Title:

Exploration of fertilizer industry wastes as potential source of critical raw materials.

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Abstract:

This paper explores the possibility of using wastes (i.e. solid phosphogypsum (PG), process waters and edge outflows) generated by a fertilizer plant in SW Spain as a source of elements of economic interest, estimating the available metal reserves and discussing the technological and economic pros and cons of this potential source of raw materials. In general, elements of economic interest are found in these wastes below of the grades commonly reported in conventional deposits. However, the huge tonnage of

Abbreviations
B, boron; B_2O_3: boron oxide; Be, beryllium; Co, cobalt; CO_2, carbon dioxide; Cr, chromium, Cr_2O_3: chromium(III) oxide; Cu, copper; D2EHPA, Di-2-ethylhexylphosphoric acid; DOPPA, di-octylphenylphosphoric acid; Eu, europium; Ga, gallium; Ge, germanium; ; HCl, hydrochloric acid; HNO_3, nitric acid; H_3PO_4: phosphoric acid; H_2SO_4, sulfuric acid; La, lanthanum; Lu, lutetium; Mo, molybdenum; Nb, niobium; Ni, nickel; Sb: antimony; Sc, scandium; Se, selenium; Sm, samarium; Ta, tantalum; Th, thorium; U, uranium; U_3O_8: triuranium octoxide; USD, US dollar; V, vanadium; Y, yttrium; Zn, zinc

wastes stockpiled constitute a significant secondary source of elements. Around 30400 t of B, 28000 t of rare earth elements (REE), 1800 t of U, 1400 t of Cr, 1300 t of V and lesser amounts of other elements of economic interest (e.g. Cu, Ni, Sc and Ga) are enclosed in the solid PG while lower amounts are found in process waters (e.g. 1360 t of Zn, 760 t of V, 630 t of U and Cr, 225 t of Cu, 160 t of Ni, 190 t of REE). Considering the market metal prices, the reserves contained in the Huelva PG stack have a potential value of around 8937 million USD, which mainly correspond to PG (97% of total value). The recovery of these elements is technically feasible, although intense research in refining processes is needed in order to increase the purity of the final product. The results of this study could be of interest in other PG stacks worldwide to provide more sustainable and cost-effective management of these wastes.

Keywords:

Phosphogypsum; lanthanides; metal recovery, waste valorization

1. Introduction

The use of phosphate fertilizers is widely extended worldwide to meet the phosphorus requirements of crops. The production of commercial phosphate fertilizer begins with the manufacturing of phosphoric acid, which is commonly accomplished by a wet digestion treatment of previously concentrated phosphate ores using sulfuric acid. However, during this industrial process a variety of by-products are produced. The main unwanted by-product is referred to as phosphogypsum (PG), a collective term for a mixture comprising major solid and minor liquid waste components (Lottermoser, 2010). PG is mainly composed of gypsum but may also contain other minor solid phases as reaction products of the acid wet process (e.g. alkali fluorosilicates and fluorides), unreacted phosphate rock and gangue mineral particles (e.g. quartz and feldspars). In addition to solid components, PG also contains industrial process waters composed by residual acids trapped in the interstices of mineral particles. During PG disposal, spent process waters are commonly pumped to the PG stacks. These acidic waters infiltrate through the PG stacks and are commonly collected in perimeter channels. However, if the draining system is not efficient, edge outflows can arise from the bottom of the stacks.

The manufacturing of phosphoric acid is a highly waste generating activity; around 5 tons of PG are produced for every ton of phosphoric acid manufactured. The huge production of these unwanted by-products, i.e. over 100–280 Mt/yr of PG worldwide (Parreira et al., 2003), has promoted the searching of new recycling alternatives. Numerous investigations have focused on the search for new uses for PG, e.g. as an additive to agricultural soils (Garrido et al., 2005), as raw material in plaster bricks, masonry walls, binders of the base for roads (Smith and Theys, 2000), in the manufacturing of sodium sulfate, soil limestone and ammonium sulfate (Gorecki et al., 1990) or for mineral CO_2 sequestration (Contreras et al., 2015). Nevertheless, such practices are limited by the high content of toxic impurities, and thus only 15% of the PG worldwide production is recycled (Tayibi et al., 2009). The remaining 85% are considered wastes that requires large disposal areas and may cause huge environmental problems due to the high content in metals, metalloids and radionuclides (e.g. Pérez-López et al., 2015; El Zreli et al., 2016). Therefore, most common waste management practices have traditionally focused on mitigating the release of contaminants by covering PG piles with impermeable materials and collecting acid effluents for further treatment.

However, these wastes could also contain high concentrations of elements of economic interest whose recovery could help offset treatment costs. Particularly relevant it would be the presence of critical raw materials (CRM), those of high economic importance and at risk of supply for European countries (EC, 2014). Thus, the occurrence of these elements and the large volume of PG generated might turn this waste into a potential commodity. For instance, it is especially significant the presence rare earth elements (REE) which have a great economic impact due to their use in technological applications (Binnemans et al., 2016). The recovery of REE in PG has been focus of much research based on hydrometallurgical (e.g. Preston et al., 1996; Lokshin et al., 2011) and solvometallurgical approaches (e.g. El-Didamony et al., 2012). However, the presence of other elements of economic interest in PG (e.g. U, Sc, Th, or B) has not been adequately explored neither the content of these metals in other wastes from the fertilizer manufacturing (i.e. process waters). The recovery of these elements could constitute a promising economic and environmental friendly solution for the management of these wastes. On the other hand, the feasibility of recovery these elements relies not only on the existence of a minable pool but also on other factors such as the availability of recovery technologies, the existence of potential buyers and other economic factors. This study examines the potential recovery of metals of economic interest in wastes generated by a fertilizer industry in SW Spain, estimating the available metal reserves and discussing the technological and economic pros and cons of this potential source of raw materials. The conclusions of this study could contribute to a cleaner production and a more sustainable waste management in fertilizer industries worldwide.

