Environmental management and potential valorization of wastes generated in passive treatments of fertilizer industry effluents

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HIGHLIGHTS

- Highly polluted phosphogypsum leachates were effectively treated with DAS technology.
- The MgO-DAS and Ca(OH)$_2$-DAS removed around 100% of PO$_4$, F, Fe, Zn, Al, Cd, U and As.
- The hazardousness of DAS wastes was depth-dependent according to the EU legislation.
- A low mobility of Cd and As was found in wastes upon different weathering scenarios.
- Solids from DAS systems could be considered a secondary source of P and calcite.

GRAPHICAL ABSTRACT
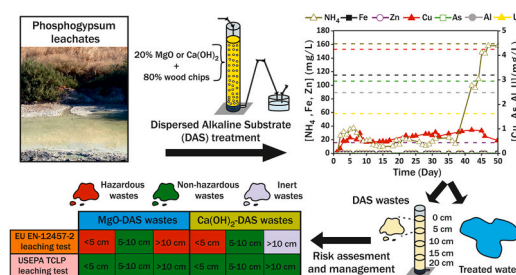
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ABSTRACT

A phosphogypsum stack located in SW Spain releases highly acidic and contaminated leachates to the surrounding estuarine environment. Column experiments, based on a mixture of an alkaline reagent (i.e., MgO or Ca(OH)$_2$) dispersed in an inert matrix (dispersed alkaline substrate (DAS) technology), have shown high effectiveness for the treatment of phosphogypsum leachates. MgO-DAS and Ca(OH)$_2$-DAS treatment systems achieved near total removal of PO$_4$, F, Fe, Zn, Al, Cr, Cd, U, and As, with initial reactive mass:volume of leachate treated ratios of 3.98 g/L and 6.35 g/L, respectively. The precipitation of phosphate (i.e., brushite, cattiite, fluorapatite, struvite and Mn$_3$Zn(PO$_4$)$_2$·2H$_2$O) and sulfate (i.e., despujolsite and gypsum) minerals could control the solubility of contaminants during the treatments. Therefore, the hazardousness of these wastes must be accurately assessed in order to be properly managed, avoiding potential environmental impacts. For this purpose, two standardized leaching tests (EN-12457-2 from the European Union and TCLP from the United States) were performed. According to European Union (EN-12457-2) regulation, some wastes recovered from DAS treatments should be classified as hazardous wastes because of the high concentrations of SO$_4$ or Sb that are leached. However, according to United States (US EPA-TCLP) legislation, all DAS wastes are designated as non-hazardous wastes. Moreover, the solids generated in the DAS systems could constitute a promising secondary source of calcite and/or P. This research could contribute to worldwide suitable waste management for the fertilizer industry.

1. Introduction

Phosphoric acid is the main raw material employed in the manufacture of phosphate fertilizers, which are essential to maintain current levels of agricultural production worldwide. Phosphoric acid is commonly obtained through the wet chemical digestion of phosphate rocks with sulfuric acid. However, during this industrial process, an unwanted waste known as phosphogypsum is generated (Cánovas et al., 2018).

The phosphogypsum (mainly gypsum, $CaSO_4 \cdot 2H_2O$) contains a high amount of toxic elements (e.g., As or Cd) and radionuclides from the U^{238} decay series (Rutherford et al., 1994; Macías et al., 2017a). These impurities are contained in the raw materials used (i.e., phosphate rock and sulfuric acid) and subsequently transferred to the final products. The solid phosphogypsum interstitial space is filled with highly-polluting residual acids (i.e., phosphoric–sulfuric–hydrofluoric acids rich in metal(loid)s), which are part of the reagents and products that cannot be recovered during the manufacturing process (Lottermoser, 2010). However, despite its environmental concern, these highly acidic wastes are usually disposed in stacks close to coastal areas where they are exposed to strong weathering processes (Tayibi et al., 2009). Furthermore, some of these stacks are not covered by any type of material and/or are dumped directly over soils without any type of insulating barrier (Kuzmanović et al., 2020; Macías et al., 2017a; Vásconez-Maza et al., 2019), therefore favoring its weathering as well as the generation of dust with high amounts of ultrafine particles and nanominerals (Lütke et al., 2020). Consequently, phosphogypsum stacks usually constitute a significant source of contamination to the surrounding environment due to the existence of polluted acid effluents from their leaching (Pérez-López et al., 2016). These leakages that commonly emerge at the edges of the stacks, known as edge outflows, are characterized by very low pH values and extremely high concentrations of SO_4, PO_4, F, and metal(loid)s such as Fe, Al, Zn, Cu, As, U, and Cd, among others (Lysandrou and Pashalidis, 2008; Pérez-López et al., 2016). Additionally, other acid effluents related to the fertilizer industry are produced during the washing of acid gases from the industrial process, which must be treated prior to their release into the environment (Affonso et al., 2020).

Recently, for the first time, Millán-Becerro et al. (2020) demonstrated the use of passive dispersed alkaline substrate (DAS) technology to successfully remove the acidity and pollutants from phosphogypsum-related leachates. This passive technology was initially designed for the treatment of acid leachates rich in SO_4 and metal(loid)s from sulfide mining wastes, the so-called acid mine drainage (AMD). This alkaline treatment is particularly interesting at orphan sites due to economic and environmental criteria (Ayora et al., 2013; Martínez et al., 2019; Pérez-López et al., 2011) and because it is considered the best sustainable upcycling solution for AMD pollution (Orden et al., 2021). The DAS system consists of a mixture of a fine-grained alkaline material with high neutralization potential and an inert matrix to provide high porosity, avoiding passivation and clogging problems associated with mineral precipitation (Ayora et al., 2016; Macías et al., 2012b). Different types of alkaline materials were tested by Millán-Becerro et al. (2020) in the design and optimization of DAS technology for phosphogypsum leachates; from conventional alkaline reagents (limestone, barium carbonate, MgO, $Mg(OH)_2$, and $Ca(OH)_2$) to waste materials (fly or biomass ashes). In that study, it was concluded that MgO and $Ca(OH)_2$ are the most effective alkaline reagents to abate the pollution from these leachates, which could be applied in other phosphogypsum waste facilities worldwide. However, these previous works highlighted the need to optimize both the operational hydraulic parameters and the alkaline reagent:acid leachate ratio to significantly increase the performance in MgO-DAS and $Ca(OH)_2$-DAS systems. On the other hand, this treatment generated significant amounts of pollutant-rich solids (Millán-Becerro et al., 2020), which may require proper and long-term management. In this sense, the mineralogical and geochemical characterization, and the potential environmental risks of these solids, must be assessed in order to minimize the environmental impacts during their management. To the best of our knowledge, this research has not been previously reported in the literature.

