2SO_4 and a maximum recovery of REEs with 3 M HNO_3. Lokshin et al. (2002) found similar results in hemihydrates PG, which was attributed to the high solubility of REE-phosphates and REE alkali metal double sulfate in HNO_3. More recently, Walawalkar et al. (2016) reported the leaching efficiency of REEs from PG using different acids (HCl, H_2SO_4 and HNO_3). However, these researchers did not report the leaching of other impurities that could limit the efficiency of further selective extraction schemes. If these impurities are not identified and removed, they can cause emulsification of extraction systems and influence product purity (Ruan et al., 1995) However, there is still no evidence about the minerals hosting REEs in PG. Thus, the main aims of this work were: i) to study REE efficiency extraction (and other elements of economic interest, such as Sc, U and Th) from PG and the

release of impurities during leaching with commercial acids (HNO_3 and H_2SO_4), especially considering the effect of leaching time on the release of target and unwanted metals; and ii) to provide some clues about the potential minerals controlling the mobility of REEs in PG. In addition, a comparative study was performed to determine the synergetic effect of acidic aqueous solutions containing diethylenetriaminepentaacetic acid (DTPA), a well-known water-soluble chelating agent (Chitry et al., 2005; Sorin et al., 2005). The results of this study may contribute to optimizing further hydrometallurgical steps, i.e. solution concentration and purification, and final metal recovery in order to achieve the sustainable valorization of PG and thus cleaner production in the fertilizer industry.

2. Methods and materials

2.1. PG characterization

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

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

environmental samples, with good recovery percentages observed with respect to total content (Sastre et al., 2002). 10 mL of aqua regia (12 mol L^{-1} HCl and 15.8 mol L^{-1} HNO_3 in the ratio 3:1) were added to 1 g of PG in Teflon reactors, which were allowed to stand for 20 h in a fume cupboard and then simmered on a hot plate for 1 h at 100 ºC. Finally, the concentrations of dissolved major and trace elements were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES Jobin-Yvon Ultima2) and inductively coupled plasma mass spectrometry (ICP-MS Agilent 7700), respectively.

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

2.2. Leaching experiments

Several leaching procedures were performed to study the release of target metals (i.e. REEs) and impurities from the PG. 3 M HNO_3 and 0.5 M H_2SO_4 were selected as leaching solutions since previous researchers (Habashi, 1985; Preston et al. 1996) have reported optimal recoveries at these acid concentrations. All leaching experiments were performed using from high purity acids solutions Merck® at a solid-to-liquid ratio of 1:20 with shaking at 500 rpm. The release of elements was studied at room temperature and different reaction times: 2, 4, 6 and 8 h. In addition, the synergistic effect of acids and chelating agents was assessed by the leaching of PG with dilute solutions of HNO_3 and H_2SO_4 with 0.05 M DTPA (from Sigma-Aldrich, 99%) adjusted to pH 3-5 to determine the optimal value for REE extraction by DTPA. DTPA is an octadentate aminopolycarboxylate chelating agent, especially for REEs (Noack et al., 2016). The best performance was obtained by adjusting pH to 3; thus, acid solutions with 0.05 M

DTPA at this pH value were used in the leaching experiments. Liquid inclusions and process waters trapped in the interstices of PG mineral particles can form efflorescent salts during sample drying. To distinguish the metal contributions of these salts from those provided by the PG, leaching with distilled water (DW) was also performed at room temperature with an L/S ratio of 1:20 and identical reaction times as the acids. The effect of Al on the REE extraction was studied by adding known amounts of Al salts (1 M solution; $Al_2(SO_4)_3$ and $Al(NO_3)_3 \cdot 9H_2O$, >99% from Sigma-Aldrich®) to the leaching solutions. The leaching solutions were removed from the residual solids by filtration (0.45 µm) before analyses.