2. Materials and Methods

2.1. Study area

Phosphate fertilizer plants operated in Huelva city (SW Spain) since 1968 and have led to the stockpiling of around 100 Mt of PG over approximately 1200 ha of surface of estuarine marshland, less than 300 m of the city (Fig. 1). The phosphate rock processed was sedimentary phosphorite imported mainly from Morocco. The implementation of a closed-circuit system promoted the existence of process water ponds on the central part of the stacks and a system of perimeter channels for collecting all leakages from the piles (Fig. 1). The main chemical difference between edges outflows emerging from the bottom of the stack and process waters stored in ponds is the concentration process suffered by the latter due to the large residence time (i.e. more than 10 years) in the close-circuit system.

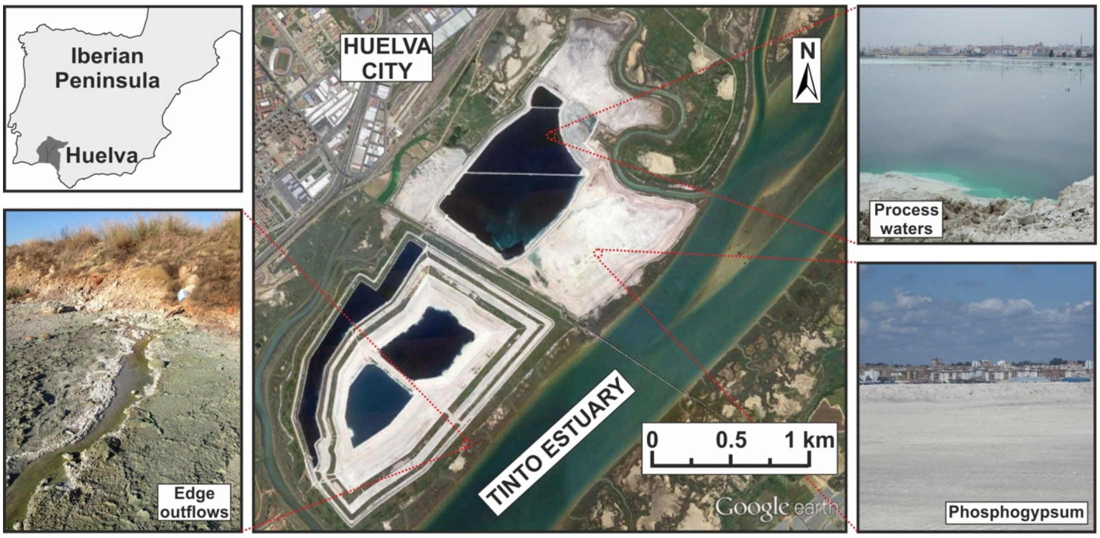

Figure 1. Location map of the Huelva PG stacks (SW Spain), showing the main wastes generated by the fertilizer plant.

The dumping of these wastes directly on bare marshland soils over 40 years have left an appalling environmental legacy; i.e. many edge outflows (Fig. 1) with a high content of toxic metals and radionuclides reach the estuary (e.g. Bolívar et al., 2002; Pérez-López et al., 2016). The restoration plan consist on the removal of process water ponds and the cover of PG stacks with impermeable materials. However, this plan is object of controversy as it is based on the assumption that the infiltration of process water stored in the ponds through the porous media and its subsequent emergence as edge outflows is the main pathway of pollutant dispersion to the estuary. This dispersion model has called into question by recent studies due to the location of the PG stacks in the tidal prism of the estuary (Pérez-López et al., 2015; 2016). The growing social and political pressure urges to explore more sustainable solutions to the management of these wastes. In this sense, Huelva PG valorization for CRMs recovery has not been explored up to know. The availability of technology metal stocks in this area, with absence of primary deposits, is of paramount importance in order to avoid the dependence from external suppliers.

2.2. Sampling and analysis

Several samplings were performed in order to collect representative samples of solid PG (n=49). Composite samples of approximately 2 kg were collected using a polypropylene shovel previously washed with distilled water, and transferred to polypropylene sterile bags. In the laboratory, samples were oven-dried (30 ºC), ground and stored in sterile polypropylene containers until analysis. The perimeter of the PG stacks was systematically monitored in order to sample edge outflows (n= 182) during all hydrological conditions. In addition, several samples of process waters (n= 13) contained in perimeter channels and ponds over the PG stacks were also collected. Water samples were filtered with 0.45 μm membrane filters, acidified with HNO_3 to pH < 1 and stored refrigerated until analysis.

Solid samples were chemically characterized after *aqua regia* digestion: 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 sample 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. The extractability of elements enclosed in PG was studied by 8h-leaching experiments with commercial acids (i.e. HCl, H_2SO_4 and HNO_3) at a solid:liquid ratio of 1:20 and room temperature. The acid concentration was selected according to previous works reported in literature (i.e. Habashi, 1985; Preston et al., 1996); 0.5, 1 and 3M for H_2SO_4, HCl and HNO_3, respectively. All samples were analyzed using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS; Agilent 7700) for the determination of elements of economic interest (e.g. B, Be, Co, Cr, Cu, Ga, Ge, Mo, Ni, Nb, Se, Sc, Sb, Ta, U, Zn, LREE (La to Sm) and HREE (Eu to Lu, plus Y)). Detection limits were 0.1 μg/L for all these elements.