Thus, the main objectives of this research were to optimize the DAS-based treatment of these leachates and to assess the stability and the potential environmental risks of these wastes while establishing the management bases for their secure disposal. In this sense, the metal-rich wastes generated during the DAS treatment of phosphogypsum leachates have been subjected to two standardized leaching tests (EN-12457-2, 2002 and US EPA TCLP, 1992) proposed by current European Union (EU) and United States (US) environmental regulations, respectively. These leaching tests were used to assess the waste hazardousness according to the regulated limits of several released pollutants. Additionally, these tests allow for the evaluation of DAS waste weathering upon different environmental scenarios (i.e., weathering by rainfalls and weathering under reducing conditions). In addition, a detailed mineralogical and geochemical study has been done to adequately characterize the wastes and to estimate metal mobility. To our knowledge, this is the first time that this methodology has been applied to this type of waste, and it should, therefore, be considered when managing similar wastes generated during the passive treatment of fertilizer industry effluents worldwide. This work fills a gap in the knowledge of the sustainable management of wastes from the fertilizer industry, contributing to the circular economy objectives in this industrial sector.

2. Materials and methods

2.1. Study area

The site investigated is a controversial phosphogypsum stack located directly above salt-marshes of the Tinto River estuary (Huelva, SW Spain). The manufacture of phosphoric acid in the Huelva phosphate fertilizer industry took place for more than forty years (from 1968 to 2010). During this period, around 100 Mt of phosphogypsum were generated. This waste, classified as a hazardous material according to EU legislation (Macías et al., 2017a), was dumped in stacks (12 km^2 of surface) located directly on the marsh soil, less than 100 m from the Huelva city. The stack is divided into four disposal modules; zones 1 and 4 are partially restored, while in zones 2 and 3 no restoration measures have been carried out yet. However, all disposal areas show edge outflows in their perimeters due to the hydraulic and chemical connection of the stack with the estuarine tidal channels and the lack of insulating materials in the stack (Pérez-López et al., 2016). The zone 4 of the stack raises a special concern since previous restoration measures were not effective and continues to release hazardous substances that poses serious threats to human health or the environment. In fact, zone 4 can be classed as an orphan site since the parties responsible for the contamination are unknown, unable or unwilling - to pay for needed remedial actions (Millán-Becerro et al., 2020). A broader description of the study area can be found in Pérez-López et al. (2016).

2.2. Column setup

Four columns made of polymethyl methacrylate (40 cm in height and 6 cm inner diameter) were built and provided with a drain pipe and a 3 cm layer of glass pearls (3 mm diameter) at the bottom to favor water drainage. Two columns were filled with MgO-DAS and the other two with $Ca(OH)_2$-DAS reactive material (20 cm of filling material each), consisting of a mixture of reagent (75.7 g of magnesia and 127 g of calcium hydroxide, respectively) with wood chips at a 1:4 ratio in volume. Each column was connected to a decantation vessel of 445 cm^3. One of the systems filled with each type of DAS reagent material (i.e., MgO-DAS and $Ca(OH)_2$-DAS) was used to study the hydrochemical evolution during the experiments, while the other DAS systems were

used to obtain the solid precipitates originated during the alkaline treatment.

Magnesia (70% periclase (MgO)) was supplied by Magnesitas de Navarra S.A, while high purity calcium hydroxide (>95% portlandite ($Ca(OH)_2$)) was provided by Fisher Chemical. The mineralogical composition and bulk chemistry of both alkaline reagents can be seen in Table S1 (Supplementary Material). Leachates from zone 4 were collected to feed the columns due to its status as an orphan site. The chemical composition and physico-chemical parameters of the input solution are shown in Table S2. During the treatment, the input water was conducted by a peristaltic pump, with a constant flow rate of 0.3 mL/min, to the top of the DAS columns, and then flowed downward through the reactive materials and out of the drain pipe into the decantation vessels.

2.3. Water sampling and analysis

Water samples were daily collected from the different treatment components; input and outputs of DAS columns and decantation vessels. Different physico-chemical parameters such as pH, electrical conductivity (EC), oxidation-reduction potential (ORP) and temperature were measured in situ with a CRISON multi-parameter portable equipment MM 40+, previously calibrated with buffer solutions of 4.01, 7.00, and 9.21 for pH and with standard solutions of 147 µS/cm, 1413 µS/cm, and 12.88 mS/cm for CE. Furthermore, the accuracy of the ORP measurements was checked using buffer solutions of 220 and 470 mV. Values of ORP were corrected according to Nordstrom and Wilde (1998) to obtain Eh values, referenced to the standard hydrogen electrode. Sampled solutions were filtered and divided into two aliquots, one non-acidified for anions and NH_4 analysis by high performance liquid chromatography (HPLC); and the other acidified with ultrapure HNO_3 (2%) at pH < 1 for cations. Major element (Fe, Zn, Al, S and P) concentrations were determined by atomic emission spectroscopy with inductively coupled plasma (ICP-AES, Jobin Yvon Ultima 2) while those of trace elements (Cu, As, Cr, U, Cd, Ni, Co and Sb) were analyzed by mass spectrometry with inductively coupled plasma (ICP-MS; Agilent 7700). All analyzes were carried out in the Laboratories of the University of Huelva. The detection limits were: 0.2 mg/L for S; 0.05 mg/L for Fe; 0.02 mg/L for Al, Zn and P; and 0.1 µg/L for trace elements. In the laboratory, home-made standards with concentrations within the range of the samples were prepared from certified materials and included in each analysis sequence to verify the analytical accuracy. In this same sense, blank solutions made with the same acid matrix as the samples were also analyzed. Furthermore, dilutions were carried out to guarantee that sample concentrations were within the concentration range of the standards. The average measurement error was better than 5% in all samples.

