Journal of Cleaner Production xxx (2016) 1–9

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

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

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ARTICLE INFO

Article history:
Received 25 October 2016
Received in revised form
15 December 2016
Accepted 16 December 2016
Available online xxx

Keywords:
Phosphogypsum
Lanthanides
Metal recovery
Waste valorization

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 wastes stockpiled constitutes a significant secondary source of elements. Around 30,400 t of B, 28,000 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.

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

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.

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http://dx.doi.org/10.1016/j.jclepro.2016.12.083
0959-6526/

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-Zrelli 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 of rare earth elements (REE) which have a great economic impact due to their use in technological applications (Binnemans et al., 2013). The recovery of REE in PG has been focus of much research based on hydrometallurgical (e.g. Preston et al., 1996; Lokshin et al., 2002) 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.

The dumping of these wastes directly on bare marshland soils over 40 years has 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 consists 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

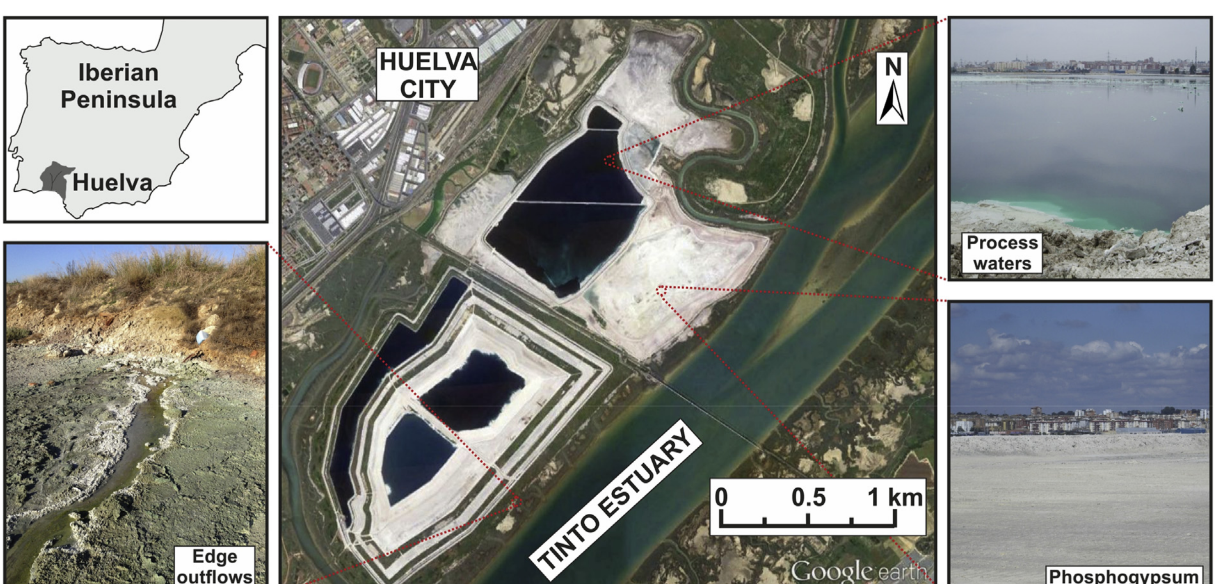

Fig. 1. Location map of the Huelva PG stacks (SW Spain), showing the main wastes generated by the fertilizer plant.

Please cite this article in press as: Cánovas, C.R., et al., Exploration of fertilizer industry wastes as potential source of critical raw materials, Journal of Cleaner Production (2016), http://dx.doi.org/10.1016/j.jclepro.2016.12.083