

Mobility of Trace Elements in Phosphogypsum Leachates During Seawater Mixing

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INTRODUCTION

The Estuary of Huelva (Spain) is greatly affected by the phosphate fertilizer industry due to the stack-piling of a waste by-product, known as phosphogypsum, directly on the salt marshes of the Tinto River, in the immediate vicinity of the town of Huelva. This dump is not totally watertight and liquid effluents from its leaching, known as edge outflows, are until nowadays a continuous source of pollution in the estuary (Pérez-López et al., 2015; Pérez-López et al., 2016).

Estuarine systems are responsible for the mass flux of elements entering the coastal areas, and eventually the deep ocean, because they are transitional environments between freshwater and seawater (Lian and Wong, 2003). During mixing, a variety of geochemical processes occurs, such as precipitation and sorption onto newly-formed solid phases or dissolution, desorption and migration, resulting in changes in the elemental concentration of solutions (Zhou et al., 2003; Hierro et al., 2014; Asta et al., 2015). The phosphogypsum leachates in the study area are subjected to seawater mixing, and subsequently, to geochemical transformations. Thus, a clear insight of the geochemical processes taking place during mixing of phosphogypsum leachates and seawater at the Estuary of Huelva is vitally important for the awareness of the metal loads transported to the Atlantic Ocean.

This research reports the effect of pH increase on the mobility of contaminants in the phosphogypsum leachates during their mixing with seawater. The aim of this contribution is to simulate and monitor in experiments: i) the behaviour of the contaminants (Al,

Cr, Fe, Co, Ni, Cu, Zn, As, Cd, Sb, Pb and U) when the leachates are released to the estuary undergoing seawater mixing and pH rise, and ii) the driving geochemical processes that take place.

METHODOLOGY

We took a sample of edge outflow at one of the disposal modules of the phosphogypsum stack. We also sampled process water ponded on the pile surface, which was used to carry the phosphogypsum to the stack as a slurry, because this industrial water is released to the estuary in some point discharges (Pérez-López et al., 2016).

We performed mixing experiments using seawater from the Espigón beach in Huelva. Several experiments were carried out for both types of waters by mixing the acidic phosphogypsum leachates and seawater to different ratios with the aim of obtaining pH values of 3, 4, 5, 6 and 7. Given the huge volume of seawater needed for the experiments, mixtures were prepared directly in the beach. Nevertheless, a titration curve was previously carried out in the laboratory in order to estimate the amount of seawater required for each target pH value.

The resulting solutions and precipitates for each mixing pH were collected. The physicochemical parameters (pH, electrical conductivity, redox potential and temperature) of the solutions were measured in situ. Then, the solutions were filtered (0.22 µm) and divided for cation -after being acidified with 1% supra pure nitric acid- and anion analysis via ICP-MS and ion chromatography, respectively. Likewise, all the water end members, including seawater and the two types of acidic waters, were analysed. The solid

precipitate samples were collected on filter paper (0.45 µm) by filtration of the solutions using a vacuum pump and were examined by SE-EDS-SEM.

RESULTS

Mixing ratios of seawater to phosphogypsum leachates

The phosphogypsum leachates displayed conditions of high acidity and extreme contamination, with pH values of 2.0 and 1.4, and electrical conductivity of 48.8 and 57.9 mS/cm, for edge outflow and process water, respectively; while seawater exhibited values of pH of 7.9 and of conductivity of 55.2 mS/cm. The results indicated that the acidity of the leachates obstructed the rise of the pH requiring large amounts of seawater to reach circumneutral values; 227 mL and 1.6 L of seawater were needed per each mL of edge outflow and process water, respectively. Even for achieving merely pH 4, around 22 mL and 190 mL of seawater were required for every mL of edge outflow and process water, respectively. For both type of acidic waters, the necessary seawater amount increased gradually until pH 6, while the increase of seawater was much more abrupt until reaching neutral pH values (Fig. 1).

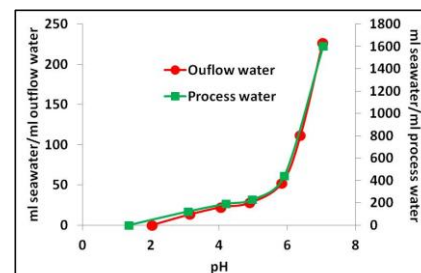


fig 1 Relation between the required volumes of seawater and acidic waters as a function of pH.

palabras clave: Movilidad de Metales, Mezcla de Agua de Mar, Contaminación de Fosfoyeso.

key words: Metal Mobility, Seawater mixing, Phosphogypsum contamination.