3. Results and discussion

3.1. Abundance of elements of economic interest in phosphoric manufacturing wastes

Figures 2 and 3 show the abundance of the main elements of economic interest in the different wastes generated by the Huelva fertilizer plant during phosphoric acid production. As can be seen in Figure 2, solid PG constitutes the major reservoir of HREE in the stacks, with an average value of 123 mg/kg. However, a high variability is observed along the stacks with minimum and maximum values of 39 and 279 mg/kg, respectively. The concentration of HREE in the process water is one order of magnitude lower than that observed in PG (average value of 11 mg/L; Fig. 2), while edge outflows showed the lowest concentrations of the PG-related wastes (average value of 0.1 mg/L). The same tendency is observed with LREE; higher concentrations were recorded in the solid by-product (average value of 160 mg/kg for PG) than in liquid ones (average values of 7.3 and 0.16 mg/L of LREE in process water and edge outflows, respectively). In the case of Sc, the higher average values were observed in solid PG (3.2 mg/kg), while quite lower contents were found in process water and edge outflows (average values of 0.86 and 0.27 mg/L, respectively; Fig. 2). The content of B observed in solid PG (average value of 304 mg/kg) is notable if compared to the rest of by-products;

around two orders of magnitude higher than those observed in process waters and edge outflows (average values of around 2.7 mg/L in both cases; Fig. 2). Although at lower quantities, the solid PG also hosts preferentially other elements such as Se (5.2 mg/kg), Ga (1.4 mg/kg), Ge (1.0 mg/kg), Be (0.68 mg/kg), Ta (0.43 mg/kg), or Nb (0.13 mg/kg) compared to liquid unwanted by-products (Fig. 2).

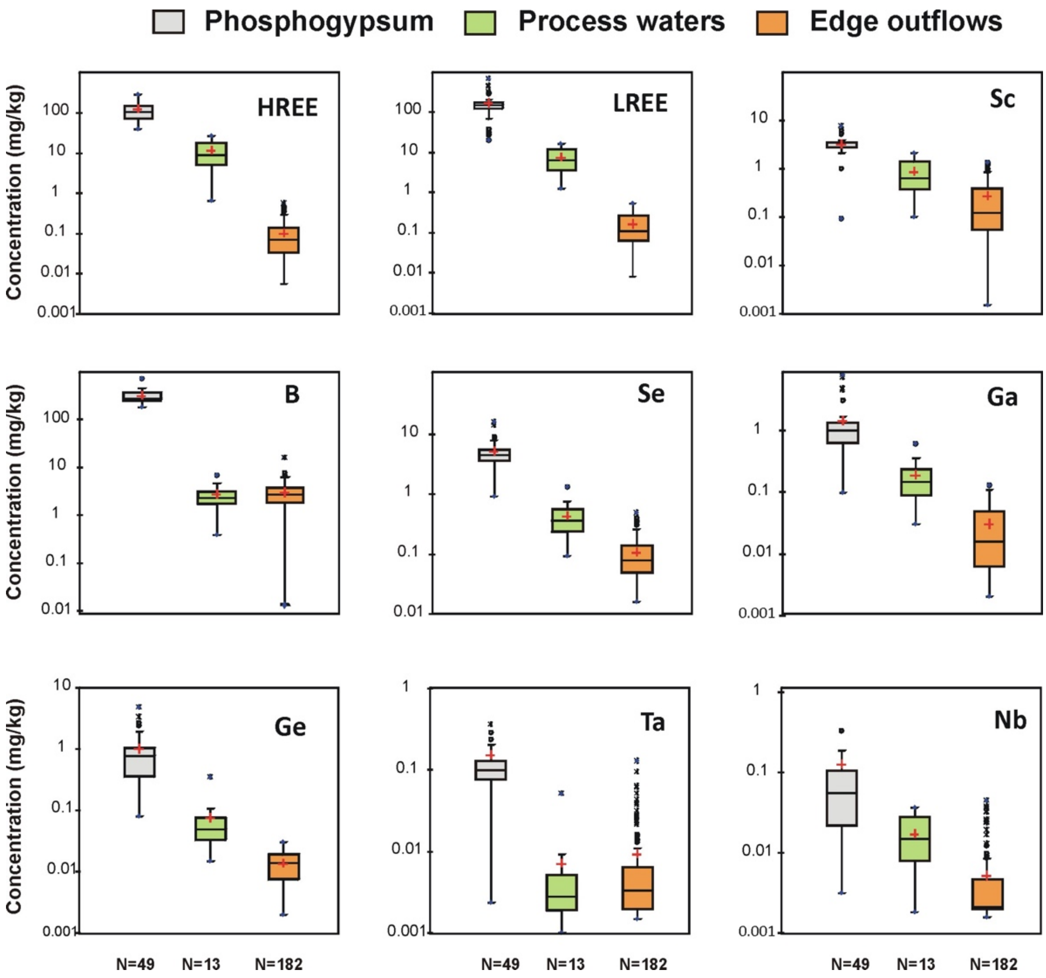

Figure 2. Box-and-whiskers plots of some elements of economic interest in solid PG (in mg/kg), process waters and edge outflows (in mg/L).

On the contrary, the process water stored in the perimeter channels and on the top of the stacks showed the highest U concentrations (average value of 64 mg/L); between 2.5 and 3.5 times higher than those observed in solid PG (18 mg/kg; Fig. 3). Process water ponds and channels also exhibit the highest concentrations for other metals, with average values of 136 mg/L for Zn, 77 mg/L for V, 63 mg/L of Cr, 23 mg/L of Cu, 17 mg/L of Mo, 16 mg/L of Ni, 1.8 mg/L of Co and 0.80 mg/L of Sb (Fig. 3). In general, the lower concentrations of elements of economic interest were found in the edge outflows, although significant concentrations of U and B were observed (Figs. 2 and 3).

