



Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: [www.elsevier.com/locate/jenvman](http://www.elsevier.com/locate/jenvman)

Research article

# Spatial distribution and leaching behavior of pollutants from phosphogypsum stocked in a gypstack: Geochemical characterization and modeling

Sara Bisone, Mathieu Gautier, Vincent Chatain, Denise Blanc\*

Université de Lyon, INSA-Lyon, DEEP (Déchets Eaux Environnement et Pollutions – Wastes Water Environment Pollutions), 20 Avenue Albert Einstein, F-69621, Villeurbanne, France

## ARTICLE INFO

## Article history:

Received 15 November 2016

Received in revised form

20 February 2017

Accepted 21 February 2017

Available online xxx

## Keywords:

Phosphogypsum  
Geochemical modeling  
Leaching behavior  
Phosphates  
Fluoride

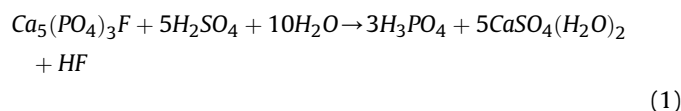
## ABSTRACT

Phosphogypsum (PPG) is the byproduct of the production of phosphoric acid and phosphate fertilizers from phosphate rocks (PR) by acid digestion. Despite the technical feasibility, the impurities present in this waste make its reuse critical and large amounts of PPG are stockpiled, resulting in the production of polluted acid leachates. The aim of the present study was to characterize the spatial variability and evolution in time of a 20-year-old gypstack and to study the geochemical behavior of the waste in order to assess the best management options. Chemical and mineralogical analyses were performed on core samples taken from 4 different depths of the stack down to 13.5 m. Despite the high homogeneity shown by chemical and mineral characterization, leaching tests revealed a different chemical behavior with depth. pH-dependent leaching tests were also performed to measure the acid neutralization capacity of the studied matrices and to determine the leachability of the elements or pollutants of concern as a function of pH. The study was focused on Ca, Fe Na, Si, Cd and Sr and on  $F^-$ ,  $PO_4^{3-}$  and  $SO_4^{2-}$  anions. The geochemical modeling of these tests with PHREEQC enabled the identification of the minor phases controlling the solubilization of the elements analyzed. Validation of the model by the simulation of a column leaching test suggested that the model could be used as a predictive tool to assess different management scenarios.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Phosphogypsum (PPG) is the byproduct of the production of phosphoric acid and phosphate fertilizers from phosphate rocks (PR) by acid digestion. PR contain high concentrations of phosphate minerals, mostly from the apatite group  $Ca_5(PO_4)_3[F, OH, Cl]$ . Among the different production processes, the dihydrate (DH) process was the most widely used (IAEA, 2013). The acid digestion with sulfuric acid at high temperature (70–80 °C) used in this process can be simplified with the following equation:



The PPG is then separated from phosphoric acid by filtration, and later washed to reduce hydrofluoric acid (HF) concentration. Phosphoric acid recovery does not reach 100%, hence residual phosphorus and HF can be found in the PPG. Phosphorus is mostly present as phosphoric acid, but it can precipitate as  $Ca_3(PO_4)_2$ ,  $Ca(H_2PO_4)_2$  and  $CaHPO_4 \cdot 2H_2O$  (Aliedeh and Jarrah, 2012). HF can react with silica to form  $SiF_4NaF$ ,  $Na_2SiF_6$ ,  $Na_2FeF_6$  and  $CaF_2$  may also be found in PPG (Aliedeh and Jarrah, 2012). Beside the residual acidity and F, some impurities may accumulate in PPG. Metals (Sr, Ba, Cu, Cd, etc.), and radio-elements ( $^{226}Ra$ ,  $^{238}U$ ) are frequently found in PPG (Abril et al., 2008; Degirmenci et al., 2007; IAEA, 2013) and make the management of this waste a complex issue.

These impurities come primarily from PR and to a lesser extent from sulfuric acid (Davister, 1998). The process used also determines the amount and the characteristics of PPG generated (Ghafoori and Chang, 1993). The DH process engenders about 4.9 t of PPG (dry mass) for every ton of phosphoric acid produced. PPG wet mass can reach 6.5 t (IAEA, 2013). In 2009, worldwide PPG

\* Corresponding author.

E-mail address: [denise.blanc@insa-lyon.fr](mailto:denise.blanc@insa-lyon.fr) (D. Blanc).

production per year was estimated to be around 100–280 million tons (Yang et al., 2009).

Phosphorus production by acid attack is widespread, but the global quantity of PPG produced per year is difficult to estimate. The IAEA (International Atomic Energy Agency) reported a total production of 6 billion t of PPG up to 2006, 37% of which was produced by the USA (IAEA, 2013).

The valorization of this waste has been widely studied. PPG has been mainly recycled in agriculture as a fertilizer, thanks to its high content of S, Ca and P. It has also proved to be efficient in reclaiming sodic soil, reducing the aluminum toxicity and acidity of subsoils and improving calcareous soils (Alcordero and Rechcig, 1993; Rutherford et al., 1994; Sfar Felfoul et al., 2002). As a substitute for natural gypsum, PPG has been recycled in building materials in the composition of cement and concrete and used to produce plaster and plasterboard (Reijnders, 2007; Tayibi et al., 2009; Zhang et al., 2013) or as a road base material (Dooris and Martin, 2000; Shen et al., 2009).