2.4. Solid samples characterization

The columns aimed to collect solid samples were stopped during the maximum effectiveness period of pollutant removal, in order to avoid possible re-dissolution processes of newly-formed precipitates after this period, which has been reported in previous studies (Millán-Becerro et al., 2020). This period of maximum effectiveness ends once the alkaline reagent is consumed or coated by these precipitated solids and, consequently, there is a sharp decrease in the pH of the leachates treated and an increase in metal concentrations.

Once the experiments were stopped, the columns were disassembled, split into 5 cm-thick slice and dried at room temperature. The solids precipitated in the decantation vessels were also collected. The main mineral phases contained in these solids were identified by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer with Cu Kα monochromatic radiation, and examined by an Electron Probe Micro-Analyzer (EPMA), via a JEOL JXA-8200 SuperProbe using a fitted Wavelength-Dispersive Spectrometer (WDS) equipment.

The pseudo-total chemical composition of the solid samples was obtained by standardized aqua regia digestion as follows: 5 mL of aqua regia (12 mol/L HCl and 15.8 mol/L HNO_3 in a 3:1 ratio) were added to 0.5 g of sample in Teflon reactors and reacted for 24 h at room temperature in a fume cupboard, and then, on a heating plate for 2 h at 130 °C.

2.5. Leaching protocols for the hazardousness classification and environmental assessment

The hazardousness of the solids collected from the DAS treatments was evaluated according to the international leaching test proposed by the EU and US EPA (US Environmental Protection Agency) regulations (EN-12457-2, 2002 andUS EPA TCLP, 1992; respectively). The EN-12457-2 leaching test is employed to assess the suitability of disposing a waste in European landfills (landfills for inert, non-hazardous and hazardous wastes; EC Decision, 2003/33/EC), based on the leached concentration of certain contaminants (i.e., SO_4, Ba, Zn, Cu, As, Cr, Mo, Pb, Ni, Se and Sb). This standardized leaching test is based on the interaction of the wastes with distilled water in a solid: liquid ratio of 1:10, followed by agitation on a shaker for 24 h. The supernatants were filtered and then analyzed to determine the dissolved contaminant concentrations.

The TCLP leaching test has traditionally been used to simulate co-disposal of materials with municipal wastes, although, its application has been extended to the management of other types of wastes (US EPA, 1998). Additionally, the concentrations of metals (As, Ba, Cd, Cr, Ni, Pb, V, Zn, Se, Sb, Be and Tl) leached during the TCLP test can also be used as a limit value to determine if a waste should be subjected to a universal treatment standard (UTS) in order to comply with land disposal restrictions (LDR, EPA 530-R-01-007) (US EPA, 2020a). This leaching test was performed based on method 1311 of the US EPA (US EPA, 1992). First, the extraction liquid was chosen based on the pH of the waste. For solids with pH < 5, a solution of CH_3COOH buffered at pH 4.93 must be employed as extractant. On the contrary, if the residues have pH > 5, a solution of CH_3COOH buffered at pH 2.88 must be used as extractant fluid. The MgO-DAS and $Ca(OH)_2$-DAS wastes collected at 0–15 and 0–10 cm depth, respectively, had a pH close to 2. On the other hand, the MgO-DAS wastes taken at 15–20 cm depth and $Ca(OH)_2$-DAS solids collected at depths deeper than 10 cm, presented pHs of 6 and 10 respectively. Following this EPA method, the suspensions were centrifuged and the supernatants were filtered and stored for their subsequent chemical analysis.

Additionally, the results obtained from these tests can also be used to study the weathering of these materials in different environment conditions. Thus, the contact of these solids with water during the EN-12457-2 test would reproduce weathering by rainfall events, while the interaction with organics acids during TCLP protocol would mimic weathering upon reducing conditions. Both leaching tests have been previously employed for the classification, management and environmental assessment of wastes generated during alkaline treatments of acidic and metal-rich waters from mining with DAS technology (Macías et al., 2012a).

2.6. Geochemical modeling

The saturation indices (SI) of solutions with respect to certain mineral phases that could be controlling the solubility of contaminants during the DAS treatments were calculated with the code PHREEQC 3.0 (Parkhurst and Appelo, 2005) using the MINTEQ.V4 thermodynamic database (Allison et al., 1991). This database was slightly amended to include thermodynamic data of fluorapatite from Lawrence Livermore National Laboratory (llnl.dat) database.

An equilibrium-based geochemical modeling was performed to estimate the amount of calcite ($CaCO_3$) precipitated in the decantation vessel during the treatment of leachates with $Ca(OH)_2$-DAS technology.

For the building of this geochemical model the "EQUILIBRIUM PHASES" data block was used, which was employed to impose the precipitation of this mineral phase if oversaturation in water were observed.

3. Results and discussion

3.1. Chemical evolution during DAS treatments

The acid leachates used in this study displayed extremely low pH values (average of 2.24) and high net acidity (of 6240 mg/L as $CaCO_3$ equivalents according to the definition of Kirby and Cravotta (2005) and modified by Millán-Becerro et al. (2020)), as well as high dissolved concentrations of pollutants, i.e., 2513 mg/L of PO_4, 5321 mg/L of SO_4, 1328 mg/L of F, 160 mg/L of NH_4, 102 mg/L of Fe, 16 mg/L of Zn, 5.5 mg/L of Cu, 3.0 mg/L of As, 2.8 mg/L of Al, 2.8 mg/L of Cr, 1.8 mg/L of U, and 0.7 mg/L of Cd, among others (Table S2).