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

3. Results and discussion

3.1. Mineralogical and chemical composition of PG

The XRD pattern (Fig. 1A) of the Huelva PG allowed identifying gypsum to be the main mineral present (above 90% of the mass; semi-quantitative analysis). The presence of quartz was also identified, although the secondary peaks were overlapped by gypsum's peaks. The low crystallinity or minor presence (below 10% of mass) of other minerals (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_2SO_4. 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_5 (PO_4, CO_3)$_3$(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 be 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

metals and metalloids such as Fe (52 mg/kg), Cu (41 mg/kg), Zn (11 mg/kg), Cr, V (5.1 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).

3.2. Investigation of leaching methods applied to PG

Figure 2A shows the leaching efficiency for REEs, Sc, Th and U related to the different aqueous solutions used. The highest leaching efficiency for both HREEs and LREEs was reached when leaching was performed in 3 M HNO_3 (86% and 82% of the total, respectively), while lower values were achieved using 0.5 M H_2SO_4 (58% and 46%, respectively). However, these values are noticeably higher than those obtained by Rychkov et al. (2018) with the same H_2SO_4 concentration, which is attributed to the preferential partitioning of REE in gypsum crystals over other minor phases in the studied PG samples. Proton concentration in the leaching solution may be one of the most important factors influencing REE efficiency, as it can lead to the dissolution of REE-hosting minerals. However, the REE extraction was not linear with H^+ concentration, which suggests that other factors (e.g. the different solubility of REE-hosting minerals, complexing, re-precipitation reactions, etc.) control the solubility of REE once dissolved in acid conditions. This accords with Rychkov et al. (2018), who reported an REE extraction efficiency of only around 10% using 3 M instead of 0.5 M H_2SO_4 concentration.

For other valuable metals such as Sc, which was almost entirely leached from PG using both acid solutions (around 99%; Fig. 2A), and Th (88% and 78% in HNO_3 and H_2SO_4, respectively), good recovery rates were also achieved. However, U was barely extracted from PG using both dilute acids (21% for 3 M HNO_3 and 10% for 0.5 M H_2SO_4).

Lower REE recovery rates from PG were obtained by adding DTPA to both 5 mM HNO_3 (22% and 18%, respectively) and H_2SO_4 (16% and 13%). Also, for Sc, the efficiency obtained by adding DTPA was considerably lower than that obtained with dilute solutions, irrespective of the acid used (43% and 36% with HNO_3 and H_2SO_4, respectively). However, the lowest rates using DTPA solutions were obtained for U

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

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

Considering individual REEs (Fig. 2B-D), leaching with 3 M HNO_3 achieved efficiencies higher than 80% for all elements except Ce (67% of total), while lower values were recorded with 0.5 M H_2SO_4 (from 62% to 38%). In the latter case, the lowest values were also observed for Ce, while the highest were obtained for the heavier elements (Yb, Lu and Y; Fig. 2D). The lower leaching performance of Ce could be attributed to the oxidation of Ce^{3+} to Ce^{4+}. The use of oxidizing acid solutions (i.e. 3 M HNO_3 and 0.5 M H_2SO_4) may enhance the oxidation and subsequent precipitation of the Ce^{4+} oxide retained in the PG (Eqs. 2 and 3). The opposite trend was observed using DTPA diluted into the acids. These solutions not only caused the lowest values of REE release (from 26% to 11%), but decreasing efficiency was also observed for the HREE group (Fig. 2D).

$$2Ce^{3+} + SO_4^{2-} + 3H_2O \rightarrow + 2CeO_2 + + SO_3^{2-} + 6H^+ \quad \text{(Eq. 2)}$$

$$2Ce^{3+} + NO_3^- + 3H_2O + \rightarrow 2CeO_2(s) + NO_2^- + 6H^+ \quad \text{(Eq. 3)}$$

Regarding impurities, the use of HNO_3 promoted a higher gypsum dissolution rate compared to H_2SO_4. Around 63% of the Ca was leached with 3 M HNO_3, while less than 6% was released using 0.5 M H_2SO_4 (Fig. 3A). The high concentration of the SO_4^{2-} anion in the H_2SO_4 leaching solution may limit the solubility of gypsum. However, adding chelating agents to H_2SO_4 and a lower SO_4^{2-} concentration (around 5 mM *vs* 0.5 M) caused a higher Ca release (15% of total) than that obtained with 0.5 M H_2SO_4.