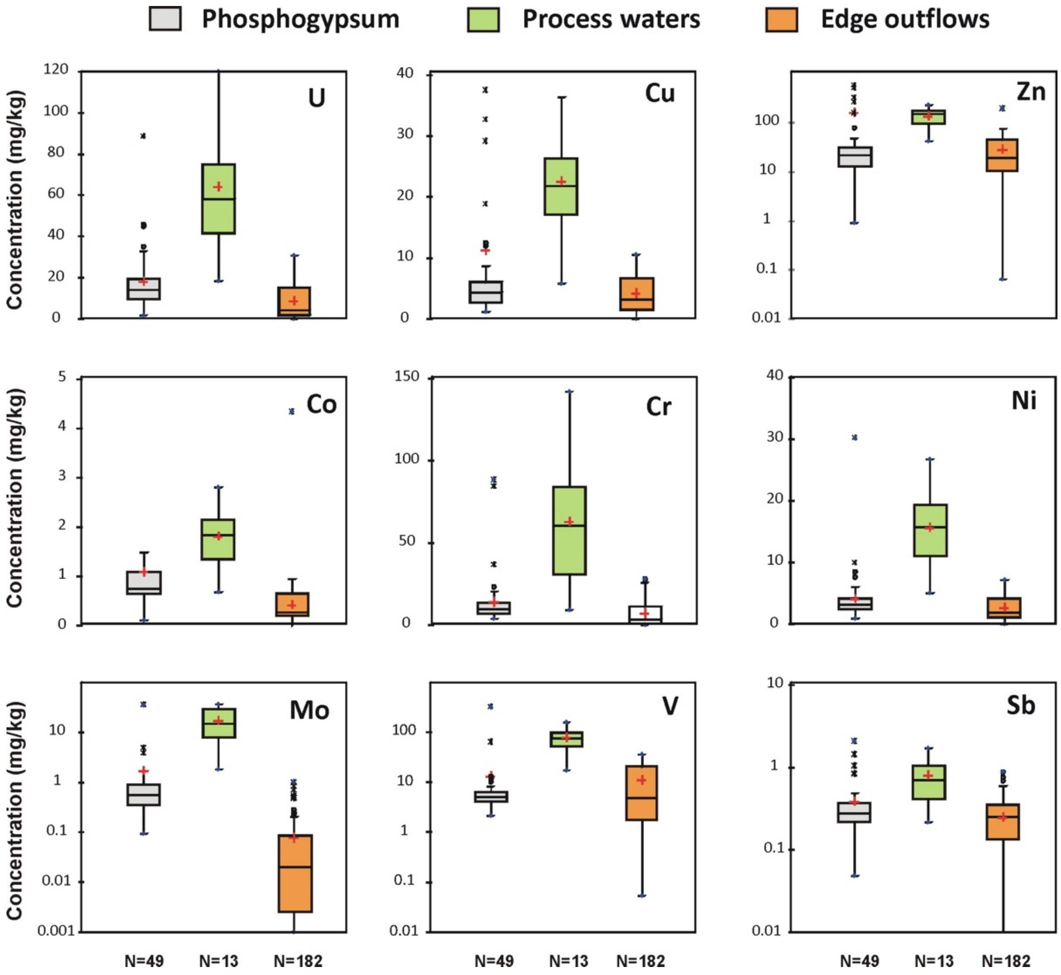

Figure 3. Box-and-whiskers plots of some elements of economic interest in solid PG (in mg/kg), process waters and edge outflows (in mg/L).

3.2. Availability of minable contents of target elements

The economic feasibility of a mining exploitation is strongly dependent on the mineral cut-off grade. Thus, the first step in the assessment of the potential valorization of these wastes should be the estimation of the grade for metals of economic interest. For instance, considering an average REE concentration in PG of 283 mg/kg, this content would yield a grade of around 0.034% of Rare Earth Oxides (REO) in PG (Table 1). If compared this value with those commonly found in conventional high to medium REE grade deposits worldwide such as carbonatites, deposits associated with alkaline igneous rocks or lateritic deposits, it would be one or two orders of magnitude lower (from 0.33 to 9.7% of REO; Table 1). However, the REE grade observed in PG is comparable to those reported for other low-grade deposits currently exploited such as marine and alluvial placers or ion-adsorption clays (Table 1).

Location	**Deposit type**	**Tonnage**	**Grade REO**
Bayan Obo (China)	Carbonatite-associated	750 Mt	4.10%
Thor Lake (Canada)	Associated with alkaline igneous rocks	64 Mt	1.96%
Olimpic Dam (Australia)	Iron-REE deposits	2000Mt	0.33%
Lehmi Pass (USA)	Hydrotermal deposits	39Mt	0.51%
Jangardup (Island)	Marine placers	30 Mt	0.046%
Horse Creek (USA)	Alluvial placers	19 Mt	0.041%
Mount Weld (Australia)	Lateritic deposits	12 Mt	9.70%
Longnan (China)	Ion-adsorption clays	< 0.01 Mt	0.03-0.35%
Huelva (Spain)	Phosphogypsum	100 Mt	0.034%

Table 1. Comparison of rare elements oxides (REO) content in PG with respect main conventional deposits worldwide. Modified from BGS (2011) compilation of data reported by Orris and Grauch (2002) and Grauch and Mariano (2008).

The content of some other elements is also generally below the levels observed in conventional deposits. For instance, the grade of B_2O_3 in solid PG is around 0.1%, which is considerably lower than those found in common deposits of colemanite and ulexite worldwide, i.e. from 20 to 45% (Kistler and Helvaci, 1994). On the other hand, the grade of Cr_2O_3 observed in PG and process water are only of 0.002% and 0.007%, respectively, well below of values commonly found in conventional deposits of chromite worldwide, i.e. median value of 45% (Mosier et al., 2012).

Vanadium occurs in deposits of phosphate rock, titaniferous magnetite, and uraniferous sandstone and siltstone, in which it constitutes less than 2% of the host rock and, hence, is typically recovered as a by-product (USGS, 2016). The grade of V in solid PG is around 0.0013%, three orders of magnitude lower than those found in the abovementioned deposits, due to V may be preferentially transferred to acid solution during the attack of phosphate rock with H_2SO_4 as evidences the high concentration of V observed in the process water (average value of 77 mg/L; Fig. 3). A similar depletion process in solid PG is observed for U, with a U_3O_8 grade in PG of 0.0021%, one order of magnitude lower than the U_3O_8 grade reported in phosphorite deposits where the PG derives from (IAEA, 2009). The Zn grades for solid PG and process waters range from 0.013 to 0.015%, well below the median value observed in felsic volcanic massive sulfides worldwide, i.e. 3.2% of Zn (Mosier et al., 2009).