MgO-DAS was run under optimal conditions for 43 days, successfully treating 19 L of leachates. The increase in pH values up to around 9.6 (Fig. 1a) promoted the total removal of F, Fe, Zn, Al, Cr, U, and Cd (around 98% of PO_4 and close to 77% for Cu) (Fig. 1a,b,c). Regarding As, the alkaline treatment showed removal percentages close to 100% for the first 32 days, reducing the removal rate to around 76% for the rest of the effective experimental runtime. Other pollutants, such as SO_4 and NH_4, showed more conservative behavior, reaching average removal rates of 15–43% (Fig. 1a and b). The sharp decrease in PO_4 and F may be due to the intense precipitation of Ca–Mg–Fe phosphates and Ca fluorides (i.e., hydroxylapatite ($Ca_5(PO_4)_3(OH)$), fluorapatite ($Ca_5(PO_4)_3F$), cattiite ($Mg_3(PO_4)_2 \cdot 22H_2O$), strengite ($FePO_4 \cdot 2H_2O$), and fluorite ($CaF_2$)) (Table S3). These minerals could also control the solubility of other contaminants, such as NH_4, Zn, Cu, As, Al, Cr, U, and Cd, by co-precipitation and/or adsorption processes. In addition, the precipitation of oxyhydroxides (e.g., goethite (FeO(OH)), lepidocrocite (FeO(OH)), $Fe(OH)_{2.7}Cl_{0.3}$, spertiniite ($Cu(OH)_2$), and diaspore (AlO(OH))) oversaturated in the outflows, according to PHREEQC (Table S3), cannot be ruled out. The slight decrease in SO_4 concentration could be attributed to gypsum ($CaSO_4 \cdot 2H_2O$) precipitation, which was close to equilibrium according to PHREEQC, and/or associated with co-precipitation processes onto the phosphate phases (Park et al., 2008). On the other

hand, the precipitation of brucite ($Mg(OH)_2$) could also take place during the alkaline treatment since equilibrium with this mineral phase was predicted by PHREEQC.

The $Ca(OH)_2$-DAS column effectively treated 20 L of acid leachates during 46 days of the experimental run. The $Ca(OH)_2$ dissolution raised the pH up to average values of 12 (Fig. 1d), allowing the total elimination of PO_4, F, Fe, Zn, As, Al, Cr, U, and Cd (Fig. 1d,e,f). In addition, around 71–73% of NH_4 and Cu was removed. The average removal of SO_4 reached 45%, which is three times greater than that achieved in the MgO-DAS system. According to PHREEQC calculations, the $Ca(OH)_2$-DAS treated waters showed oversaturation with respect to calcium phosphates and fluoride (i.e., hydroxylapatite, fluorapatite, and fluorite) (Table S4). These minerals could play a key role in the elimination of toxic pollutants, such as F, NH_4, Fe, Zn, Cu, As, Al, Cr, U, and Cd, according to the removal rates observed in Fig. 1. However, as in the case of MgO-DAS, the precipitation of oxyhydroxide minerals (i.e., goethite, lepidocrocite, $Fe(OH)_{2.7}Cl_{0.3}$, and spertiniite) is predicted to occur with this treatment. Gypsum was oversaturated in treated waters (Table S4), which could explain the higher removal percentages with respect to the MgO-DAS system, where this mineral phase was found to be undersaturated. Finally, the solutions from the $Ca(OH)_2$-DAS system showed oversaturation with respect to brucite and calcite ($CaCO_3$).

The results described above indicate that $Ca(OH)_2$-DAS technology is the most effective remediation strategy for phosphogypsum leachates, achieving an initial reactive mass:volume of leachate treated ratio of 6.35 g/L. The MgO-DAS treatment system also showed high effectiveness at removing pollutants, with a mass:volume ratio of 3.98 g/L. These data represent an improvement in the volume of leachate treated per mass of reagents used with respect to those reported by Millán-Becerro et al. (2020) (i.e., 36.3 g/L for $Ca(OH)_2$-DAS and 7.57 g/L for MgO-DAS). This improvement involves obtaining ratios that are 6 and 2 times lower, respectively, than the reported rates by these authors.

3.2. Mineralogical characterization

In the MgO-DAS treatment system, periclase (MgO), dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$) (inherited from the original reactive material; Table S1) were identified by XRD along the depth profile of the
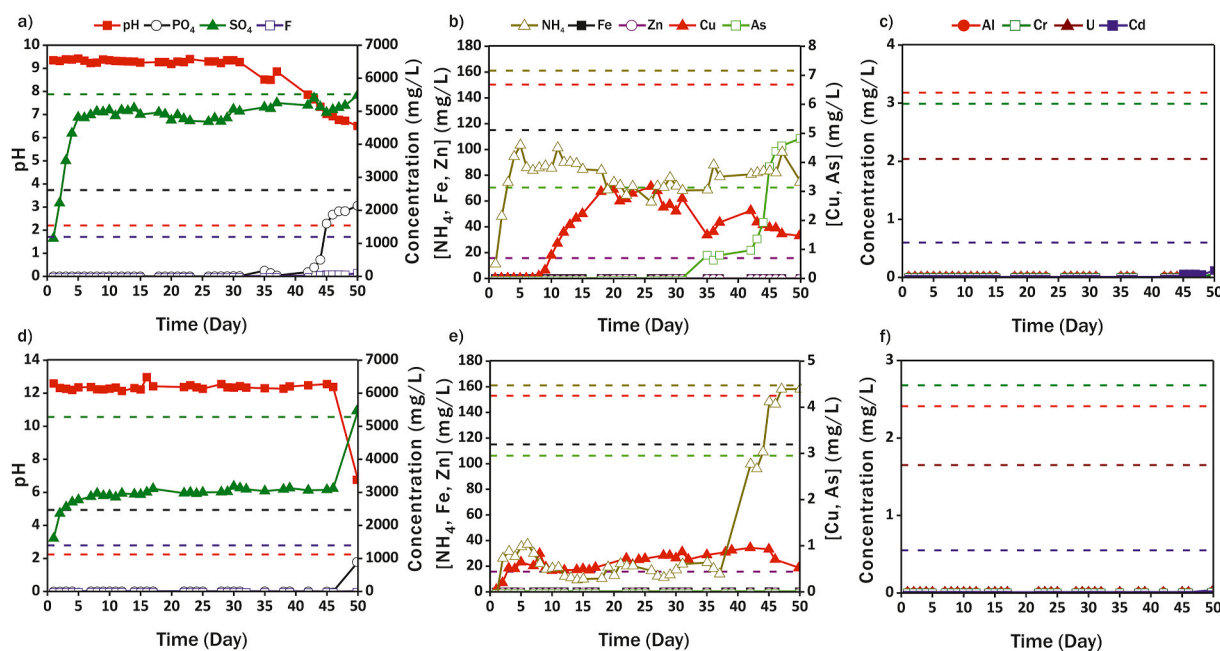