Behaviour of Contaminants

The initial concentrations of the main contaminants in the edge outflow were around 80 mg/L of Fe, 20 mg/L of As and Zn, 10 mg/L of Al, 5 mg/L of U, Cu and Cr, 2 mg/L of Cd and Ni, and 0.5 mg/L of Sb, Pb and Co. Concentrations in the process water were even between 3 and 10 times higher than those found in the edge outflow. This is because process water comes directly from the industrial process and is concentrated in a closed-circuit system.

The results of this study indicated a similar behaviour of the contaminants between the two types of phosphogypsum leachates during the mixing experiments (Figs. 2 and 3). Concentrations of Fe and Al decreased with increasing mixing ratio. Most of the Fe and Al were depleted from the solution at pH around 4 and 6.5, respectively. These pH values are consistent with buffering zones observed in other acidic systems, which are related to the hydrolysis and precipitation of Fe and Al during acid neutralization (Carrero et al., 2015). Lead behaves similarly to iron so it must be retained in these precipitates by sorption processes.

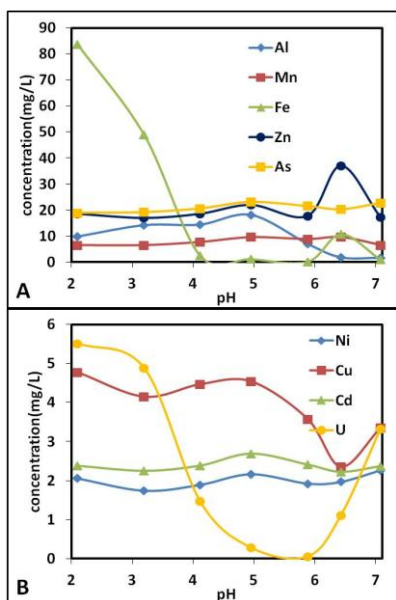


fig 2. Contaminants concentration in the edge outflow water during the mixing. Note that the values were corrected by the dilution factor.

On the contrary, the remaining toxic elements exhibited a conservative behaviour through the sorption processes during seawater mixing and do not participate in them; i.e. around 80-100% of Zn, As, Cd, Ni and Sb and Co

were kept into solution until neutral pH (Figs. 2 and 3). Uranium concentrations exhibited a different behaviour as they decreased in solution until being depleted at pH 6, but then they increased at the end of both experiments due to desorption processes, resulting to a positive flux.

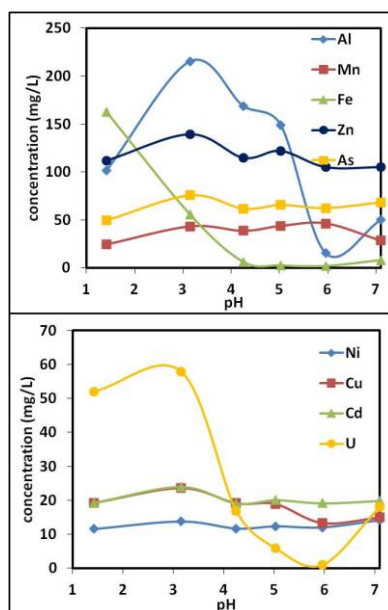


fig 3. Contaminants concentration in the process water during the mixing. Note that the values were corrected by the dilution factor.

CONCLUSIONS

In synthesis, contaminants that pose serious threat to the environmental welfare are contained in the toxic phosphogypsum leachates, which discharge into the Estuary of Huelva and undergo seawater mixing.

The current research reports two main conclusions through experimental simulation of mixing of phosphogypsum wastewaters with seawater: i) the high acidity of the leachates hinders the rise of the pH requiring enormous amounts of seawater to achieve circumneutral values, and ii) contaminants such as Ni, Cu, Zn, As, Cd and Sb behave conservatively in solution, whereas Fe, Al and Pb decreased significantly.

The findings of this study have provided important insight into the problematic of the phosphogypsum waste in Huelva and have highlighted the threat of the toxic contaminants in the leachates even during seawater mixing. It is, therefore, urgent to adopt effective restoration measures to minimize the impact of the phosphogypsum stack on

the estuarine environment.

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