



Effects of seawater mixing on the mobility of trace elements in acid phosphogypsum leachates



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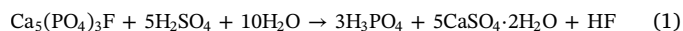
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ABSTRACT

This research reports the effects of pH increase on contaminant mobility in phosphogypsum leachates by seawater mixing, as occurs with dumpings on marine environments. Acid leachates from a phosphogypsum stack located in the Estuary of Huelva (Spain) were mixed with seawater to achieve gradually pH 7. Concentrations of Al, Fe, Cr, Pb and U in mixed solutions significantly decreased with increasing pH by sorption and/or precipitation processes. Nevertheless, this study provides insight into the high contribution of the phosphogypsum stack to the release of other toxic elements (Co, Ni, Cu, Zn, As, Cd and Sb) to the coastal areas, as 80–100% of their initial concentrations behaved conservatively in mixing solutions with no participation in sorption processes. Stable isotopes ruled out connexion between different phosphogypsum-related wastewaters and unveiled possible weathering inputs of estuarine waters to the stack. The urgency of adopting effective restoration measures in the study area is also stressed.

1. Introduction

The phosphate fertilizer industry produces huge amounts of a waste by-product, known as phosphogypsum (mainly gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) through the wet chemical digestion of phosphate ore (fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$) with sulphuric acid (H_2SO_4) to generate phosphoric acid (H_3PO_4). The theoretical overall chemical reaction is (Eq. (1)):



Most of the contaminants in the raw phosphate ore are transferred to the phosphoric acid during the wet chemical process (Bolivar et al., 2009; Pérez-López et al., 2010). Phosphogypsum has high acidity and concentration of contaminants due to the occurrence of residual phosphoric acid that has not been fully separated during the industrial process and that remains trapped in the interstices of gypsum grains. The waste also contains other chemical reagents and products from reaction (1), such as sulphuric and hydrofluoric acids, ammonium hydroxide or amine (Lottermoser, 2010). These impurities strongly limit

the potential of phosphogypsum for recycling, e.g. as agricultural additives or for building materials (see review in Cánovas et al. (2018)).

Phosphogypsum wastes are often dumped directly in the marine environment and considered one of the major sources of seawater contamination, as occurs in the Gulf of Gabes (SE Tunisia) (El Zrelli et al., 2015). They are transported as an aqueous slurry and without any prior treatment are usually stockpiled in coastal areas close to phosphate fertilizer plants, where they are exposed to weathering conditions (Tayibi et al., 2009) and physical and geochemical processes associated with coastal systems (Sanders et al., 2013). These stacks are considered as a significant source of environmental contamination under leaching conditions (Lottermoser, 2010; Pérez-López et al., 2016).

Coastal systems are responsible for the mass flux of elements entering the deep ocean, because they serve as transition zones between freshwater and seawater environments. At coasts, significant modifications of seawater chemistry occur concerning salinity, ionic composition and redox conditions depending on the tidal cycles and the temporal variations in freshwater inputs (Hierro et al., 2014; Liang and

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Wong, 2003). During mixing of wastewaters and seawaters, a variety of geochemical processes take place, such as precipitation and adsorption onto newly-formed solid phases or dissolution, desorption and migration, resulting in the change of elemental concentrations in solution (Asta et al., 2015; Hierro et al., 2014; Zhou et al., 2003). Given the frequent dumping of phosphogypsum on coastal systems worldwide, their leachates are often subjected to changes of pH induced by mixing with seawater, and subsequently to geochemical processes that regulate the behaviour of trace elements and control their partitioning into dissolved concentrations and solid phases. Thus, a clear insight into the geochemical processes occurring during the mixing of phosphogypsum leachates with seawater at coastal environments is vital for the assessment of the total metal loads transported to the oceans.

One of the principal parameters during the seawater mixing is the pH, which controls the resulting chemical composition of waters and the mineralogy and the precipitated solid phases. Therefore, this research focuses on the effect of pH increase on the mobility of contaminants in phosphogypsum leachates during seawater mixing. The aim of this contribution is to simulate and evaluate: i) the behaviour of contaminants including Al, As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, U and Zn when the leachates are released to the coast undergoing seawater mixing and pH rise, and ii) the driving geochemical processes that take place in these solutions. The main motivation of this study resides in the importance to understand the impact of seawater mixing on metal concentrations in phosphogypsum leachates before they attain the open oceans.

2. Materials and methods

2.1. Site description

A huge waste facility of phosphogypsum is located near the Atlantic coast of SW Spain, in an estuary formed by the confluence of the Odiel and Tinto Rivers (Huelva province), co-existing with one of the most important marsh ecosystems in Europe (Borrego et al., 2013). Although this first order ecological value, the Estuary of Huelva is one of the most polluted aquatic systems in the world due to the impacts of the abandoned mining industry in the Iberian Pyrite Belt (IPB) and the current activity in the Huelva Industrial Estate. The contamination related to abandoned mines is caused by the high concentrations of sulphates, metals and metalloids produced by the aqueous oxidation of sulphide-rich wastes -a process known as acid mine drainage (AMD)-, which are transported through the Tinto and Odiel Rivers (Nieto et al., 2013), while the industrial activity is responsible for, among others, the dumping of phosphogypsum wastes (Perez-Lopez et al., 2011).