Fig. 1. Evolution in the pH and output concentration of anions and cations dissolved in the phosphogypsum leachates during the neutralization experiments with both treatment systems; i.e., MgO-DAS (a,b,c) and $Ca(OH)_2$-DAS (d,e,f). The dashed lines indicate the initial concentration of the different pollutants. The data error bars are smaller than the symbols used, therefore not shown.

reactive column (Fig. 2a). Brushite (CaHPO$_4$·2H$_2$O), despujolsite (Ca$_3$Mn(SO$_4$)$_2$(OH)$_6$·3H$_2$O), and brucite were the predominant newly-formed minerals at shallower depths (<10 cm), while at deeper depths (>10 cm) several phosphate minerals were identified (i.e., fluorapatite, cattiite, struvite (NH$_4$MgPO$_4$·6H$_2$O), struvite-(K) (KMgPO$_4$·6H$_2$O), and Mn$_3$Zn(PO$_4$)$_2$·2H$_2$O together with the aforementioned sulfate phase (i. e., despujolsite). On the other hand, the minerals precipitated in the decantation vessel correspond to evaporitic salts (halite (NaCl) and hexahydrite (MgSO$_4$·6H$_2$O); Fig. 2a). The EPMA analyses of some selected solid samples (taken at 0–5 and 10–15 cm depths; Fig. 3a and b, respectively) showed the existence of sub-micrometer granular aggregates chemically constituted mainly of P, Ca, and Mg, which is indicative of brushite and cattiite. Other pollutants (Fe, Zn, Mn, K, and S) were detected in the same aggregates, suggesting the precipitation of strengite, Mn$_3$Zn(PO$_4$)$_2$·2H$_2$O, struvite-(K), and despujolsite, or the co-precipitation and/or adsorption of these elements on these phosphate minerals (i.e., brushite and cattiite). It should be noted that the identification of individual phases was not possible due to the cryptocrystalline size of the solids. The evaporitic salts of the decantation vessel appeared as pure phases, with no presence of pollutants, which would confirm the efficiency of the treatments.

The solids collected in the Ca(OH)$_2$-DAS column were identified as unreacted portlandite (Ca(OH)$_2$) (Fig. 2b) and a variety of newly-formed solids including phosphate (brushite), sulfate (gypsum), hydroxide (brucite), and carbonate (calcite) minerals (Fig. 2b). The high

concentration of OH$^-$ groups and Mg from the reagent dissolution and the phosphogypsum leachates, respectively, may favor brucite precipitation. In the case of calcite, this mineral may have precipitated after the dissolution of atmospheric CO$_2$ in the high pH and Ca-rich solutions. The newly-formed precipitates in the decantation vessel were identified by XRD as calcite, gypsum, and halite (Fig. 2b). The EPMA analysis performed on the newly-formed solids collected at a depth of 5–10 cm showed aggregates composed mainly of P, Ca, Mg, and S (Fig. 3c), which might suggest the precipitation of brushite, brucite, and gypsum. The solid precipitated inside the decantation vessel showed sub-rounded granular aggregates constituted mainly of Ca (Fig. 3d), indicative of calcite, and monoclinic aggregates of gypsum, confirming the results obtained by XRD. As in the case of MgO-DAS, the presence of pollutants was not detected in the phases precipitating in the decantation vessel, which is in agreement with the hydrochemical results.

According to the mineralogical information, the newly-formed solids in the Ca(OH)$_2$-DAS treatment could be considered a resource of raw materials due to the presence of calcite and brucite, which are alkaline reagents commonly used for the treatment of AMD waters, i.e., limestone and magnesium hydroxide (Ayora et al., 2013; Masindi et al., 2017). To quantify the presence of these minerals within the precipitated solids, a semi-quantitative mineralogical analysis of the crystalline phases was performed. This analysis estimated a percentage (in weight) of calcite and brucite in the precipitated solids of less than 11% and 7%, respectively, while the remaining 82% are mainly sulfate and phosphate phases rich in metallic impurities. On the other hand, the mineralogical composition of the precipitates in the decantation vessel was close to 54% of gypsum and 44% of calcite, with minor proportions of halite.

3.3. Risk assessment and management of solids generated in DAS treatment

The efficient treatment of the pollutant leachates led to the generation of metal-rich solid wastes. To assess their hazardousness for safe disposal, avoiding potential environmental impacts, these solids were subjected to different standardized leaching tests. This characterization was only performed on solids collected inside the columns due to the following: 1) more than 95% of total solids was generated in the columns and 2) the absence of toxic elements accumulated in the decantation vessels.

The hazardousness of solids generated in MgO-DAS treatment is depth-dependent (Table S5). The shallowest solids (<5 cm) should be classified as hazardous wastes due to the high concentration of SO$_4$ leached (21,126 mg/kg), exceeding the limit for disposal in non-hazardous waste landfills. The solids collected at a depth of 5–10 cm should be classified as non-hazardous wastes since the concentration of SO$_4$ and Sb released (8324 and 0.52 mg/kg, respectively) exceeded the threshold values for inert wastes. At depths deeper than 10 cm, the waste material should also be classified as hazardous waste considering the high concentration of Sb leached (0.81 mg/kg).

A decreasing hazardousness pattern with depth of solids from the Ca (OH)$_2$-DAS treatment was observed according to EU legislation (Table S5). At depths lower than 5 cm, the solids should be considered hazardous wastes due to the high release of SO$_4$ (24,508 mg/kg). Regarding solids recovered at a depth of 5–10 cm, they should be deposited in landfills for non-hazardous wastes since the SO$_4$ and Sb leached (11,050 and 0.12 mg/kg, respectively) exceed the limit for their disposal as inert wastes. Finally, the solids collected at depths deeper than 10 cm should be classified as inert wastes since they did not exceed any threshold value.

