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Fractionation and fluxes of metals and radionuclides during the recycling process of phosphogypsum wastes applied to mineral CO₂ sequestration

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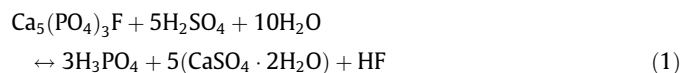
ABSTRACT

The industry of phosphoric acid produces a calcium-rich by-product known as phosphogypsum, which is usually stored in large stacks of millions of tons. Up to now, no commercial application has been widely implemented for its reuse because of the significant presence of potentially toxic contaminants. This work confirmed that up to 96% of the calcium of phosphogypsum could be recycled for CO₂ mineral sequestration by a simple two-step process: alkaline dissolution and aqueous carbonation, under ambient pressure and temperature. This CO₂ sequestration process based on recycling phosphogypsum wastes would help to mitigate greenhouse gasses emissions. Yet this work goes beyond the validation of the sequestration procedure; it tracks the contaminants, such as trace metals or radionuclides, during the recycling process in the phosphogypsum. Thus, most of the contaminants were transferred from raw phosphogypsum to portlandite, obtained by dissolution of the phosphogypsum in soda, and from portlandite to calcite during aqueous carbonation. These findings provide valuable information for managing phosphogypsum wastes and designing potential technological applications of the by-products of this environmentally-friendly proposal.

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1. Introduction

Industrial production of fertilisers from phosphate rock ore by the wet process produces a gypsum-rich by-product called phosphogypsum (PG, CaSO₄·2H₂O). It is generated in the production of phosphoric acid (H₃PO₄) during the acid attack of apatite (mainly fluorapatite, Ca₅(PO₄)₃F) with sulphuric acid (H₂SO₄) (Rutherford et al., 1994). The chemical reaction of the industrial process can be written as follows:



Worldwide phosphogypsum production is estimated to be around 280 Mt per year (Yang et al., 2009). However, only 15% of the phosphogypsum is recycled (Kim, 2010) because of existing contaminants, such as organic substances, metals and other potentially toxic elements and natural radionuclides from the ²³⁸U decay

series (Mas et al., 2006; Pérez-López et al., 2007). The remaining 85% is often stored in large stacks in areas close to fertiliser plants (Tayibi et al., 2009). Spanish phosphoric acid production began in the city of Huelva (SW Spain) in 1968, and since then the PG waste has been slurried with water, pumped out of the fertiliser plant by a pipe system and then dumped on a nearby disposal site in the salt-marshes of the Tinto River (1200 ha containing about 120 Mt) without any commercial application (Bolívar et al., 2009a, 1995). The proximity of the waste to Huelva, less than 1 km away, is an important concern because of its alleged implications for the health of the local population of roughly 150,000 inhabitants. After looking unsuccessfully for sustainable solutions to the stockpiling of wastes, the fertiliser plant ceased dumping phosphogypsum in December 2010. However, the waste piles still remain in the area without an apparent solution. The urgent need to perform the current study is related to the great social interest in an action plan proposing solutions to the problem of the phosphogypsum stacks.

The main restrictions on reusing PG are related to its relatively high content of radionuclides and metallic elements, and evidence

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the need for in-depth radiochemical studies prior to the search for future applications. During the chemical attack of the phosphate rock, the impurities are partitioned according to their respective elementary chemical behaviours. Between 85% and 95% of most of the trace elements, including uranium and thorium, goes into the phosphoric acid fraction (liquid fraction), and therefore into the phosphate fertiliser, whether no purification processes are applied to remove these impurities. Conversely, more than half of the Sr and Y content and radium-isotopes such as ^{210}Pb and ^{210}Po co-precipitate with the PG since they are chemically very similar to calcium (Pérez-López et al., 2010; Bolívar et al., 2009b; Mazzilli et al., 2000). The concentration of some impurities in the PG, such as P_2O_5 , Cd or Y, has been found to exceed that of the typical uncontaminated soils, but others, such as Cr or Pb, have been observed to fall below uncontaminated typical soils (Pérez-López et al., 2010; Rudnick and Gao, 2003). Nevertheless, these results may vary significantly depending on the phosphate rock origin (Tayibi et al., 2009).

Despite these drawbacks, environmentally friendly applications are already being investigated. One of them is based on the use of PG as a calcium source for CO_2 mineral sequestration in the framework of the mitigation of greenhouse gases emissions. It is well known that some calcium-rich compounds can be considered as efficient sinks of carbon dioxide by carbonation reactions. Mineral sequestration is a promising strategy for permanently fix carbon dioxide (Seifritz, 1990; Power et al., 2013) which involves a naturally occurring reaction in geological formations where aqueous ions (mainly Ca and Mg resulting from silicates or oxides) react with CO_2 to form stable carbonate minerals. The speed of the reaction and the costs associated with the scale-up from laboratory to industry are the major drawbacks of this technology. However, this carbonation reaction can be accelerated by using sequester agents with high specific surface areas (Santos et al., 2009) and the costs could be reduced by using industrial alkaline wastes (Kirchofer et al., 2013) as Ca and Mg sources, e.g. municipal solid waste bottom-ash (Rendek et al., 2006), paper mill wastes (Pérez-López et al., 2008) or coal combustion fly-ash (Montes-Hernandez et al., 2009). Moreover, neither high pressure nor high temperature are needed because some waste slurries, such as acetylene production wastes (Morales-Flórez et al., 2011), are able to capture CO_2 in very soft conditions, even at atmospheric concentrations. In addition, mineral sequestration is able to fix not only carbon dioxide from localised sources but also that from diffuse pollution sources such as road traffic and past emissions.