Around 100 Mt of phosphogypsum were produced from 1968 to 2010 and stored in piles on 1200 ha of salt marshes at the right margin of the Tinto River without any type of isolation (Fig. 1). Phosphogypsum piles contain highly-contaminated groundwaters that are retained at depth by the marsh surface, forcing them to flow laterally and reach the edge of the stack. These acidic polluted leakages emerge, forming the so-called edge outflows, which are until nowadays a continuous source of pollution in the estuary (Pérez-López et al., 2015, 2016). Another source of contamination is the water stored on the surface of the piles, known as process water. The process water was used to slurry the phosphogypsum produced and transport it from the industry to the stack in a closed-circuit system implemented in 1997 for ensuring no wastage of water. Before 1997 phosphogypsum was transported using seawater in an opened-circuit system. Phosphogypsum stacks lie within the tidal prism of the estuary (Pérez-López et al., 2015), so that interaction of acid wastewaters and seawater occurs and the fate of contaminants after mixing must be elucidated.

Currently, four zones are recognised at the disposal area (Fig. 1). Zones 1 and 4 (3 m and 8 m of waste thickness, respectively) are considered already restored, as the piles are covered by natural soil and do not have surface process water ponds. On the contrary, zones 2 and 3

(30 m and 8–15 m of waste thickness, respectively) are still directly exposed to weathering conditions and are not totally watertight at present, with process water accumulated on their surface and numerous edge outflows reaching the estuary. However, the a priori restorations and the future restoration plans are not sufficient for preventing the phosphogypsum leachates reaching the estuary (Pérez-López et al., 2015, 2016), as zone 4, and to a lesser extent zone 1, discharge edge outflows ending up to the estuary.

2.2. Sampling and seawater mixing experiments

Seawater mixing experiments were performed to study the geochemical processes occurring when phosphogypsum leachates reach the estuary. Three leachate samples were collected to conduct such experiments. Two edge outflow waters were sampled at discharge points of the zones 3 and 4. This allows the comparison between restored and non-restored phosphogypsum areas in terms of mobilization of metals during seawater mixing. Process water from the surface pond of the zone 3 was also sampled for the mobility experiments, as this industrial water is released to the estuary in some point discharges (Pérez-López et al., 2016). To avoid additional contamination, seawater samples for the experimental mixtures were collected closer to the ocean coast in a contamination-free underway.

Fifteen experiments were carried out in total for the three different types of acidic phosphogypsum leachates (edge outflow waters from zones 3 and 4, and process water from zone 3) by mixing them with seawater to different ratios for obtaining pH values of approx. 3, 4, 5, 6, and 7. The adequate amounts of wastewaters, that would provide sufficient newly-formed precipitates for their characterisation, required huge volumes of seawater in order to obtain the target pH values. Therefore, mixtures were prepared directly on the coast site using plastic containers of 15 L. Titration curves were previously carried out in the laboratory for all the leachates in order to estimate the amount of seawater required for each target pH value.

The resulting solutions and precipitates from each mixing experiment were collected for further analyses. The pH, electrical conductivity and redox potential of the mixing solutions were in situ measured using a portable multi-parameter electrode (Hach, sensION™ + MM150). Measured redox potential was referenced to standard hydrogen electrode (Eh) as proposed by Nordstrom and Wilde (1998). In the laboratory, two aliquots were subsequently separated in polyethylene vials after filtering through 0.45 µm pore size filters; one for analysis of cation concentrations after being acidified with 1% suprapure nitric acid, and another unacidified for anion analysis. Two filtered aliquots were also collected in polyethylene vials for isotope analysis; one for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of H_2O and another for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulphates. Seawater and original phosphogypsum wastewaters were prepared in a similar manner as their mixtures. The solid precipitate samples for the different pH values were collected on filter paper (0.45 µm of pore size) by filtration of the total amount of the solutions using a vacuum pump. These solid samples were examined for mineralogical characterisation of newly-formed phases.

2.3. Analytical methodology

Major element (Ca, K, Mg and Na) concentrations were obtained via Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) by a Jobin Yvon Ultima 2 instrument at the University of Huelva (Spain). Concentrations of anions (F^- , Cl^- , Br^- , SO_4^{2-} , PO_4^{3-}) and ammonia were also analysed at the University of Huelva by a high performance liquid chromatography system (HPLC) using a Metrohm 883 basic ion chromatograph (IC) equipped with Metrosep columns. Aluminium, Fe, Mn and trace elements (Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb, and U) were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) by an Agilent 8800 Triple quadrupole device at the Andalusian Institute of Earth Sciences (IACT) in Granada (Spain).

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