According to the US regulation, all the solids sampled should be classified as non-hazardous wastes since the TCLP limits were not exceeded (Table S6). Furthermore, these solids did not exceed the UTS limits; thus, they could be directly disposed of in a non-hazardous waste landfill, without additional treatments.

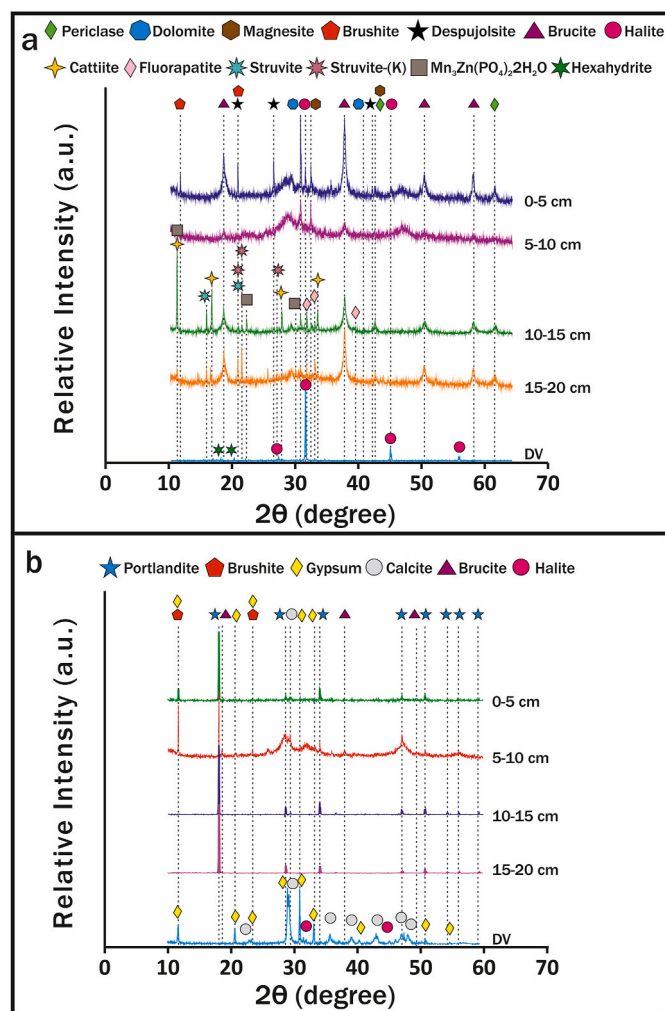These discrepancies between both regulations have already been

Fig. 2. XRD spectra of the solid precipitates collected from the MgO-DAS system (a) and the Ca(OH)$_2$-DAS system (b).
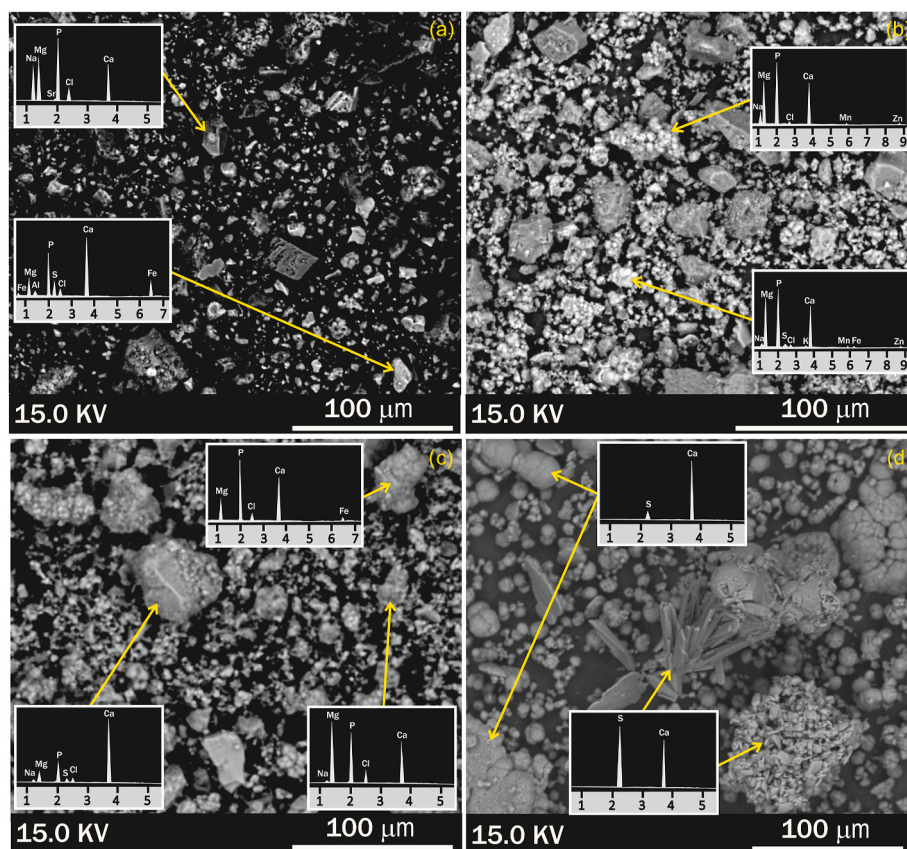
Fig. 3. EPMA images and WDS spectra of the solid precipitates recovered from the MgO-DAS system (a,b) and the Ca(OH)$_2$-DAS system (c,d).