A similar case was observed for Sr and Ba, which usually replace Ca in the gypsum lattice. Around 77% and 41% of both elements were released with 3 M HNO_3 and only 18% and 1.0% were mobilized with 0.5 M H_2SO_4 solution (Fig. 4A). The high SO_4^{2-} concentration in the leaching solution also limited the solubility of Pb. Thus, around 60% of Pb was released with 3 M HNO_3, while less than 11% was extracted with 0.5 M H_2SO_4, a lower value than those obtained with DTPA solutions (27% and 15%, respectively). Appreciable differences in the rate of P release were also observed depending on the acid used. Around 84% of P was dissolved using 3 M HNO_3, but only 25% was dissolved with 0.5 M H_2SO_4. These differences may be related to the increasing dissolution rates from the acidity of phosphate present in the PG as minor minerals (although this was not observed by SEM).

The addition of DTPA to dilute acids provided similar leaching efficiencies (or even higher) than those obtained with more concentrated acids for different metals such as Mg, Mn, Cu and Zn, although with different leaching percentages (Fig. 3B). More than 80% of Mg, around 60% of Mn and lower values for Zn (32-42%) and Cu (less than 10%) were observed. However, the high values obtained with DW suggest the efflorescent salts originated from liquid inclusions trapped in the lattice interstice as the main contributor of these metals. Arsenic also seems to be linked to efflorescent salts; around 75% was leached with DW and around 90% using other leaching solutions (Fig. 3B). The presence of these elements (i.e. Cu, Zn, As and Mn) in PG as liquid inclusions could be related to the sulfuric acid used during phosphoric acid manufacturing in Huelva, which was mainly obtained by pyrite roasting and SO_2 recovery, which may lead to the accumulation of these elements as impurities (Macías et al., 2017)

Although considerable amounts of Fe and, to a lesser extent, Se and Al were released from the water-soluble fraction, the leaching of these elements may be governed by acid concentration: the greater the acidity, the higher the release into the liquor solution (Fig. 3C). Higher releases were observed for Co and V using 3 M HNO_3 (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_2SO_4 (and
300 in some cases with 3 M HNO_3) 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_2SO_4 and 3 M
303 HNO_3. 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_2SO_4, respectively. The REE leaching rates with 3 M HNO_3
306 were slightly higher than those obtained when 0.5 M H_2SO_4 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_2SO_4 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_3.

312 The different leaching efficiencies for Ca obtained with 0.5 M H_2SO_4 and 3 M HNO_3
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_3; 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_2SO_4 and 3 M HNO_3, 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

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

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

The siting of trace elements, metals and metalloids in PG is variable and has been previously discussed. For instance, the presence of Cd and Sr has been linked to gypsum by Ca substitutions in the crystal lattice (Rutherford et al., 1994), while U and Se may be adsorbed onto the surfaces of gypsum and Fe oxyhydroxides, respectively (Arocena et al., 1995). However, there is controversy as to which minerals host REE in PG. Some authors, e.g. Borges et al. (2016), have pointed to different minerals, such as sulfates, carbonates, fluorides and phosphates, as the main carriers of REE. However, other authors have suggested a single mineral phase as the REE carrier in PG. Gypsum, the main mineral phase in PG, is commonly considered to be the principal REE carrier in PG. Habashi (1985) observed the impossibility of recovering all REEs contained in PG without destroying the PG lattice. However, Walawalkar et al. (2016) did not find REEs in the surface gypsum using spectroscopy techniques. Lokshin et al. (2002) arrived at the same result; based on PG leaching with 96% HNO_3, they concluded that the REEs are not incorporated in gypsum, but rather exist as separate phases. The results obtained in this work agree well with these findings: high REE extraction was observed during H_2SO_4 leaching despite the low gypsum dissolution (5.7%).

