Science of the Total Environment xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

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

Mobility of rare earth elements, yttrium and scandium from a phosphogypsum stack: Environmental and economic implications

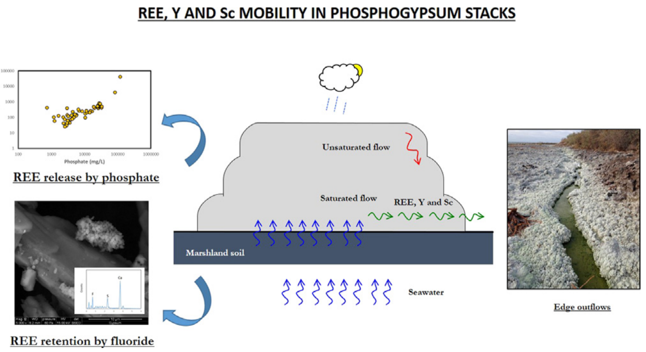
Carlos Ruiz Cánovas *, Francisco Macías, Rafael Pérez López, José Miguel Nieto

Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment (RENSMA), Faculty of Experimental Sciences, Avda. Fuerzas Armadas s/n, 21071 Huelva, Spain

HIGHLIGHTS

- The mobility of REE, Y and Sc has not been properly addressed in phosphogypsum stacks.
- Leaching tests showed a low mobility of REE, Y and Sc in the stack.
- Phosphate minerals may host REE and Y in the phosphogypsum stack.
- Fluoride minerals may exert a solubility control of REE, Y and Sc in pore waters.
- Phosphogypsum is a secondary source of REE, Y and Sc that could be exploited.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 April 2017
Received in revised form 22 July 2017
Accepted 21 August 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Leaching test
Fractionation processes
REE scavenging
REE fractionation

ABSTRACT

This paper investigates the mobility and fluxes of REE, Y and Sc under weathering conditions from an anomalously metal-rich phosphogypsum stack in SW Spain. The interactions of the phosphogypsum stack with rainfall and organic matter-rich solutions, simulating the weathering processes observed due to its location on salt-marshes, were simulated by leaching tests (e.g. EN 12457-2 and TCLP). Despite the high concentration of REE, Y and Sc contained in the phosphogypsum stack, their mobility during the leaching tests was very low; <0.66% and 1.8% of the total content of these elements were released during both tests. Chemical and mineralogical evidences suggest that phosphate minerals may act as sources of REE and Y in the phosphogypsum stack while fluoride minerals may act as sinks, controlling their mobility. REE fractionation processes were identified in the phosphogypsum stack; a depletion of LREE in the saturated zone was identified due probably to the dissolution of secondary LREE phosphates previously formed during apatite dissolution in the industrial process. Thus, the vadose zone of the stack would preserve the original REE signature of phosphate rocks. On the other hand, an enrichment of MREE in relation to HREE of edge outflows is observed due to the higher influence of estuarine waters on the leaching process of the phosphogypsum stack. Despite the low mobility of REE, Y and Sc in the phosphogypsum, around 104 kg/yr of REE and 40 kg/yr of Y and Sc are released from the stack to the estuary, which may imply an environmental concern. The information obtained in this study could be used to optimize extraction methods aimed to recover REE, Y and Sc from phosphogypsum, mitigating the pollution to the environment.

1. Introduction

Rare earth elements (REE) are a group of chemically similar metallic elements (i.e. lanthanide series). Although traditionally scandium (Sc)

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* Corresponding author.
E-mail address: carlos.ruiz@dgeo.uhu.es (C.R. Cánovas).

https://doi.org/10.1016/j.scitotenv.2017.08.220
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Please cite this article as: Cánovas, C.R., et al., Mobility of rare earth elements, yttrium and scandium from a phosphogypsum stack: Environmental and economic implications, Sci Total Environ (2017), https://doi.org/10.1016/j.scitotenv.2017.08.220

and yttrium (Y) were also included in this group, only Y is currently considered as lanthanide (Chakhmouradian and Wall, 2012), forming a group known as REY elements (Ayora et al., 2016). This group of elements, arbitrarily divided into light (LREE: La to Nd), medium (MREE: Sm to Gd) and heavy (HREE: Tb to Lu plus Y) (Hatch, 2012), are becoming increasingly important in the transition to a green, low carbon economy due to their essential role in permanent magnets, lamp phosphors, rechargeable NiMH batteries, catalysts and other applications (Binnemans et al., 2013). REE are not considered as essential elements for living organisms, although they may have unknown functions in the organisms, especially in innumerable biochemical processes (Migaszewski and Galuszka, 2015). On the contrary, some studies suggested that high concentrations of REE may cause significant environmental impacts on living organisms (e.g. Oral et al., 2010; Pagano et al., 2015). The growing use of these elements by industry has led to an inherent increase of REE emissions into the environment. Thus, it is of paramount importance to address the potential release and transport of REE during all stages of industrial processes. A potential source of REE, Y and Sc to the environment is the fertilizer industry which produces the phosphoric acid needed for fertilizer manufacturing. Phosphoric acid is commonly produced by the chemical reaction of the phosphate rock with sulfuric acid, a process known as wet chemical treatment, responsible for around 90% of the worldwide phosphoric acid production (USGS, 2016). As a result, a by-product known as phosphogypsum is generated. Phosphogypsum is mainly composed of gypsum ($CaSO_4 \cdot 2H_2O$) although may also contain other minor solid phases such as reaction products of the wet process (e.g. alkali fluorosilicates and fluorides), unreacted phosphate rock and gangue mineral particles (e.g. quartz, organic matter and feldspars) (Lottermoser, 2010). The presence of wastewaters from the industrial process, mainly phosphoric, sulfuric, and hydrofluosilicic acids, trapped in the interstices of mineral particles confers to phosphogypsum its acidic nature. In addition, this residual water contains high levels of metals, metalloids and radionuclides (Luther et al., 1993). Due to the high level of impurities, phosphogypsum are often stockpiled in stacks close to the factories and finally covered, and rarely recycled.

