Science of the Total Environment 907 (2024) 168078

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Towards circular and sustainable restoration of a deeply polluted river basin: The Odiel River catchment (SW Spain)

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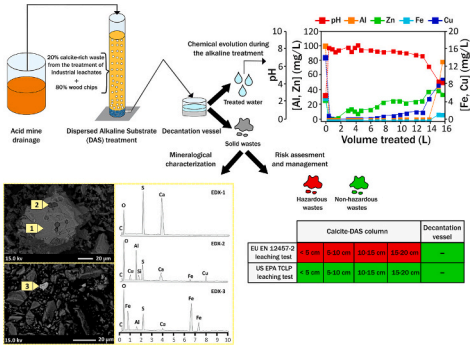
HIGHLIGHTS

- The performance of a calcite-rich waste for the DAS treatment of AMD was evaluated.
- The calcite-DAS treatment removed around 90–100 % of Fe, Al, and Cu from the AMD.
- Oxyhydroxysulfate and carbonate minerals were the main sinks of pollutants.
- SO_4, Zn, and Cu contained in the newly-formed solids showed a high mobility risk.
- The proposed calcite-rich waste may be suitable to replace limestone in DAS systems.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Damià Barceló

Keywords:
Highly polluted waters
Column experiment
Dispersed alkaline substrate
Contaminants removal

ABSTRACT

The Ría de Huelva estuary located in SW Spain is heavily polluted by acid mine drainage leachates and phosphate fertilizer industry effluents. This study assesses the effectiveness of a solid waste rich in calcite originated during the remediation of industrial effluents using the passive dispersed alkaline substrate (DAS) technology, for the treatment of highly acid and polluted mine drainages. The research consists of flowing the mine leachates through a column loaded with a combination of an alkaline reagent (i.e., calcite-rich waste resulting from the treatment of industrial leachates) scattered in a non-reactive matrix (i.e., wood chips) to increase the pH of acidic water while decreasing the solubility of dissolved pollutants. The alkaline treatment achieved average removal percentages of 100 % for Al and Fe, and close to 90 % for Cu. However, the treatment was not effective for other metals present in mine drainages such as Co and Ni. These results are comparable to those achieved in the DAS treatment with commercial limestone. The precipitation of oxyhydroxysulfates (i.e., schwertmannite and basaluminite) and carbonates (i.e., malachite and hydrozincite) minerals could be controlling the solubility of pollutants during the treatment. The solid wastes from the DAS treatment were subjected to two standardized leaching tests (EN 12457-2 from the European Union and toxicity characteristic leaching procedure (TCLP) from

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https://doi.org/10.1016/j.scitotenv.2023.168078
Received 7 September 2023; Received in revised form 20 October 2023; Accepted 21 October 2023
Available online 26 October 2023

the United States) in order to ensure suitable management and avoid potential environmental impacts. According to European Union legislation, the high mobility of Cu, Zn and SO_4 confers some solid wastes from the DAS treatment the hazardous waste classification. However, according to United States regulation, these same solids are considered non-hazardous wastes. This research could help to improve the environmental sustainability of acid mine drainage treatment with DAS technology by replacing marketable limestone with a low-cost alkaline waste.

1. Introduction

A world case scenario of metallic pollution transition between fluvial systems and oceans is the Ría de Huelva estuary, a coastal wetland formed by the confluence of the Tinto and Odiel Rivers (SW Spain), where several continuous sources of pollution occur at the same time (Kerl et al., 2023). Around 100 million tonnes of phosphogypsum wastes from the fertilizer industry are stockpiled over 12 km^2 of Tinto River marsh soils, which release significant volumes of highly-polluted acidic leakages into the estuarine system due to its exposure to weathering processes (Pérez-López et al., 2016). However, the main source of pollution comes from both Tinto and Odiel Rivers, whose watersheds are extremely acidic due to the man-made stress related to the mining of the Iberian Pyrite Belt (IPB) (Nieto et al., 2013; Cánovas et al., 2021), considered to be one of the biggest massive sulfides metallogenic provinces (Sáez et al., 1999). The IPB is well known for its intense mining history, with a legacy of >80 abandoned mines (Grande, 2016), where significant volumes of sulfide-rich wastes are exposed to water and oxygen, causing the generation of acidic and SO_4-metal(loid)s-rich leachates, known as acid mine drainage (AMD). Discharges of AMD into the Tinto and Odiel Rivers cause an almost irreparable deterioration in the quality of their waters and end up severely polluted by AMD, and subsequently they act as main vectors of pollutant transfer to the Ría de Huelva estuary. As a comparison, the fluvial (Olías et al., 2006) vs. phosphogypsum stack (Millán-Becerro et al., 2023) contributions of contaminants to the estuary are 7922 vs. 76 t/year of Fe, 3475 vs. 11 t/year of Zn, 1721 vs. 1.7 t/year of Cu, 36 vs. 6.9 t/year of As, and 11 vs. 1.1 t/year of Cd, respectively, among others.