previously reported by Millán-Becerro et al. (2019) during the hazardousness classification of solids from the active treatment of phosphogypsum leachates. In addition, these discrepancies have been observed during the classification of other wastes, such as those from passive and active treatments of AMDs (Macías et al., 2012a, 2017b) or solid phosphogypsum (Macías et al., 2017a). The lack of agreement between both environmental legislations comes from the use of different extracting solutions and the differences between the restrictive levels established by each legislation, i.e., the organic solutions used in the TCLP leaching tests have a higher leaching capacity (Tables S7 and S8). Nevertheless, their threshold values are less restrictive. Hence, it would be highly advisable to use additional assessment protocols to achieve a more

accurate hazardousness evaluation for these wastes. Among these complementary protocols, the study of possible adverse effects on aquatic life will be approached. For this purpose, the results obtained during the different leaching tests mimicking weathering after rainfalls (i.e., EN-12457-2) and reducing conditions (i.e., TCLP) were compared with the threshold values of the Criterion Continuous Concentration (CCC) issued by the aquatic life criteria of the US EPA (US EPA, 2020b). The CCC is the limit value of concentration above which a certain pollutant present in water poses an unacceptable effect to aquatic organisms upon chronic exposure. As seen in Fig. 4a, CCC limits were not exceeded after the interaction of MgO-DAS and Ca(OH)$_2$-DAS wastes with rainwater, highlighting their chemical stability upon rainwater
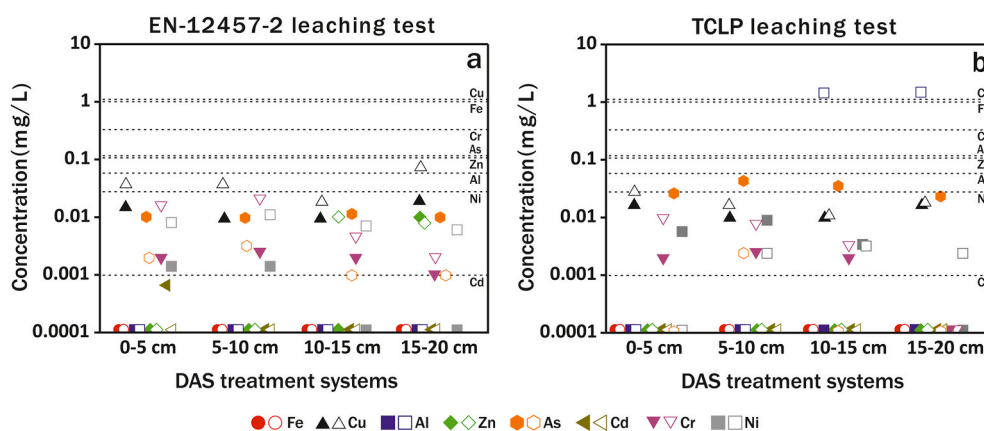

Fig. 4. Metal(loid)s concentrations released after EN-12457-2 test (a) and TCLP test (b). Continuous Concentration Criteria (CCC) limits for those pollutants are included (horizontal dashed lines). The solid markers indicate that the leached element comes from the MgO-DAS waste whereas the hollow markers indicate that the contaminant comes from the Ca(OH)$_2$-DAS solid. The data error bars are smaller than the symbols used, therefore not shown.

weathering. On the other hand, most metal concentrations remained below the CCC limits after interaction of treatment wastes with organic acids, except for Al in the Ca(OH)$_2$-DAS profile, which exceeded the limits below 10 cm (Fig. 4b). Therefore, these wastes should not be co-disposed with municipal wastes or covered with vegetation or organic-rich amendments to avoid weathering under reducing conditions.

A rough estimation of the contaminants released from the treatment wastes after rainfall weathering and reducing conditions can be made (Tables S7 and S8). In this sense, the low mobility of metal(loids) contained in DAS wastes is striking, with values below 2%, except for Al in the deeper layers of the Ca(OH)$_2$-DAS profile, where release rates close to 70% were observed (Table S8). On the other hand, the high release of SO$_4$ from both wastes is remarkable (58–70% in MgO-DAS wastes, Table S7; 5–46% in the Ca(OH)$_2$-DAS profile), being slightly higher upon reducing conditions. By comparing these results with those obtained after applying the same leaching schemes to solid phosphogypsum (Macías et al., 2017a), the low mobility of Cd and As from the treatment wastes compared with the latter waste is especially noticeable. This implies that DAS treatment must be considered an efficient stabilization method for these highly toxic metalloids.

3.4. Environmental and economic implications

Acidic leachates arising from the Huelva phosphogypsum stack constitute an important source of contamination to the Ría de Huelva estuary (Pérez-López et al., 2016). In this context, DAS technology is an effective and environmentally sustainable solution for the treatment of these acid leachates. Considering the total annual volume of edge outflows that emerges from the phosphogypsum stack, i.e., approximately 335,000 m^3 (Pérez-López et al., 2016), treatment using DAS technology could avoid the release of significant amounts of pollutants to the estuary; around 842 tons/yr of PO$_4$, 445 tons/yr of F, 48 tons/yr of NH$_4$, 42 tons/yr of Fe, 12 tons/yr of Zn and Al, 6.7 tons/yr of As, 4.2 tons/yr of U, 3.5 tons/yr of Cr, 1.6 tons/yr of Cd, 1.3 tons/yr of Cu, and 0.9 tons/yr of Al. To achieve effective treatment of the total volume of phosphogypsum leachate, around 1335 tons of magnesia or 2127 tons of calcium hydroxide would be necessary. Although the Ca(OH)$_2$-DAS system requires almost twice the reactive mass of the MgO-DAS system per volume of leachate treated, the cost of calcium hydroxide is 7–10 times lesser than magnesia (INAP, 2021). Thus, considering a market price for calcium hydroxide of 60–100 USD/t (INAP, 2021), the annual cost related to the purchase of this may vary between 128,000 and 213,000 USD. On the other hand, if the alkaline reagent selected was magnesia, this would imply an economic cost associated with its purchase that could reach values around 0.56 and 1.34 MUSD. Therefore, the selection of Ca(OH)$_2$ as an alkaline reagent for the treatment of phosphogypsum leachates would imply an annual economic cost that is 4–6 times lower.