However, the radioactivity and the occurrence of leachable metals represent a potential danger for its application, particularly in agriculture (Al-Hwaiti and Al-Khashman, 2015; Ammar et al., 2016; Elloumi et al., 2015). The presence of residual acidity and impurities imposes some technical limits on its reuse as building material. A pretreatment is usually recommended but subsequently reuse material becomes less cost-effective, especially in countries with natural gypsum deposits. More recent phosphoric acid production methods generate a purer waste, which can be easily reused and recycling facilities are sometimes integrated in the production process (Hilton, 2013; Zhang, 2010). Despite these efforts, most of the PPG produced has been stockpiled (between 42 and 62% of the world production up to 2006) (IAEA, 2013) or discharged in water bodies. Stockpiles are current in all countries where the production of phosphoric acid by wet process is used (USA, Europe, China, Morocco and Tunisia) (Gázquez et al., 2009; Greenpeace, 2013; IAEA, 2013). Stockpiles are land-consuming and their operating costs are substantial since the high production of acid leachates concentrated in metals demands management of the stock and treatment of the wastewater. Hilton and Astley (2005) estimate, for Florida, an approximate handling and storage cost of 1.50 \$ per ton of PPG produced, giving a life-time storage cost of around 25 \$ per ton (Hilton, 2010). Finding the best management options for this waste is still a challenge.

Previous studies focused mainly on PPG characterization at the end of the production process (Al-Masri et al., 2004; Sfar Felfoul et al., 2005), on superficial samples of PPG stocks (Rentería-Villalobos et al., 2010), or on the study of gypstack leachates (Gázquez et al., 2014; Papanicolaou et al., 2009; Pérez-López et al., 2010, 2016). Very few studies have investigated the spatial characterization of stockpiled PPG (Al-Hwaiti et al., 2005). The study of the variability of stocked PPG is important in assessing the best management options. The objective of the present study was to contribute to the knowledge of the geochemical characteristics and leaching behavior of stocked PPG. The results of this study are based on PPG samples coming from a 20-year-old gypstack. The variability of PPG characteristics with stack depth was evaluated. Investigations focused especially on the distribution and mobility of the PPG main constituents (calcium and sulfates) and the elements that are more problematic for the wastewater treatment of stockpiles (phosphates and fluoride). The approach was based on the use of a mineralogical study, batch leaching tests and geochemical modeling. This study aims to provide a reliable instrument to evaluate different management scenarios for stockpiled PPG.

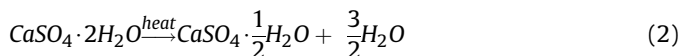
## 2. Materials and methods

### 2.1. Sampling

Four core samples (SC1, SC2, SC3, and SC4) at depths ranging from 11 to 13.8 m were collected by sonic drilling from a French gypstack operating in the 1980s and – 1990s. The total surface of the stack is about 30 ha and the cores were taken at different points of the stack in order to obtain central and peripheral samples. For each core, three samples were selected for this study: a superficial one, one from the middle of the core, and a deeper one. The following 12 samples were obtained (depth is expressed as distance from the top of the stack): SC1 (0–2 m); SC1 (11–12 m); SC1 (13–13.5 m); SC2 (0–2 m); SC2 (6–8 m); SC2 (13–13.8 m); SC3 (0–2 m); SC3 (6–8 m); SC3 (11–12 m); SC4 (0–2 m); SC4 (6–8 m); SC2 (13–13.5 m). For core SC1 the depth 11–12 m was chosen instead of the middle of the core as this layer had a different appearance (darker color). For the superficial samples the first 0.5 m were discarded. Samples were homogenized and stored at 4 °C in the dark.

### 2.2. Physico-chemical and mineralogical characterization

Moisture content of PPG was measured after drying at 55 °C for 72 h. This temperature was chosen to avoid the transformation of gypsum into hemihydrate calcium sulfate that may occur from about 60 °C (Hitachi, 1985; Popescu et al., 1985; Van der Merwe et al., 1999), according to (2).



pH, oxidation reduction potential (ORP) and conductivity of each sample were measured from a solution of deionized water with a liquid/solid ratio of 10 and after a contact period of 30 min pH was measured with a WTW® combined glass electrode after calibration. The redox potential (ORP) was measured in the same solution using a Rodier electrode (Ag-AgCl/KCl, + 220 mV vs. NHE).

The analysis of trace and major contents were performed by the Service d'Analyse des Roches et des Minéraux (SARM) of the Centre de Recherches Pétrographiques et Géochimiques (CRPPG). After digestion by LiBO<sub>2</sub> fusion, total content elements samples were analyzed by ICP-OES for major and ICP-MS for trace elements. Organic carbon and total sulfur were analyzed after separation by a CS analyzer, fluorine by potentiometry after fusion with Na<sub>2</sub>CO<sub>3</sub>.

A representative selection of samples grounded to powder (<50 μm) was analyzed by X-ray diffraction on a Bruker D8 Advance instrument equipped with a VANTEC-1 “SUPER SPEED” detector and a copper anticathode. The samples were scanned on an angular range from 3° to 70° with steps of 0.022°. Results were processed with the DIFFRAC.EVA® software (V3.0) using the Powder Diffraction File database distributed by the International Centre for Diffraction Data (ICDD).

Mineralogical characterization was completed by thermogravimetry-differential thermal analysis (TG/DTA) using a Labsys 1600 instrument by SETARAM. 20 ± 1 mg of PPG dried at 55 °C were analyzed in duplicate. Samples were heated at a constant heating rate of 10 °C · min<sup>-1</sup> up to 1500 °C under nitrogen and up to 850 °C under air. Results were processed with the SETSYS software by SETARAM. The mass of gypsum in the waste was estimated on the basis on the mass loss associated to water evaporation during the transformation of gypsum to hemihydrate between 100 and 150 °C (Eq. (2)). It was found that moisture was completely evaporated at T < 60 °C.

Download English Version:

<https://daneshyari.com/en/article/5116860>

Download Persian Version:

<https://daneshyari.com/article/5116860>

[Daneshyari.com](https://daneshyari.com)