Currently, the Odiel River basin is subject to strong social and legislative pressures due to the future construction of the Alcolea reservoir intended for irrigation, with serious doubts about the water quality reaching the reservoir given the severe AMD affection of the watershed (Olías et al., 2011); as well as the need to comply with the European Water Framework Directive (WFD, 2000/60/CE). The main objective of the WFD was to achieve good chemical and ecological quality of all water bodies of the European Community by the year 2015 (EU Commission, 2000). However, this deadline could be extended in specific cases such as the Odiel River basin, where due to the magnitude of the AMD pollution it was technically and economically impossible to achieve a good chemical quality of its waters. For this reason, the regional authorities managed to postpone the WFD deadline until the year 2027 (Macías et al., 2017c). In order to improve the water quality of the Odiel watershed, the implementation of various dispersed alkaline substrate (DAS) passive treatment plants, similar to those currently located in Mina Concepción and Mina Esperanza (Martínez et al., 2019; Orden et al., 2021), throughout the basin is needed. DAS technology consists of a mixture of a fine-grained alkaline material (usually limestone) to prevent passivation by enhancing the dissolution rate of the reagent and a coarse-grained inert matrix (wood chips) to avoid clogging problems related with mineral precipitation (Macías et al., 2012c; Ayora et al., 2013). This technology is currently considered the best passive option to treat severely polluted AMD leachates according to environmental and economic criteria (Ayora et al., 2013; Orden et al., 2021). As mentioned above, limestone is the most used alkaline reagent in treatment of highly acidic and metallic mine drainages using DAS technology (Macías et al., 2012b; Orden et al., 2021). The limestone dissolution generates alkalinity capable of increasing the pH of the leachate to values around 6.5, promoting the precipitation of trivalent metals (i.e., Fe and Al) (Cortina et al., 2003; Rötting et al., 2008). It should be noted that the mineral precipitation of these metals together with SO_4 control the hydrochemistry of the waters affected by AMD (Caraballo et al., 2009). However, the use of limestone to remediate AMD implies economic and, more importantly, environmental costs because it is a marketable resource that must be mined. In this sense, in the Odiel River basin, the annual economic cost associated with the purchase of limestone could be roughly estimated at around 100,000 €, taking into account the costs related with filling the limestone-DAS mixture in the Mina Esperanza treatment plant (Orden et al., 2021), as well as the need to implement around a dozen of these treatment plants throughout the basin (Macías et al., 2017c). On the other hand, the use of limestone from quarries has a negative impact on the environmental footprint of the DAS system mainly due to the mining operations (Martínez et al., 2019). Therefore, the use of a low-cost alkaline waste that could replace the commercial reagent would be especially attractive, improving the environmental and economic sustainability of the treatment. In this sense, Millán-Becerro et al. (2022) reported that during the DAS treatment of leachates from the phosphogypsum stacks using portlandite ($Ca(OH)_2$) as an alkaline reagent, a solid waste was generated, consisting mainly of gypsum ($CaSO_4{\cdot}2H_2O$) and calcite ($CaCO_3$), with no metallic impurities. This calcite-rich waste could constitute a promising alkaline reagent to remediate highly acidic and polluted mine drainages. Thus, the valorization of this newly-formed calcite-rich solid could turn this waste into a valuable resource and represent a promising step towards the zero waste goals of the phosphate fertilizer industry. To the best of our knowledge, this is the first time that a waste generated during the passive treatment of acidic and polluted industrial wastewater, without any a prior use, has been used as an alkaline reagent in a DAS treatment system for the remediation of AMD.