Shivaramaiah et al. (2016) reported that Eu is not incorporated into the gypsum lattice, 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_3 (84%; Fig. 3) obtained in this study, but
354 not with H_2SO_4 (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_3 and H_2SO_4), 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_3 solution (above 80%); a high concentration
387 of impurities (i.e. Ca, SO_4, 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_2SO_4 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_3 liquor (Table 3). As a result, the extraction with 0.5 M H_2SO_4 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_3 and 0.5 M H_2SO_4, 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-

unwanted elements, the question to be answered is if this increase of leaching efficiency is worth the energy and time consumption. Still, further steps are needed to concentrate and separate REEs. The results obtained in this study show that the washing of PG with water considerably reduces the contents of impurities in the solid: around 80% of the total content of Mg, Mn and As, 40% of Fe, and 30% of Cd and Zn. Another possibility, not tested in this study, is the leaching of the residual PG (containing both target metals and impurities; Table 3) with recycled acid solutions from subsequent recovery steps. In light of these results, a potential leaching process could be proposed (Fig. 6). The PG samples should be initially washed with freshwater to reduce impurities. Then, the washed PG would be leached with 0.5 M H_2SO_4 solutions for 2h (Fig. 6). The resulting acid liquor would be used in further selective recovery schemes for REEs (and other elements of economic interest). After this step, the acid liquor could be recycled to improve the REE extraction rates and the removal of impurities. As a result, an REE-rich acid liquor solution and a clean PG could be obtained (Fig. 6).

3.6. Technical and economic limitations of the recovery process

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

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

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

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

Conclusions

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

The best REE leaching performance was obtained using a solution 3 M HNO_3 (above 80%) which caused a dissolution rate of 63% of gypsum originally present. The use of 0.5 M H_2SO_4 extracted between 46 and 58% of REE contained in PG, dissolving less 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_4, 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^{3+} and subsequent precipitation of Ce^{4+} 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

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Conflict of Interest Statement