Accordingly, the elements of economic interest enclosed in PG are found in one or several orders of magnitude lower than in conventional deposits. However, the long period of phosphoric acid manufacturing (i.e. 40 years) has caused the stockpiling of a huge tonnage of PG near the fertilizer plant (around 100 Mt). In addition, around 10 Mm^3 of process water is currently deposited on the top of the stacks and around 0.48 Mm^3 of edge outflows are annually released from the bottom of the stacks. These huge amounts of wastes enclose significant amounts of elements of economic interest that could be subject to recovery even despite being at low concentrations. This possibility is especially appealing for countries with absence of primary deposits. For the sake of simplicity, average values of elements have been considered in order to estimate the total reserves contained in wastes generated by this fertilizer plant. Table 2 shows the estimated reserves of CRMs and other elements of economic interest (OEIs).

		Tonnage			Valuation (Million USD)		
		Phosphogypsum	*Process waters*	*Edge outflows*	*Phosphogypsum*	*Process waters*	*Edge outflows*[1]
		100 Mt	10 Mm^3	0.48 Mm^3/yr	8721	213	2.4
Critical raw materials	*Price*[1] *(USD/kg)*						
B	4.6	30425	73	1.38	12	0.03	0.001
LREE	35	16005	74	0.077	584	1.9	0.002
HREE	206	12297	114	0.048	1116	7.6	0.004
Cr	17	1374	627	3.27	24	11	0.056
Co	28	109	18	0.21	3.0	0.51	0.006
Sb	8.4	38	8.0	0.12	0.32	0.07	0.001
Be	508	22	4.0	0.04	11	2.1	0.019
Nb	42	13	0.17	0.002	0.53	0.01	0.0001
Elements of economic interest							
Zn	1.4	15897	1362	13.55	23	2.0	0.020
U	61	1807	639	4.20	111	39	0.258
V	8.8	1278	769	5.25	11	6.7	0.046
Cu	4.9	1126	225	2.02	5.5	1.1	0.010
Se	53	518	4.3	0.05	27	0.22	0.003
Ni	8.6	405	164	1.29	3.5	1.4	0.011
Sc	15000	316	8.6	0.13	4738	130	1.9
Ga	197	151	1.9	0.01	30	0.37	0.003
Ge	1906	104	0.7	0.01	198	1.4	0.012
Mo	18	82	4.5	0.02	1.5	0.08	0.000
Ta	320	45	0.1	0.004	14	0.02	0.001

Table 2. Estimated reserves (tons) and valuation (million USD) of elements of economic interest in unwanted by-products generated by the Huelva fertilizer plant (SW Spain). 1 Reserves calculated in edge outflows are expressed as ton/yr. Valuation estimated according to the metal prices for 2015 listed in the London Metal Exchange (LME, 2015) and those reported by USGS (2016).

Owing to its huge tonnage, solid PG is the main source of elements; around 30400 t of B, 16000 t of LREE and Zn, 12000 t of HREE, 1800 t of U, 1400 t of Cr, 1300 t of V and lesser amounts of other elements of economic interest (e.g. Cu, Ni, Sc and Ga) are enclosed in the stacks (Table 2). The process water ponds also contain significant reserves of some elements of economic interest; around 1360 t of Zn, 760 t of V, 630 t of U and Cr, 225 t of Cu, 160 t of Ni, 110 t of HREE and lesser quantities of other elements (e.g. LREE, B, Sc, Co, Sb, Mo and Be) are found dissolved in this wastewater (Table 2). The outflows emerging from the edge of the stacks constitute modest reserves of elements of economic interest if compared to the rest of wastes; around 14 t of Zn, 5.3 t of V, 4.2 t of U, 3.3 t of Cr, 2.0 t of Cu are annually discharged to the estuarine environment (Table 2). However, edge outflows could be considered as a quasi-renewable source of elements if current conditions remain in the stacks.

3.3. Economic considerations

Economic considerations may drive the interest in metal recovery from such low-grade industrial by-products. For this reason, the first step before undertaking a great investment to develop and put into operation pilot plants for metal recovery is to calculate the value of the metal reserves subject to exploitation. Metal prices on the market vary considerably depending on purity, quantity and other criteria. An estimation of the value of metal reserves contained in the fertilizer wastes (i.e. solid PG, process waters and edge outflows) has been performed considering the tonnage previously calculated and the metal prices published for 2015 by the London Metal Exchange market (LME, 2016) and USGS (2016), as shown in Table 2. According to this estimation, metal reserves enclosed in these wastes would have a total valuation of 8937 million USD, of which 97.6% corresponds to solid PG (Table 2). Despite being in lower concentration than most elements, Sc reserves reached the highest valuation (i.e. 4738 million USD) due to the high price of Sc on the market (15000 USD/kg, Table 2). Other profitable sources of elements are REE, with a total valuation of 1116 and 584 million USD for HREE and LREE, respectively. Germanium and U reserves enclosed in solid PG also reach a significant valuation with around 198 and 111 million USD (Table 2). The reserves of the rest of elements did not exceed the value of 30 million USD.

In the case of the process water, the valuation estimated for the whole elements accounts for 213 million USD (Table 2), a 2.4% of the total valuation. As well as in the case of solid PG, Sc constitutes the most valuable reserve in the process water (Table 2) with a total valuation of around 130 million USD, followed by U (39 million USD) and Cr (11 million USD). Lower values were estimated for HREE (7.6 million USD), V (6.7 million USD), Zn (2.0 million USD), LREE (1.9 million USD) and other elements of economic interest (Table 2). On the other hand, edge outflows that are released from the bottom of the stacks and contaminate the estuarine waters have an estimated valuation of 2.4 million USD per year (Table 2), due mainly to the Sc reserves (appraised at around 1.9 million USD). Significant values for U (0.26 million USD/yr), Cr (56120 USD/yr), V (46000 USD/yr), Zn = Be (around 19000 USD/yr), Ge (12165 USD/yr) and lesser valuations for other elements of economic interest were estimated (Table 2). In this latter case, despite the lower valuation in comparison with the rest of wastes, it is worth to insist on the quasi-renewable nature of this source if current conditions remain in the stacks.