The main aim of this study is to demonstrate the potential use of a calcite-rich solid waste generated during the treatment of phosphogypsum leachates to remediate waters affected by AMD. For this purpose, the behavior of the acidity and the main pollutants dissolved in the Odiel watercourse has been evaluated using the DAS technology. Additionally, the solid wastes formed during the AMD treatment have been adequately characterized from a mineralogical and geochemical point of view. Moreover, the risk assessment and management of the solid wastes have been done for their proper environmental management. The idea proposed in this work is especially attractive from an environmental point of view, since it is intended to replace limestone, a mined raw material commonly used in AMD treatments with DAS technology, with a solid waste from the treatment of industrial leachates, without application so far, thus promoting a circular economy. The results obtained in this research work could be extended to other areas of the world affected by both environmental problems such as China and Brazil, among others (de Oliveira et al., 2007; Li et al., 2018; Xue-Fang et al., 2018; Pereira et al., 2020).

2. Materials and methods

2.1. Column experiment

In the laboratory, a DAS system was built to treat AMD that consisted of the following components: (1) a 5000 cm^3 storage tank for the acid leachate connected to a peristaltic pump that drives water at a rate of

0.3 mL/min through a pipe towards (2) a column of polymethyl methacrylate (6 cm in diameter and 40 cm in length) filled with 20 cm of DAS reagent material (80 % (v/v) wood chips and 20 % (v/v) calcite-rich waste (i.e., around 84 g) resulting from the treatment of phosphogypsum-related leachates (Millán-Becerro et al., 2022). The column was provided with a drain pipe and a layer of 3 cm glass beads (3 mm diameter) at the bottom to facilitate drainage. The column is connected to (3) a decantation vessel, with a capacity of 445 cm^3 (see Fig. S1), which promotes chemical equilibrium and allows colloids and precipitates to decant. The flow of AMD through the DAS system was constant and uninterrupted throughout the experiment, demonstrating the absence of clogging problems. Before building the aforementioned DAS system, phosphogypsum leachates were treated with a $Ca(OH)_2$-DAS treatment system in the laboratory (Millán-Becerro et al., 2022), in order to generate calcite-rich precipitates for later be used in the treatment of AMD. In this sense, around 6 g of calcite-rich solids precipitated