Conflict of Interest – None

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FIGURE CAPTIONS

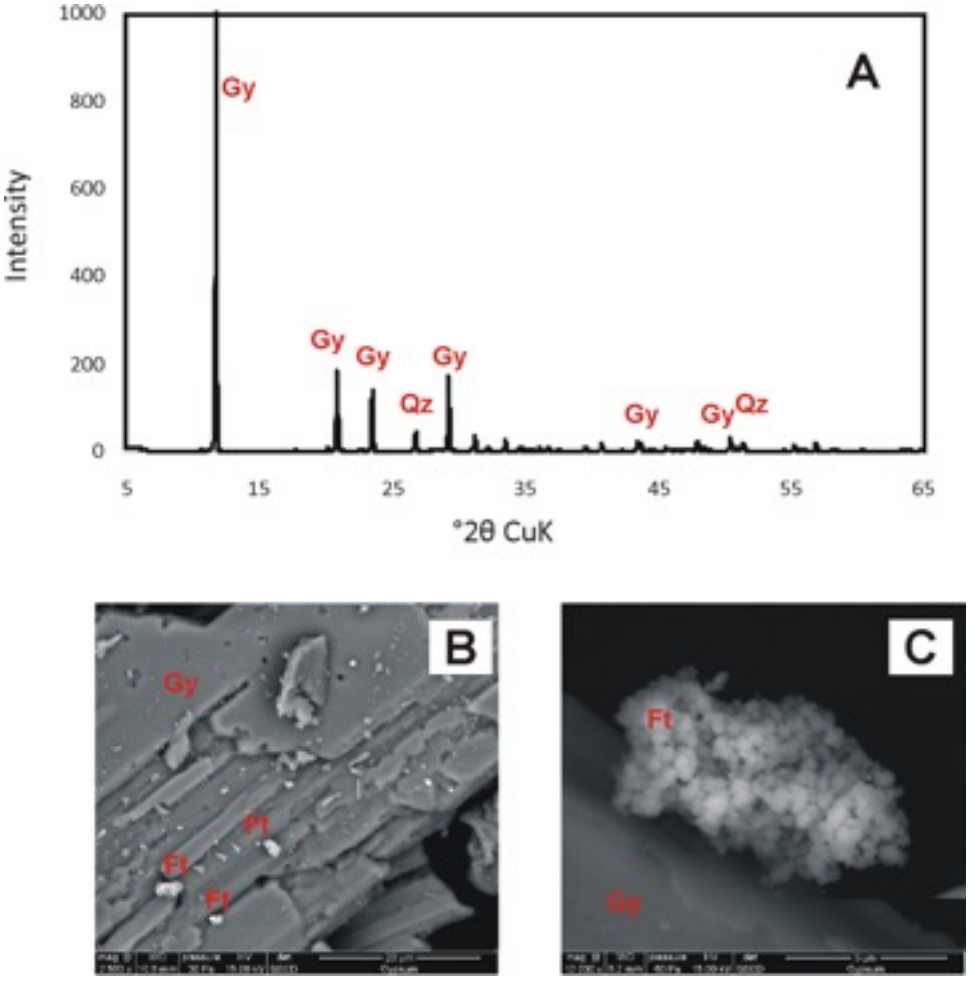
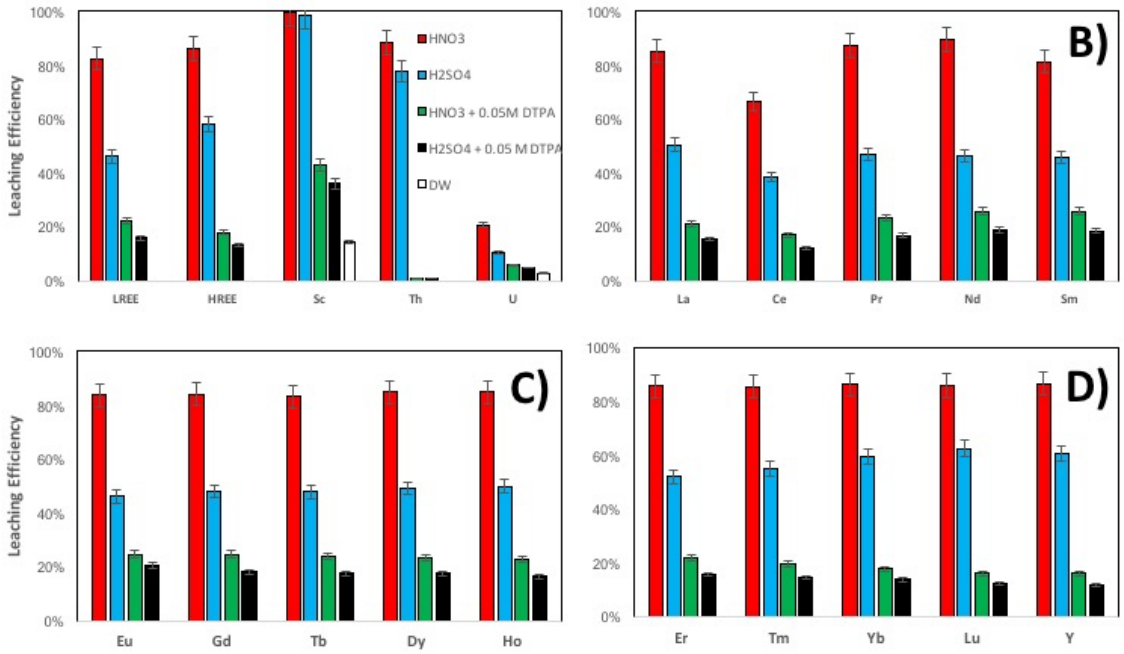
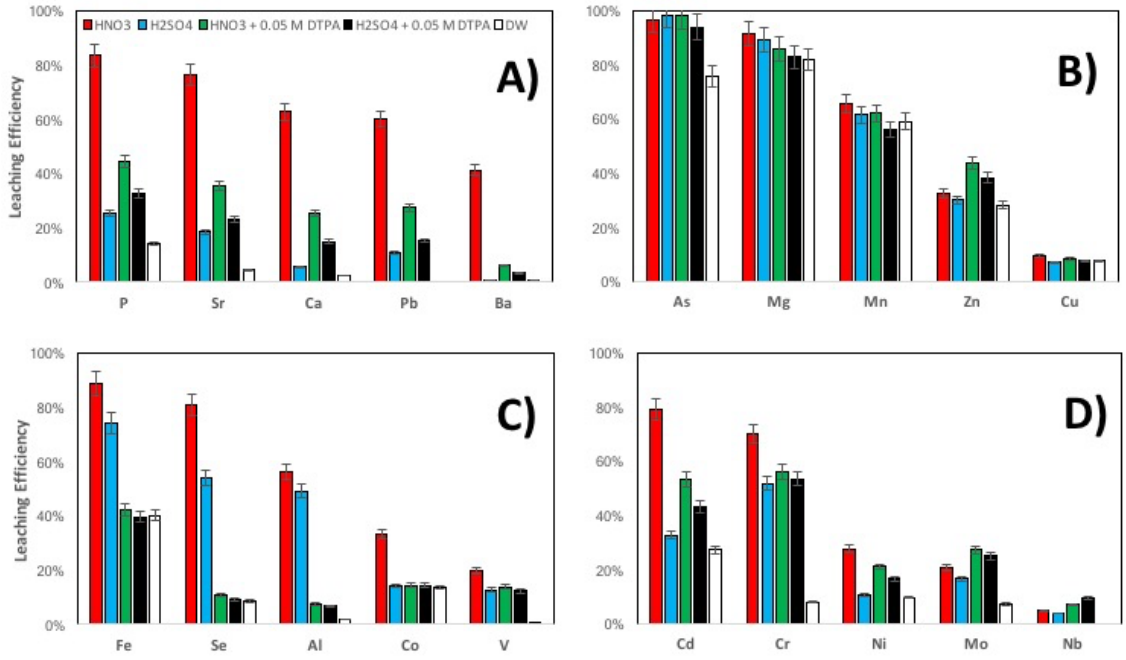