However, could the abovementioned figures be considered realistic? This estimation is based on the current prices established on the metal market assuming a high purity and total recovery of elements enclosed in the wastes. Obviously, this situation is clearly far from reality. The extraction of target metals from the ore is often limited by technical or economic factors. Quite the same may occur during the selective recovery of target elements from aqueous solution, especially for REE whose selective separation is complex as individual REE are chemically similar, and the solution of this problem can put the cost-effectiveness of the recovery scheme into risk. However, the most critical step in the recovery process may be the feasibility to obtain a marketable product according to the buyer requirements. Many attempts of waste valorization have failed to obtain a final product meeting the required specifications of the industry. For these reasons, the abovementioned figures can be considered as upper limits of metal reserves valuation contained in these wastes. In this sense, Smith et al. (2013) reported a case study of Zn selective recovery in a mine water treatment plant in the Wellington Oro Mine (Colorado, US). The product obtained, which contained around 50-57% of Zn on a dry weight basis, was purchased by a smelter who paid around 0.33 USD/kg of Zn content, assuming also the shipping costs (0.31 USD/kg of Zn content). As a result, the smelter paid for the products around 30% of the average 2010 LME price. Thus, the value of metals contained in the wastes must be only a fraction of the price established by markets. If we assume the correction proposed by these authors, total treatment cost for each element subject to recovery may not exceed a third of the metal prices listed in Table 2. A lower correction factor was applied by Kulczycka et al. (2016) who discussed the feasibility of recovering REE from PG in a Polish fertilizer plant by a novel method based on PG leaching with H_2SO_4 and subsequent REE concentration. As a result, they obtained several products (i.e. REE concentrate, supersulfate cement, H_2SO_4 and H_3PO_4) which can be commercialized. In the case of REE, these authors considered a price of 0.8 €/kg of REE concentrate, a value noticeably lower than the third of the price established in the market. The estimation of such arbitrary value must be related to the low purity of the product obtained. In this sense, the obtaining of a product of high purity must increase the market value. Despite such low value, these authors concluded that the application of this technology turned to be cost-effective but required significant financial investment and was subject to a relatively high degree of risk (i.e. fluctuations of REE prices, feasibility to scale up the technological process). Despite the necessary application of a correction factor, it seems to be worth the recovery of elements contained in fertilizer wastes. However, some questions need to be answered; are there available technologies to recover these elements? And equally important, which total cost should not exceed the recovery scheme in order to avoid becoming a sub-economic activity? In this latter case, an estimation of the total costs for each recovery scheme must be performed, considering all stages, including those related to raw material processing such as material preparation, personnel, reagents, energy or maintenance, and those related to bring the product on market such as financial costs, infrastructure, permits, fees or shipping costs.

3.4. Availability of recovery technologies

Despite the lower grades of metals observed in these by-products in comparison with conventional deposits, these metal stocks (Table 2) could be exploited if cost-effective and selective methods of recovery are developed. The first stage in the recovery process is the extraction of valuable metals from metal-bearing materials, which is frequently performed by the use of aqueous extractants. This step would be eased in the case of process waters and edge outflows where the elements are already in solution, which implies the main advantage of these wastes. Figure 4 shows the extractability of CRMs and OEIs in the solid PG using different acids, ordered according to the estimated tonnage. It can be noted a high leaching performance (from 70 to 99%) using 3M HNO_3 for HREE, LREE, Cr, Sb, Be, Se and Sc and lower values (below 60%) for the rest of elements. Among them, the extraction efficiency of B, the most abundant element in PG (Table 2), was around 50%. The extraction with 1M HCl was less efficient for REE (around 65-70%) and B (14%), however a significant improvement was observed for V and Zn (around 60%; Fig. 4). Lower efficiencies were observed using 0.5M H_2SO_4, with an extraction performance of around 60% for HREE and Sb, and 50% for LREE, Cr and Se (Fig. 4). It is striking the high extraction efficiency for Sc (around 100%), the most valued element (Table 2), irrespective to the acid solution used (Fig. 4).