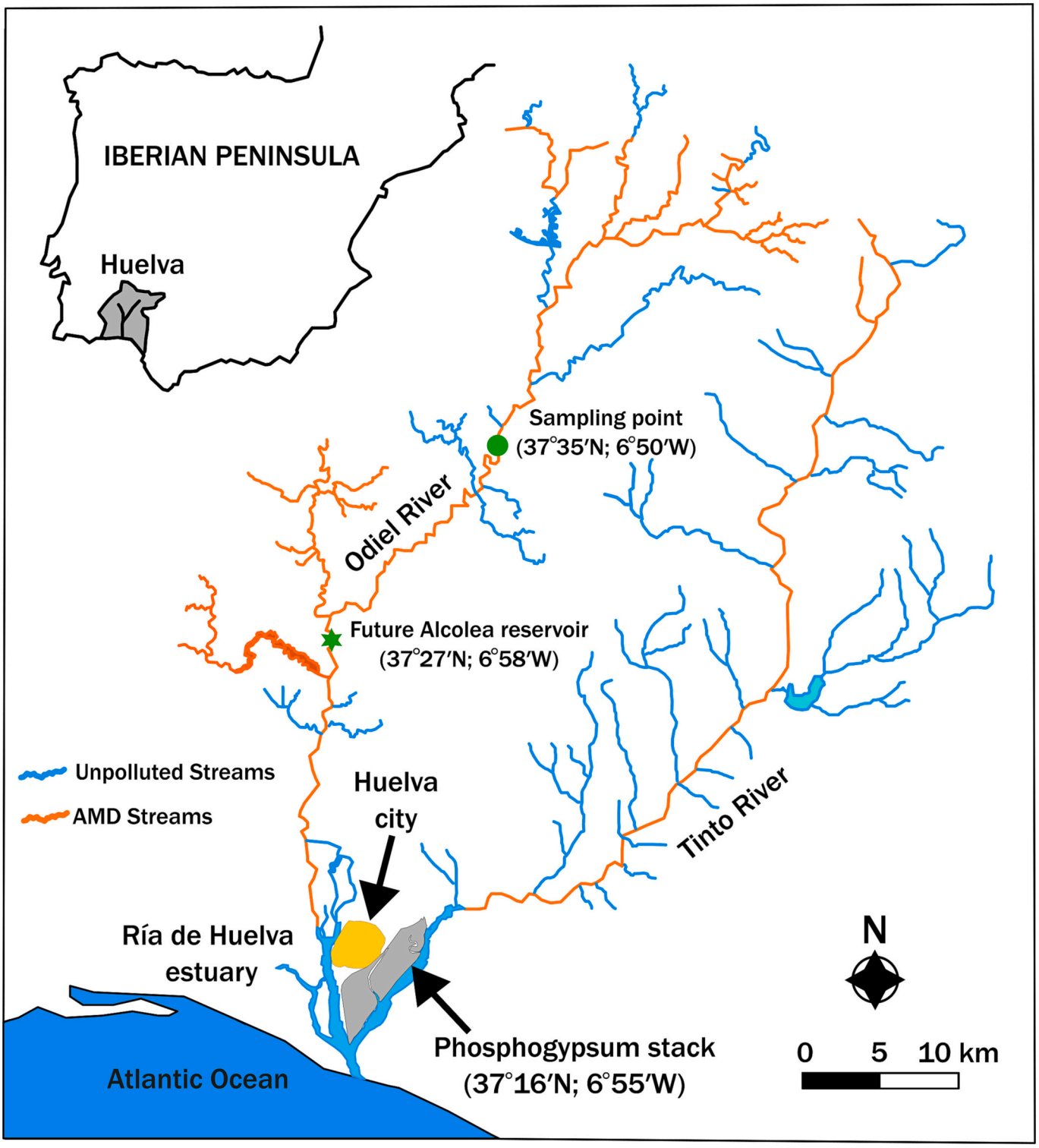

Fig. 1. Location map of the study area, showing the phosphogypsum stack, location of the point where the AMD sample was taken for this study and of the future Alcolea reservoir, as well as the main water courses affected by AMD in the Tinto and Odiel river basins.

in the decantation vessel for each 1 L of treated phosphogypsum leachates.

Input solutions for the column experiment were collected in the middle part of the Odiel River basin (Fig. 1), near Sotiel Coronada village (Huelva), just at the upstream point that will feed the future Alcolea reservoir. There is no controversy from a scientific point of view about the poor quality of the future water that will be stored in the Alcolea reservoir (Olías et al., 2011), which makes it extremely necessary to treat the water for its final use in irrigation. Fresh samples of AMD leachates were collected using 5 L sterile polyethylene bottles. To mimic field conditions, unfiltered water was used in the column experiment. Fresh input leachate to feed the DAS column was collected every 10 days to avoid water degradation.

Liquid samples were collected daily for 40 days in the different steps of the calcite-DAS treatment system (i.e., input leachate, reactive column output, and decantation vessel). However, to achieve a better understanding of the effectiveness of the alkaline waste to remedy AMD in this work, only the period of effectiveness of the treatment (i.e., 32 days) will be discussed. Since the alkaline reagent used was calcite, it is considered effective while the trivalent metals (i.e., Fe and Al) are retained in percentages close to 100 %. The pH, electrical conductivity (EC), redox potential (ORP) and temperature of the samples were measured in situ with a portable Multiparametric CRISON MM 40+ equipment. Calibration was performed using buffer solutions for pH (4.01, 7.00, and 9.21), and EC (147 μS/cm, 1413 μS/cm, and 12.88 mS/cm), while ORP was controlled using standard solutions of 220 and 470 mV. ORP measurements were corrected to obtain the Eh, referenced to the standard hydrogen electrode (Nordstrom and Wilde, 1998). The water samples were filtered at 0.45 μm with Teflon filters, acidified to pH < 1 with ultrapure HNO_3 (2 %) and refrigerated until their chemical analysis.

Once the experiment was finished, the calcite-DAS column was disassembled, divided into 5 cm thick slices and dried at room temperature for their subsequent mineralogical and geochemical characterization, and for the evaluation of their potential environmental risk according to the waste management rules. The newly-formed precipitates in the decantation vessels were also sampled for further characterization.

2.2. Analytical methodology

The concentrations of major elements (Fe, Al, Zn and S) in the solutions of the column experiment were analysed by atomic emission spectroscopy with inductively coupled plasma (ICP-AES, Jobin Yvon Ultima 2) while those of trace elements (Cu, As, Cr, Co, Ni and Cd) were determined by mass spectrometry with inductively coupled plasma (ICP-MS; Agilent 7700). The analyses were performed at the Central Research Services of the University of Huelva, Spain. The detection limits were: 0.2 mg/L for S; 0.05 mg/L for Fe; 0.02 mg/L for Al and Zn; and 0.1 μg/L for trace elements. In the laboratory, home-made standards prepared with concentrations within the range of the water samples from the column experiment were employed to check the analysis quality. In each analysis sequence, blank solutions with the same matrix as the sampled solutions were also analysed. In addition, dilutions were made to guarantee that the concentration of the samples was within the concentration range of the standards. The analyses were carried out in triplicate to evaluate their precision, being better than 5 % in all samples.