Figure 1. XRD pattern (A) and SEM images of the PG raw sample (B). Gy: gypsum; Ft: fluorite.



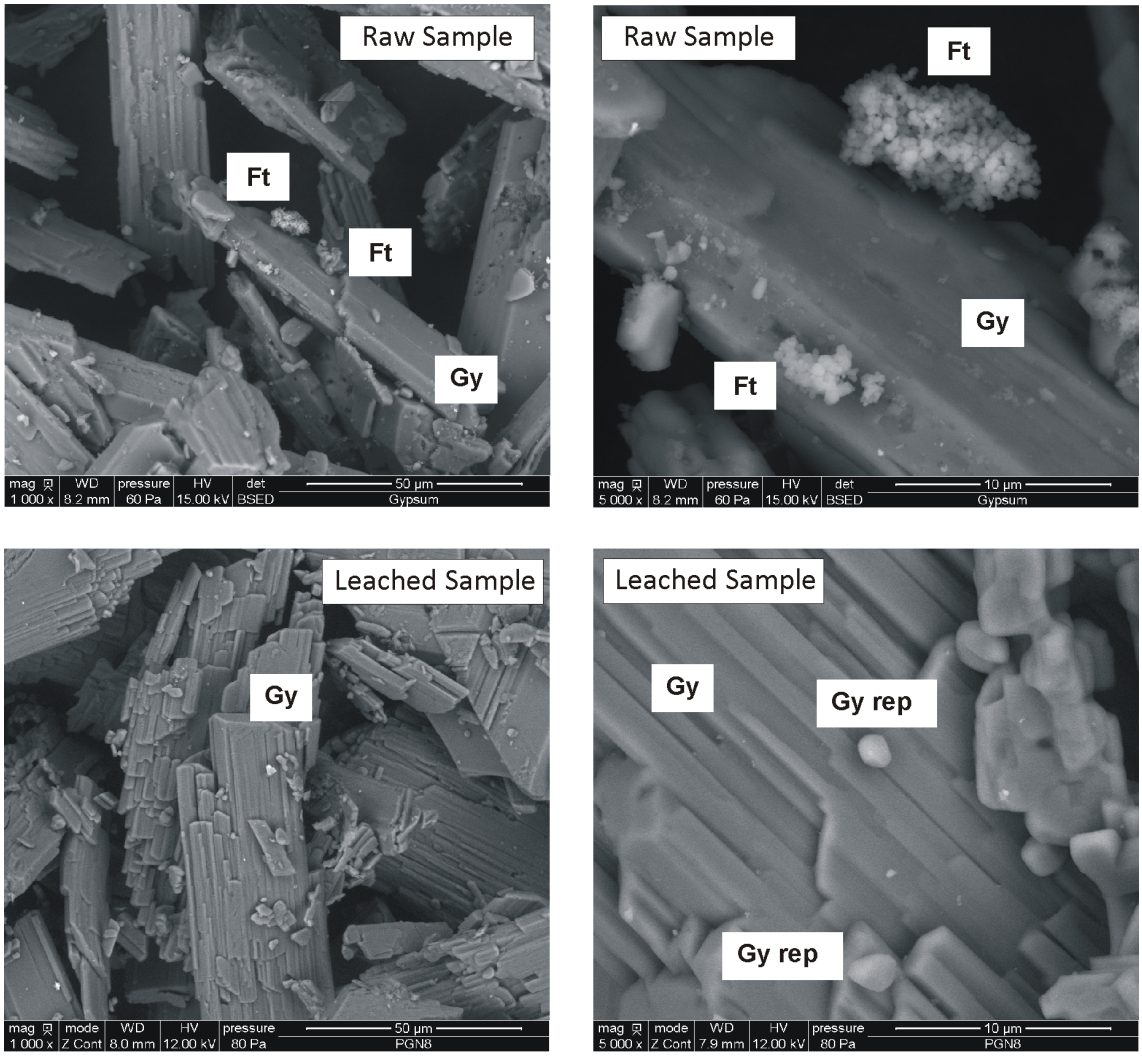
640

641 **Figure 2.** Leaching efficiency (with error bars) for REE, Sc, Th and U using different
642 aqueous solutions: 3 M HNO_3 (red bars), 0.5 M H_2SO_4 (blue bars), HNO_3 + 0.5 M DTPA
643 (green bars), H_2SO_4 + 0.5 M DTPA (black bars) and distilled water (DW, white bars).
644 Leaching time: 8 h.



645

646 **Figure 3.** Leaching efficiency (with error bars) for main impurities using different aqueous
647 solutions: 3 M HNO_3 (red bars), 0.5 M H_2SO_4 (blue bars), HNO_3 + 0.5 M DTPA (green
648 bars), H_2SO_4 + 0.5M DTPA (black bars) and distilled water (DW, white bars). Leaching
649 time: 8 h.



650

651 **Figure 4.** SEM images of raw and HNO_3 treated PG samples. Gy: gypsum; Ft: fluorite;
652 Gy rep: reprecipitated gypsum.