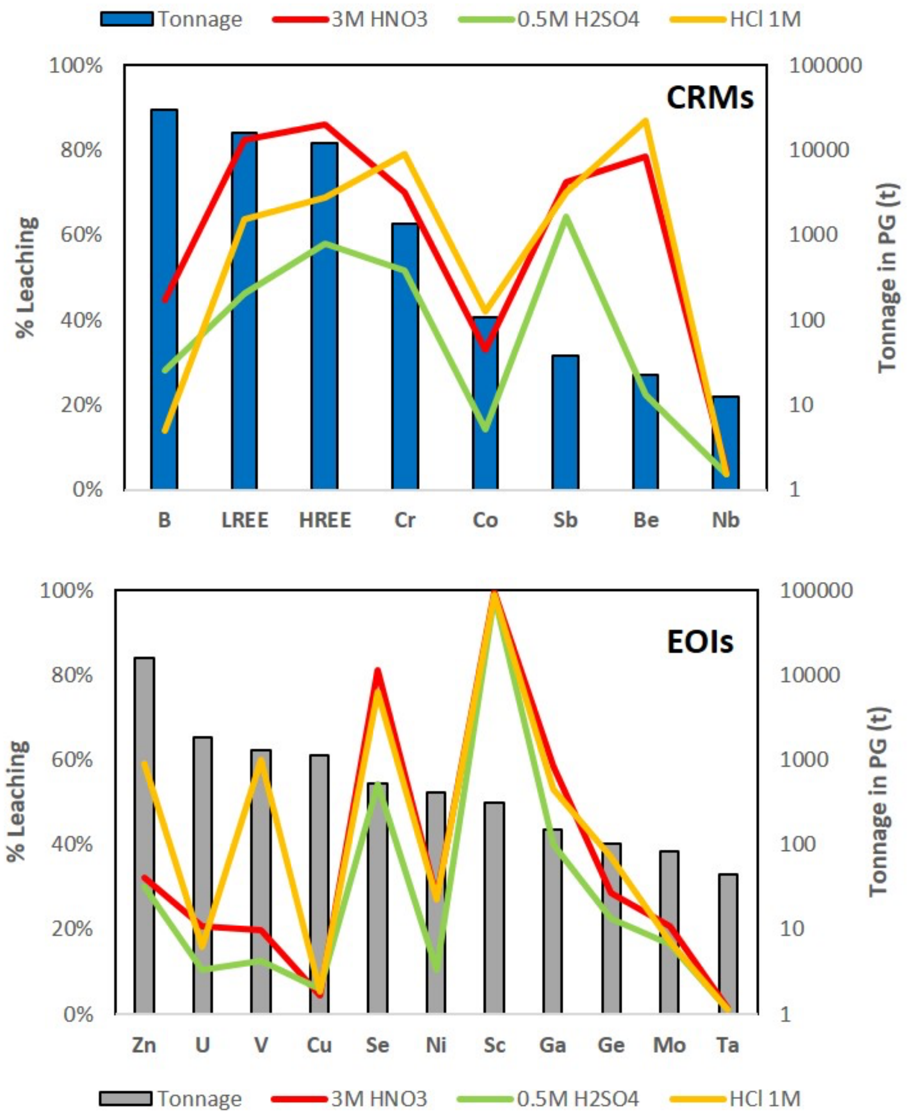

Figure 4. Leaching rates of some elements of economic interest from PG using different acid solutions (i.e. 0.5M H_2SO_4, 1M HCl and 3M HNO_3).

Once dissolved, further steps are needed to concentrate and separate elements of interest. The final goal is to obtain the highest purity by refining and purifying the element to achieve a marketable product. The pressing need of finding secondary sources of elements such as REE and U has promoted the research on selective recovery methods from PG. Thus, not surprisingly most recovery methods found in literature dealt with these elements. Jarosinski et al. (1993) studied the recovery of REE from PG by both solvent extraction with nonyl–phenyl phosphoric acid (NPPA) and selective precipitation with HF, obtaining a final product with around 40% of REE oxide. Preston et al. (1996) approached this issue by solvent extraction with tri-n-butyl phosphate (TBP) and di-n-butyl n-butylphosphonate (DBBP), reaching a mixed REE oxide product of high purity (94-98%). Koopman and Witkamp (2000) reported recovery efficiencies of up to 53% of REE during acid phosphoric production using an ion exchange resin composed of sulfonic acid functional groups.

Several methods have been investigated to extract selectively U from phosphoric acid manufactured by the fertilizer industry. Mayyas et al. (2014) reported a value of 91% of U recovery using a synergistic mixture of di-ethylhexyl phosphoric acid and trioctyl phosphine oxide (DEPA–TOPO) diluted in kerosene. Other methods addressed this matter by different methods such as ion-exchange, membrane separation and liquid-liquid extraction (e.g. Singh et al., 2010; Kumar et al., 2011), being the latter the most widely used method. However, Turgis et al. (2013) obtained improved selectivity than previous systems for U recovery in phosphoric acid using bifunctional amidophosphonic acid ligands. The use of organic solvents may decrease the consumption of acids and the volume of leaching solutions, while improving the selectivity for metal recovery compared to conventional hydrometallurgical leaching methods. In this way, El-Didamony et al. (2012) reported the recovery of around 80% of REE using tri-butyl phosphate (TBP) and tri-octyl phosphine oxide (TOPO) in kerosene.

Some recovery schemes have been implemented even at pilot scale. This is the case of the pilot plant operated by Solvay since 1983, which recovers U and REE from wet-process phosphoric acid using a mixture of DOPPA and TOPO, obtaining a final product with around 26% of REE oxide and 7.9% of U (Rollat, 2016). Kulczycka et al. (2016) studied the feasibility of recovering REE from PG in a Polish fertilizer plant by a novel method based on leaching with H_2SO_4 and chemical REE precipitation. These authors concluded that although this scheme is feasible technically, the large initial investment required might presently limit its implementation.

In contrast to REE and U, the recovery of other elements from the wastes of fertilizer plants have received much less attention and, to our knowledge, recovery schemes have not been still proposed. However, promising research has been performed in the last years for the recovery of these elements from other matrices, and thus, these methods could be successfully applied to fertilizer wastes in the near future. Solvent extraction has been frequently shown as a very efficient technique to extract and concentrate other target metals. For instance, the use of 2-ethylhexanol as extractant to recover B yielded an extraction efficiency of 99.5% in brines with a purity of 95.5% (Zhang et al., 2016). Wang et al. (2013) reported selective Sc extraction (around 99%) using D2EHPA over a H_2SO_4 liquor from the acid attack of red mud at aqueous/organic phase of 5:1 and 40ºC. Nusen et al. (2015; 2016) reported a selective recovery of up to 68% and 92% of Ga and Ge from acid solutions of zinc refinery residues by the performance of synergetic solvent extractions (SSX). On the other hand, Ning et al. (2014) studied the extraction of V and Cr from leaching solutions of chromium-bearing vanadium slags (V–Cr slag) using primary amine LK-N21. They reported an extraction over 90% of V while more than 90% of Cr remained in the raffinate. Even higher extraction efficiency was obtained by Zaky et al. (2005) for Be using TOPO, which was subsequently stripped with NaOH and precipitated at pH 9 up to obtain Be hydroxide of 99.7%. In the same way, Zhu et al. (2015) reported a selective recovery of V and Mo from acid sulfuric solutions by solvent extraction. They obtained an efficient extraction of Mo in the pH range of 0.5–2.0, while efficient V extraction was at pH over 1.8. In the same sulfuric matrix, Nayl (2010) extracted and separated efficiently Co and Ni using different forms of Aliquat 336 diluted with kerosene. On the other hand, El-Hussaini et al. (2004) recovered up to 69% and 79% of Nb and Ta, respectively, from a 0.5M H_2SO_4 solution using a tertiary amine.