During the wet process, elements contained in the phosphate rock are released from their host phases into solution and partitioned into phosphoric acid or phosphogypsum, according to their solubility (Rutherford et al., 1994). Uranium, Th and Pb-210 concentrate in the phosphoric acid whereas most of the Ra-226 and Po-210 are finally contained in phosphogypsum (Lottermoser, 2010). According to different authors (e.g. Rutherford et al., 1994; Al-Masri et al., 2004; Pérez-López et al., 2011), metals (e.g. Cd, Cu and Zn) are preferentially transferred into phosphoric acid. In the case of REE, around 70–85% originally present in phosphate rocks are concentrated in solid phosphogypsum (Binnemans et al., 2015). The weathering of phosphogypsum stacks constitutes an environmental concern due to the release of pollutants into the surrounding environment (e.g. Bolívar et al., 2002; Tayibi et al., 2009; Pérez-López et al., 2015; El-Zrelli et al., 2016). Unlike metals, metalloids and radionuclides, the mobility of REE in phosphogypsum stacks has not been studied in detail nor have their fluxes into the environment been quantified, despite the potential interest for recovery of these elements from phosphogypsum (e.g. Binnemans et al., 2015; Cánovas et al., 2017). This issue is especially significant taking into account the worldwide growing production of phosphogypsum to support the increasing levels of farming production; around 100–280 Mt of this by-product is generated per year (Parreira et al., 2003) and deposited near the industries due to its limited recycling. An improved understanding of REE behavior during low-temperature water–rock interaction in industrial waste landfills is needed. Thus, this study investigates the factors controlling the mobility of REE under weathering conditions in a phosphogypsum stack in SW Spain and quantifies the REE fluxes to the environment.

2. Methods

2.1. Site description

A fertilizer plant was operating via wet treatment near Huelva city (SW Spain) during almost 40 years (from 1967 to 2010). Sedimentary phosphorite was imported mainly from Morocco to manufacture the phosphoric acid. As a result, around 100 Mt of phosphogypsum were directly dumped on 12 km^2 of salt-marshes of the Tinto River estuary, <100 m from the city (Fig. 1). The implementation of a closed-circuit system in 1997 promoted the existence of process water ponds in the central part of the stacks and a system of perimeter channels for collecting all leakages from the piles (Fig. 1). The singularity of this phosphogypsum stack relies on the facts that wastes were deposited over the marshland without any type of isolation and within the tidal prism of the estuary. Under these circumstances, this stack is strongly weathered not only by a downward flow of rainwater during rainy episodes but also by an upward flow of seawater during tidal cycles. In case of weathering by rainwater, these episodes are especially significant as rainfall events in Mediterranean regions are scarce but intense. In addition, the absence of composite liners in the bottom of the stack causes the interaction of these wastes and their weathering agents with the organic matter-rich marshland. As a result, the weathering of the phosphogypsum can occur under oxidizing conditions in the shallowest part and under reducing conditions in the deepest part in contact with the marsh (Pérez-López et al., 2015). Moreover, this phosphogypsum contains anomalously high concentrations of some toxic elements in comparison to others around the world (Macías et al., 2017). In order to avoid the release of pollutants to the estuary during rainy events, the stack has been partially restored. Despite the decrease in the pollutant release observed, these measures seem to be insufficient as permanent edge outflows continue being released from the toe of the stack (Pérez-López et al., 2016). The main chemical difference between edge outflows emerging from the bottom of the stack and process waters stored in surface ponds is the higher element concentration in the latter due to the large residence time in the close-circuit system and to evaporation. Detailed descriptions of physical and environmental setting of Huelva phosphogypsum stack can be found in Pérez-López et al. (2007, 2015, 2016) and Macías et al. (2017).

2.2. Sampling and analytical techniques

2.2.1. Water and solid samples

Edge outflows were sampled along the perimeter of the phosphogypsum stack during the dry and rainy seasons (June and November 2014). In addition, some samples of process water contained in central ponds and perimeter channels of the stacks were taken (Fig. 1). In total, 121 water samples were collected during both campaigns. The pH, redox potential (ORP), electrical conductivity (EC) and temperature were measured in the field using a portable Multiparametric Crison MM 40+ equipment. Measured ORP values were referenced to the standard hydrogen electrode (Eh), as proposed by Nordstrom and Wilde (1998). Water samples were filtered with 0.10 μm membrane filters and divided into two aliquots; one unacidified for anion and ammonia determination and the other acidified with HNO_3 to $pH < 1$ for major and trace element analysis. From an operational point of view, concentrations determined in filtrates were considered to be dissolved.

Concentrations of anions (PO_4, Br, Cl and F) and ammonia in unacidified aliquots were analyzed by high performance liquid chromatography (HPLC) using a Metrohm 883 basic ion chromatograph (IC) equipped with Metrosep columns. The acidified samples were analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; Jobin Yvon Ultima 2) for major elements (Al, Ca, K, Mg, Na and S) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS; Agilent 7700) for REE, Y and Sc. Detection limits were: 0.2 mg/L for S; 0.1 mg/L for Na; 0.05 mg/L for K and Mg; 0.02 mg/L for Al and Ca; and 0.1 μg/L for

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