

# Stable isotope insights into the weathering processes of a phosphogypsum disposal area

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## ABSTRACT

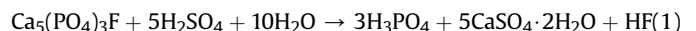
Highly acidic phosphogypsum wastes with elevated potential for contaminant leaching are stack-piled near coastal areas worldwide, threatening the adjacent environment. Huge phosphogypsum stacks were disposed directly on the marshes of the Estuary of Huelva (SW Spain) without any impermeable barrier to prevent leaching and thus, contributing to the total contamination of the estuarine environment. According to the previous weathering model, the process water ponded on the surface of the stack, initially used to carry the waste, was thought to be the main washing agent through its infiltration and subsequently the main component of the leachates emerging as the edge outflows. Preliminary restorations have been applied to the site and similar ones are planned for the future considering process water as the only pollution agent. Further investigation to validate the pollution pathway was necessary, thus an evaluation of the relationship between leachates and weathering agents of the stack was carried out using stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , and  $\delta^{34}\text{S}$ ) as geochemical tracers. Quantification of the contribution of all possible end-members to the phosphogypsum leachates was also conducted using ternary mixing via the stable isotopic tracers. The results ruled out ponded process water as main vector of edge outflow pollution and unveiled a continuous infiltration of estuarine waters to the stack implying that is subjected to an open weathering system. The isotopic tracers revealed a progressive contribution downstream from fluvial to marine signatures in the composition of the edge outflows, depending on the location of each disposal zone within the different estuarine morphodynamic domains. Thus, the current study suggests that the access of intertidal water inside the phosphogypsum stack, for instance through secondary tidal channels, is the main responsible for the weathering of the waste in depth, underlying the necessity for new, more effective restorations plans.

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## 1. Introduction

The phosphate fertilizer industry is responsible for the generation of a waste by-product, known as phosphogypsum (mainly

gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), during the production of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) via the wet chemical digestion of phosphate ore (fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) with sulphuric acid ( $\text{H}_2\text{SO}_4$ ). The overall chemical reaction can be written ideally as (Eq. (1)):



The phosphate rock containing potentially toxic metal (loid)s and radionuclides as impurities is pre-concentrated by flotation, a process enhanced by reagents such as ammonium hydroxide or amine (Rutherford et al., 1994). Elevated concentrations of contaminants from the raw phosphate ore are then transferred into the

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resulting phosphogypsum (Rutherford et al., 1994; Bolívar et al., 2009; Pérez-López et al., 2010). Phosphogypsum, also, contains residual reagents and products from the industrial process trapped in its interstices, mainly phosphoric acid which is not fully separated in the factory, but also sulphuric and hydrofluorosilicic acids, increasing the acidity of the waste (Lottermoser, 2010). Thus, phosphogypsum is considered as a significant source of environmental contamination (Pérez-López et al., 2016).

The phosphate fertilizer industry is witnessing growth in order to maintain the farming production worldwide. Thus, huge amounts of phosphogypsum are also produced, while potential applications do not often meet the condition of high-consumption (Cánovas et al., 2018). The wet process that produces phosphoric acid requires a large volume of water, commonly known as process water, for a multitude of uses in the industrial complex. Process water is used, for instance, to slurry the phosphogypsum produced and transport it to storage in large stacks close to the fertilizer plants that are exposed to weathering conditions. Additionally, process water is often stored in ponds maintained on top of the stacks, forming a waste facility that can pose serious threat to the adjacent environment due to their potential leaching (Tayibi et al., 2009). Nevertheless, there are no formal regulations for the management of such hazardous material (Macías et al., 2017), despite its worldwide impact in many phosphogypsum disposal areas (see review in Tayibi et al., 2009).

Phosphoric acid plants and, hence, phosphogypsum stacks are often located in coastal areas, due to their relatively flat surface for the industrial activity, the nearby water availability and the proximity of the sea as a means of communication (Lysandrou and Pashalidis, 2008; Sanders et al., 2013; El Samad et al., 2014; El Zrelli et al., 2015). One of these paradigmatic phosphogypsum disposal areas is located at the Huelva Estuary (SW Spain), formed by the confluence of the Tinto and Odiel Rivers (Fig. 1a). Phosphogypsum was stack-piled on the salt-marshes of the right margin of the Tinto River estuary; however, similar, nearby salt marshes in the Odiel River, were declared as UNESCO Biosphere Reserve and RAMSAR-NATURA wetland with high-priority protection status. Acidic liquid effluents from the leaching of the stack, known as edge outflows, are highly concentrated in toxic elements and are a major source of contamination to the estuarine environment (Pérez-López et al., 2015). The Estuary of Huelva is, additionally, polluted by the Tinto and Odiel Rivers that are highly affected by acid mine drainage (AMD) resulting from sulphide oxidation in wastes from the abandoned mining activity in the Iberian Pyrite Belt (IPB) (Niето et al., 2013).