All these examples found in similar matrices evidence the existence of available techniques to recover selectively the elements of interest contained in wastes from the phosphate fertilizer manufacturing. Notwithstanding, these processes should be tested and optimized under different conditions (e.g. pH, aqueous/organic phase ratio, temperature) considering the interferences among elements. The development of procedures to increase the purity and quality of the final product is encouraged, as they are the key factors controlling the market value.

Conclusions

The PG stacks deposited in the vicinity of the Huelva city (SW Spain) currently release many edge outflows with a high content of toxic metals and radionuclides into the adjacent estuary. This paper explores the possibility of using these wastes as a source of elements of economic interest, which could constitute a promising economic and environmental friendly solution to this quandary. Three different wastes from the fertilizer plant were studied: i) solid PG, ii) process waters currently deposited in perimeter channels and ponds on the top of the stacks, and iii) edge outflows released from the bottom of the stacks.

In general, elements of economic interest are found in these wastes below of the grades commonly reported in conventional deposits. However, the manufacture of phosphoric acid during four decades has originated a huge tonnage of wastes, i.e. around 100 Mt of solid PG, 10 Mm^3 of process water and 0.48 Mm^3/year of edge outflows. As a result, around 30400 t of B, 16000 t of LREE and Zn, 12000 t of HREE, 1800 t of U, 1400 t of Cr, 1300 t of V and lesser amounts of other elements of economic interest (e.g. Cu, Ni, Sc and Ga) are enclosed in the solid PG within the stacks. The process water ponds also contain significant reserves of some elements of economic interest; around 1360 t of Zn, 760 t of V, 630 t of U and Cr, 225 t of Cu, 160 t of Ni, 110 t of HREE and lesser quantities of other elements (e.g. LREE, B, Sc, Co, Sb, Mo and Be) are dissolved in this wastewater.

The recovery of these elements from these wastes is technically feasible, as promising research in metal recovery schemes have been performed in last years. The high price of some elements such as HREE, LREE, Sc or U encourages the development of recovery schemes and the study of the costs associated. Intense research must be done on the development of refining processes to increase the purity of the final product, which may control its market value. This study highlights the existence of minable stocks of elements of economic interest in PG stacks which could be of interest for the fertilizer industry to provide more sustainable and cost-effective management of these wastes.

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Tables

Location	Deposit type	Tonnage	Grade REO
Bayan Obo (China)	Carbonatite-associated	750 Mt	4.10%
Thor Lake (Canada)	Associated with alkaline igneous rocks	64 Mt	1.96%
Olimpic Dam (Australia)	Iron-REE deposits	2000Mt	0.33%
Lehmi Pass (USA)	Hydrotermal deposits	39Mt	0.51%
Jangardup (Island)	Marine placers	30 Mt	0.046%
Horse Creek (USA)	Alluvial placers	19 Mt	0.041%
Mount Weld (Australia)	Lateritic deposits	12 Mt	9.70%
Longnan (China)	Ion-adsorption clays	<0.01 Mt	0.03-0.35%
Huelva (Spain)	Phosphogypsum	100 Mt	0.034%

Table 1. Comparison of rare elements oxides (REO) content in PG with respect main conventional deposits worldwide. Modified from BGS (2011) compilation of data reported by Orris and Grauch (2002) and Grauch and Mariano (2008).

		Tonnage			**Valuation (Million USD)**		
		Phosphogypsum	*Process waters*	*Edge outflows*	*Phosphogypsum*	*Process waters*	*Edge outflows* [1]
		100 Mt	10 Mm^3	0.48 Mm^3/yr	8721	213	2.4
Critical raw materials	*Price [1] (USD/kg)*						
B	4.6	30425	73	1.38	12	0.03	0.001
LREE	35	16005	74	0.077	584	1.9	0.002
HREE	206	12297	114	0.048	1116	7.6	0.004
Cr	17	1374	627	3.27	24	11	0.056
Co	28	109	18	0.21	3.0	0.51	0.006
Sb	8.4	38	8.0	0.12	0.32	0.07	0.001
Be	508	22	4.0	0.04	11	2.1	0.019
Nb	42	13	0.17	0.002	0.53	0.01	0.0001
Elements of economic interest							
Zn	1.4	15897	1362	13.55	23	2.0	0.020
U	61	1807	639	4.20	111	39	0.258
V	8.8	1278	769	5.25	11	6.7	0.046
Cu	4.9	1126	225	2.02	5.5	1.1	0.010
Se	53	518	4.3	0.05	27	0.22	0.003
Ni	8.6	405	164	1.29	3.5	1.4	0.011
Sc	15000	316	8.6	0.13	4738	130	1.9
Ga	197	151	1.9	0.01	30	0.37	0.003
Ge	1906	104	0.7	0.01	198	1.4	0.012
Mo	18	82	4.5	0.02	1.5	0.08	0.000
Ta	320	45	0.1	0.004	14	0.02	0.001

Table 2. Estimated reserves (tons) and valuation (million USD) of elements of economic interest in unwanted by-products generated by the Huelva fertilizer plant (SW Spain). 1 Reserves calculated in edge outflows are expressed as ton/yr. Valuation estimated according to the metal prices for 2015 listed in the London Metal Exchange (LME, 2015) and those reported by USGS (2016).