In this context, a recent work has offered the first approach to the use of phosphogypsum wastes as a Ca source for carbon dioxide mineral sequestration (Cárdenas-Escudero et al., 2011). It reports the very high efficiency of the process and the behaviour of the main metals; however, as far as we know, no thorough study concerning fractionation and flow of trace metals and radionuclides throughout the complete carbonation process using phosphogypsum has been conducted. To bridge this information gap, the present study focuses on the characterisation of the contents of metallic impurities and radionuclides in raw materials and products during the complete procedure. The obtained results provide very useful information which should help with the development of technological solutions to this environmental problem.

2. Materials and methods

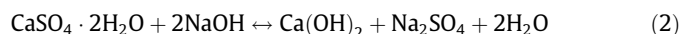
2.1. Phosphogypsum sampling and pretreatment

After preliminary characterisation of the phosphogypsum stacks in Huelva (Rentería-Villalobos et al., 2010), a representative sample was collected (≈ 2 kg at 0–15 cm depth). To develop the

chemical, mineralogical and radioactive characterisation an aliquot of the original PG sample was dried at 60°C until it reached constant weight, ground and homogenised in a planetary mill at 400 rpm for 20 min. Drying at 60°C removes free water from the sample without losing structural water in gypsum.

2.2. Experimental carbonation procedure

The experimental carbonation procedure was made using the original PG material, in order to reproduce it under real conditions. The process can be conceptually divided into two steps: (a) PG dissolution, and (b) subsequent carbon sequestration. In Fig. 1, the entire experimental procedure is sketched; full details of the methodology can be found elsewhere (Cárdenas-Escudero et al., 2011). The first process started with the dispersion of PG in distilled water at room pressure and temperature with a $\text{PG}/\text{H}_2\text{O}$ mass ratio of four, and then NaOH (pellets PA-ACS-ISO, PANREAC Química SAU, 98% chemical purity) was added to reach an $\text{OH}^-/\text{Ca}^{2+}$ molar ratio of two under constant magnetic stirring for 3 h. The chemical reaction of this first step can be written as:



This procedure resulted in the PG's dissolution and the precipitation of a whitish solid phase labelled 'S1', ($\text{Ca}(\text{OH})_2$, Eq. (2)) and a transparent supernatant liquid labelled 'L1'. The S1 was obtained by filtration, and the L1 was evaporated to dryness on a hot plate, yielding transparent salts labelled 'S2' (Na_2SO_4 , Eq. (2)).

The second process began with the dispersion of sample S1 in distilled water under magnetic stirring in a reactor with a $\text{S1}/\text{H}_2\text{O}$ mass ratio of 1/20. A CO_2 flux (~ 1 bar, $20\text{ cm}^3\text{ s}^{-1}$) was bubbled through the suspension for 15 min at room pressure and temperature. Afterwards, the sample was left to rest overnight in the CO_2 -rich water. The carbonation reaction can be written as:



The resulting solid phase labelled 'S3' (CaCO_3 , Eq. (3)) was separated by centrifugation and dried in air at 80°C . The supernatant was labelled 'L2'. It was evaporated to dryness, yielding a precipitate labelled 'S4'. The carbonation experiments were repeated five times so their reproducibility could be analysed and uncertainties associated with the experimental procedure evaluated.

2.3. Analytical techniques

The mineral characterisation of the raw materials (PG and sodium hydroxide) and the final solid products was performed by X-ray diffraction (XRD, powder method) with a Bruker diffractometer (D8-Advance with Cu $K\alpha$ radiation). Diffractometer settings were 40 kV, 30 mA, a scan range of $3\text{--}65^\circ$ (2θ) with a step size of 0.02° and a counting time of 0.6 s per step. Analysis of diffraction patterns was performed with the X Powder software (Martín-Ramos, 2004). By using the original PG sample, the particle size analysis was performed by laser granulometry in wet suspensions with water as dispersant, using a Malvern Mastersizer 2000 particle sizer with Hydro 2000 M accessory. Furthermore, morphological analyses of the samples were obtained by the use of a JEOL JSM 5410 scanning electron microscope (SEM) working at 20 kV.

Major elements were analysed by X-ray fluorescence (XRF) with a Bruker spectrometer S4 Pioneer equipped with an X-ray tube of 4 kW (front window), anode of Rh, five analyser crystals (LIF200, Ge, PET, OVO 55 and OVO C) and both flow and scintillation detectors. Trace elements were determined by ICP-MS (inductively coupled plasma mass spectrometry) after four-acid digestion at the Activation Laboratories Ltd (ACTLABS, Ontario, Canada), which meet the ISO/IEC 17025 Quality System standard. The quality control method included the use of a reagent blank, standard reference

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