Preliminary restorations have been already applied in some of the phosphogypsum modules and similar ones are planned for the future. These actions are based on the assumption that edge outflows originate mainly from the process water ponded on surface that infiltrates the piles and reaches the edge of the stack, hence, they focus on eliminating only that agent. However, Pérez-López et al. (2015) suggested that both types of phosphogypsum leachates are poorly connected using Cl/Br ratios and rare earth elements (REE) as geochemical tracers. Indeed, the absence of process water ponded on the surface of a 'supposedly' restored zone has not prevented the presence of numerous discharge points reaching the estuary until nowadays, which demonstrate the inefficiency of the restorations (Pérez-López et al., 2016). These authors proposed a possible pollutant dispersion pathway associated with the leaching of the phosphogypsum in depth through the input of estuarine waters.

Therefore, the current research aims to corroborate these previous studies by providing a full insight into the weathering processes occurring in the disposal area, to validate the main pollution pathway on which restorations should be based and more

importantly, quantify the exact contribution of all the possible end-members as washing agents. Stable isotopes are widely used in many environmental studies as one of the most powerful tool for determining water sources and fluxes in a variety of systems (Peterson and Fry, 1987). One of their applications is the determination of the proportional contribution of more than one end-member to a final solution for the identification of pollution sources (Phillips, 2001; Zencich et al., 2002; Phillips and Gregg, 2003), hence in the present study they served as undeniable tracers for determining the main pollution source of the phosphogypsum waste. Stable hydrogen, oxygen and sulphur isotopes were used for the first time as geochemical tracers regarding the phosphogypsum, in order to identify and quantify –using ternary mixing–the contribution of the possible weathering agents (process water, seawater and river water) that lead to the formation of edge outflows. The validation of the pollution pathway would be of paramount importance for future effective restoration plans, as the appliance of the current measures does not prevent the contaminated leachates from reaching the estuarine and the coastal environments. The proposed methodology and the results obtained could be useful for further knowledge of the pollution pathway in phosphogypsum stacks located in coastal areas worldwide.

## 2. Study area

The industrial production of phosphoric acid in Huelva led to the disposal of around 100 Mt of phosphogypsum waste, between 1968 and 2010, directly on the salt marshes without any impermeable barrier to prevent leaching. Until 1997, phosphogypsum was transported as aqueous slurry to several decantation zones, in an open-circuit system, using seawater that was poured into the estuary after use. However, due to the enforcement of more strict environmental regulations, the factory was forced to avoid any direct discharge to the estuary according to the OSPAR convention (OSPAR, 2002; 2007). As such, from 1997 to 2010, the new waste management plan included the deposition of phosphogypsum in a large pyramidal pile over a single zone using a closed-circuit system with freshwater as process water. In this latter system, large superficial ponds were created on the stacks in order to contain the process water and lose it by evaporation, along with perimeter channels to collect all leachates from the piles.

At present, the disposal area is clearly divided into four zones (Fig. 1a and b); the zones 1 (35 Mt; 400 ha and 2–3 m in height) and 4 (30 Mt; 280 ha and 8–10 m in height) are currently considered as restored areas, i.e. without process water and with a top cover. In particular, zone 1 is covered by natural soil and vegetation, while zone 4 has a more complex cover including building wastes, industrial wastes and topsoil. On the other hand, the zones 2 (25 Mt; 240 ha and up to 30 m in height) and 3 (15 Mt; 200 ha and 8–12 m in height) are directly exposed to weathering without restoration actions, i.e. uncovered and with surface ponds of process water. The phosphogypsum of zones 1, 3 and 4 was deposited using the open-circuit system with seawater; on the other hand, the dumping sequence in the pyramidal zone 2 comprises a first filling stage with seawater before 1997 and a second stage with process water after 1997. As stated before, all disposal modules are source of numerous edge outflows discharging into the estuarine environment (Pérez-López et al., 2016).

The stacks are located within the tidal prism of the Huelva Estuary, which is between 37 and 82 hm<sup>3</sup> during a half cycle (6 h) (Grande et al., 2000). Its localization and the lack of composite liners at the bottom of the pile, could have a great influence on the possible weathering model of the phosphogypsum wastes by means of estuarine water, as can be elucidated simply by looking at the marshlands prior to the dumping. In 1956, numerous secondary

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