During Ca(OH)$_2$-DAS treatment, calcite and brucite are generated, which have several environmental applications (e.g., passive treatment of acid mine waters). However, such practice could be limited for the precipitated solids inside the DAS column due to the low amounts of these mineral phases (11% calcite, 7% brucite) and the high content (around 82%) of sulfate and phosphate phases rich in metallic impurities. Therefore, the potential valorization of solids collected only in the decantation vessel appears to be more suitable. These solid are mainly composed of gypsum (54 wt%) and calcite (44 wt%), with no metal(loid)s impurities. In addition, the simple distilled water washing of these solids allows for an increased concentration of calcite of up to 80% due to the high solubility of gypsum (Fig. S1). The precipitation of calcite is generated by the natural sequestering of CO$_2$, which is one of the main greenhouse gases (Morales-Flórez et al., 2011). According to the PHREEQC calculations, around 0.5 g of calcite precipitates in the decantation vessel after the treatment of 1 L of leachates, which would equate to a rough generation of 173 tons/yr of calcite and a CO$_2$ sequestration of around 34 tons/yr of atmospheric CO$_2$ if all leachates (i.

e., 335,000 m^3/yr) were treated with Ca(OH)$_2$-DAS.

The calcite generated is an alkaline reagent is currently used for the treatment of extremely acidic and polluted mine waters (Martínez et al., 2019; Orden et al., 2021). Thus, the generation of this raw material during phosphogypsum leachate treatment could be used as a reagent in AMD treatment by DAS technology. According to Orden et al. (2021), 57 tons of calcite were used to successfully treat highly polluted AMD from Mina Esperanza (SW Spain) over the course of 840 days (close to 25 tons/yr of calcite used). In this sense, the potential treatment of the whole volume of phosphogypsum leachates by Ca(OH)$_2$-DAS treatment would generate the calcite needed (173 tons/yr) for around 7 DAS plants of AMD waters.

On the other hand, the solid wastes generated during DAS treatments may constitute a secondary source of P, taking into account the abundance of phosphate minerals. Thus, phosphate rock, a marketable resource, would be replaced by waste for the production of phosphoric acid so that a circular economy could be achieved. Phosphorous is considered a critical raw material (European Commission, 2020), with a worldwide production of phosphate rock in 2013 of around 210 Mt (Sverdrup and Ragnarsdóttir, 2014). Although, this value is expected to increase until reaching an annual production of around 520 Mt in 2050 (Nedelciu et al., 2020). Therefore, the search for secondary sources of phosphorus is of paramount importance, especially in countries with the absence of primary deposits. In this sense, a potential source of phosphorus could be wastewater (Cordell and White, 2014; Shaddel et al., 2020). Currently, the main methods for the recovery of phosphorus from wastewater are biological treatment, electrochemical processes, and chemical precipitation (Cichy et al., 2019; Deng et al., 2020; Lei et al., 2019; Li et al., 2018; Martin et al., 2020). In this same sense, the treatment of the leachates released using DAS technology could generate around 842 tons/yr of PO$_4$ by passive chemical precipitation, which would be otherwise released into the estuary. The recovery of phosphorous from these newly-formed phosphate phases (e.g., brushite, cattiite, and fluorapatite, among others) could help to achieve the principles of a circular economy in the fertilizer industry as well as to contribute to the mitigation of the supply risk worldwide. The high amount of impurities contained in these phosphates could be a barrier for the recovery of P in a marketable product. However, the development of innovative recovery schemes in the last year opens the door to the recycling of P from the generated wastes. For example, the improved hard process is an innovative phosphorus recovery technology, where a reduction reaction releases P at around 1250 °C, eliminating the impurities and achieving highly pure P (Worrell et al., 2017). These phosphates may contain not only a high concentration of impurities but also of valuable metals. For example, Millán-Becerro et al. (2021) reported concentrations of up to 4092 mg/kg of rare earth elements (REE), 2974 mg/kg of V, and 164 mg/kg of Sc in solids precipitated during the neutralization of these leachates with Ca(OH)$_2$. The selective recovery of these valuable metals could improve the environmental and cost-effectiveness performance of the proposed water treatment.

4. Conclusions

Different techniques for chemical and mineralogical characterization and standardized leaching protocols have been applied to optimize a sustainable treatment of fertilizer industry leachates and to assess the stability and the potential environmental impact of this treatment wastes. This study confirms the efficiency of dispersed alkaline substrate technology in the passive treatment of acidic leachates generated in phosphogypsum waste piles from the fertilizer industry. The findings revealed that Ca(OH)$_2$ is by far the most suitable alkaline chemical for the treatment based on effectiveness and economic criteria. During treatment, metals pass from the soluble forms to an insoluble solid waste mineralogically composed of phosphate (i.e., brushite, cattiite, fluorapatite, struvite, and Mn$_3$Zn(PO$_4$)$_2$·2H$_2$O) and sulfate (i.e., despujolsite and gypsum) phases. Calcite precipitation also occurs due to

atmospheric CO_2 dissolution in the treated leachates. The hazardousness of these solid wastes was assessed for proper management using EU and US regulations based on leaching tests. According to current EU legislation, the high mobility of SO_4 and Sb confers these metal-rich solids the classification of hazardous waste in some zones of the treatment. However, according to US regulation, these same solids can be considered non-hazardous wastes. The discrepancies observed between both international legislations justify the need of complimentary tools to evaluate the hazardousness of these wastes. In this sense, the comparison between leaching tests and limit values established by the EPA Continuous Concentration Criterion (CCC) revealed the stability of the wastes upon rainfall weathering but a noticeable environmental risk when interacting with organic acids, which recommends avoiding their co-disposal with municipal wastes or the use of organic amendment-based covers. On the other hand, solid wastes can be injected back into the economy as secondary raw materials as a source of calcite, brucite, gypsum, phosphate minerals, or even valuable metals (e.g., REE, Sc, or V), improving the environmental and cost-effectiveness performance of the treatment. Thus, the results obtained in this paper could also contribute to achieve the principles of sustainability and the circular economy in the fertilizer industry.

Credit author statement

Ricardo Millán-Becerro: Investigation, Data Curation, Writing-Original Draft, Visualization. **Francisco Macías**: Funding acquisition, Conceptualization, Writing - review & editing. **Carlos Ruiz Cánovas**: Funding acquisition, Project administration, Writing - review & editing. **Rafael Pérez-López**: Funding acquisition, Methodology, Writing - review & editing. **José María Fuentes López**: Investigation & Data Curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.133876.

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