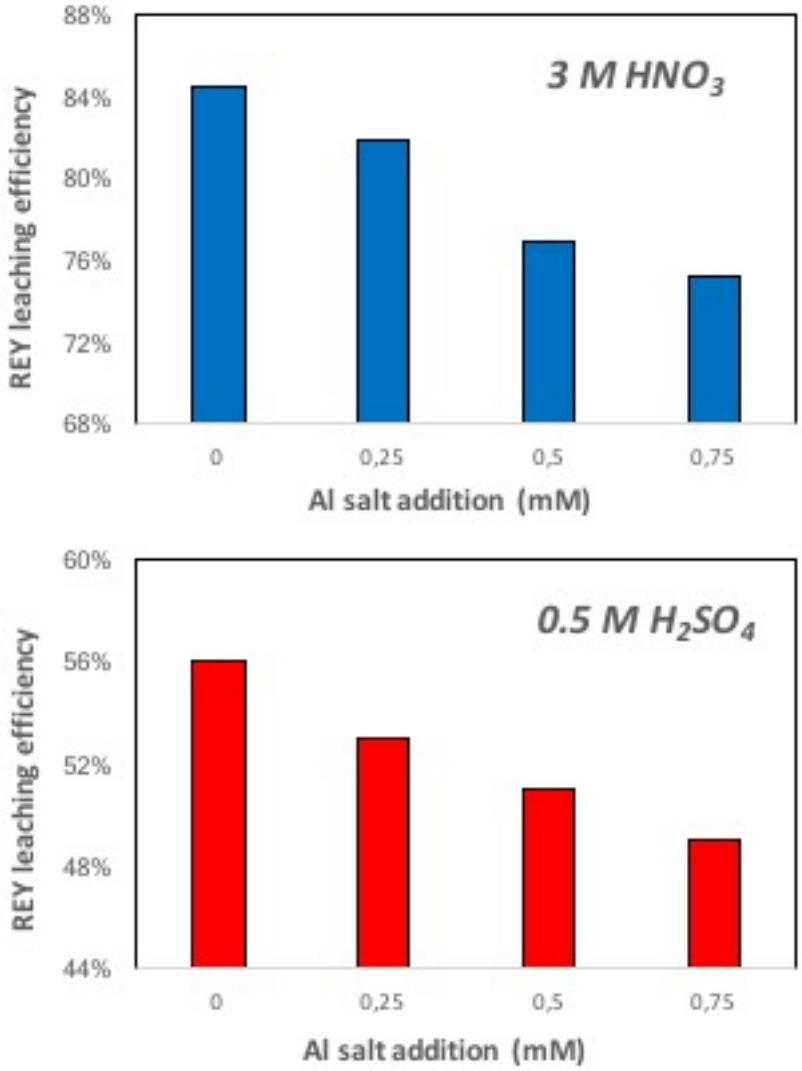


Figure 5. Effect of the addition of Al salts to the acid leaching solutions (0.5 M H_2SO_4 and 3 M HNO_3) on the REE extraction efficiency.

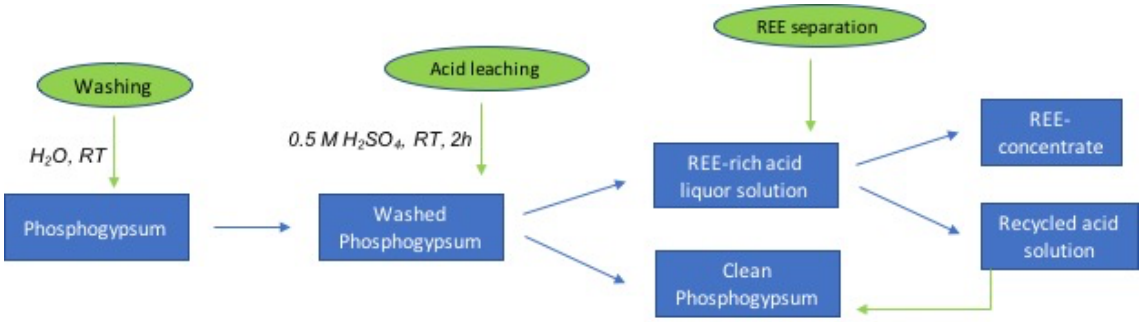


Figure 6. Flowsheet of the leaching process proposed based on results obtained in this study.

TABLES

Leaching solution		0.5M H_2SO_4				3M HNO_3			
Time		2h	4h	6h	8h	2h	4h	6h	8h
Element	*Total (mg/kg)*								
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%
Average Increase		-	4.0%	6.9%	7.4%	-	5.4%	5.9%	8.1%

Table 1. Effect of leaching time on the release of rare earth elements (REE) and yttrium in the acid liquor (0.5 M H_2SO_4 and 3 M HNO_3).

Leaching solution		0.5M H_2SO_4				3M HNO_3			
Time		2h	4h	6h	8h	2h	4h	6h	8h
Element	*Total (mg/kg)*								
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%
Sr	526	15%	16%	18%	18%	69%	73%	75%	77%
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%
Average Increase		-	1.0%	3.0%	6.1%	-	3.2%	2.6%	6.4%

Table 2. Effect of leaching time on the release of unwanted elements in the acid liquor (0.5 M H_2SO_4 and 3 M HNO_3).

		0.5 M H_2SO_4		3 M HNO_3		Fertilizer
	Phosphogypsum	Liquor solution	Residue	Liquor solution	Residue	Limit value
Weight (g)	*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	

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