The saturation indices of solutions with respect to potential mineral phases, that could be precipitating and therefore controlling the pollutants solubility during the treatment, were estimated with the code PHREEQC 3.0 (Parkhurst and Appelo, 2005) using the WATEQ4f thermodynamic database (Allison et al., 1991). This database was amended to include thermodynamic data of schwertmannite and hydrozincite from Sánchez-España et al. (2011) and Schindler et al. (1969), respectively.

The mineralogical characterization of the solid samples i.e., the calcite-rich waste used as reactive material and the precipitates originated during calcite-DAS AMD treatment, was performed by X-ray diffraction (XRD) via a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. Furthermore, the solid samples were also examined by JEOL JSM-IT500HR Field Emission Scanning Electron Microscope coupled with Oxford X-Max 150 Energy Dispersive System (FESEM-EDS). The samples analysed by FESEM were previously mounted on carbon tape and carbon coated. Both mineralogical analysis techniques were carried out at the Research Services of the University of Huelva. To estimate the percentage (by weight) of calcite contained in the waste from the phosphogypsum leachates treatment, a semi-quantitative mineralogical analysis of the crystalline phases was performed from the XRD spectrum, using the XPowder code (Martin, 2004).

2.3. Leaching protocols for the hazardousness classification and environmental assessment

A hazardousness classification of the solid samples was carried out following the standardized leaching tests proposed by the European Union (EU) (En 12457-2, 2002) and by the United States (US) Environmental Protection Agency (US EPA, 1992). The EN-12457-2 leaching test is used in the EU to determine the type of landfill suitable for the waste deposit, according to the leached concentration of certain elements (i.e., As, Ba, Cd, Cr, Cu, Mo, Ni, Pb and Sb, among others): landfills for inert, non-hazardous and hazardous wastes (EC Decision 2003/33/CE). This test consists of a solid waste leaching process with distilled water in a 1:10 solid:liquid ratio under agitation for 24 h on a shaker at room temperature.

The US standardized leaching test (i.e., TCLP) has been traditionally employed to simulate co-disposal with municipal wastes. However, its use has been extended to the management of wastes from mineral processing. In addition, the concentrations of certain contaminants (As, Ba, Cd, Cr, Ni, Pb, V, Zn, Se, Sb, Be and Tl) released after the TCLP test can be used as threshold values to establish if a waste should be subjected to a standard universal treatment (UTS) to comply with land disposal restrictions (LDR, EPA 530-R-01-007) (US EPA, 2023a). The TCLP leaching test was carried out following US EPA method 1311 (US EPA, 1992). Firstly, the extraction liquid was selected based on the pH of the solution resulting from the interaction of the waste with distilled water in a ratio of 1:10 for 10 min at laboratory temperature. For solid wastes with pH < 5, a solution of CH_3COOH buffered at pH 4.93 must be used as extraction liquid. On the contrary, if the solids have pH > 5, a solution of CH_3COOH buffered at pH 2.88 must be employed as extractant. Once the appropriate extracting fluid was selected, the solid samples were leached in a 1:20 solid-liquid ratio under agitation for 18 h at room temperature.

3. Results and discussion

3.1. Alkaline material characterization

The reactive material used for the DAS mixture is constituted by angular particles with an average grain size between 1 and 100 μm. According to the XRD spectrum (Fig. S2a), these solids are mainly composed of gypsum (54 wt%), calcite (44 wt%) and minor amounts of halite (2 wt%). On the other hand, the mineralogical study by FESEM revealed the presence of angular granular aggregates chemically composed of O, S and Ca indicative of gypsum and sub-rounded aggregates constituted of O and Ca indicative of calcite, with no apparent metal(loid)s impurities (Fig. S3). According to current EU and US environmental legislations (EN-12457-2 and US EPA TCLP tests, respectively), the alkaline waste rich in calcite may be considered as a non-hazardous waste (Tables S1 and S2).

3.2. Chemical evolution of the DAS treatment

The AMD sample used for the DAS columns showed a pH value of 2.73, a net acidity of 754 mg/L as $CaCO_3$ equivalents (Kirby and Cravotta, 2005) and high concentrations of dissolved pollutants (i.e., 2090 mg/L SO_4, 100 mg/L Al, 26 mg/L Zn, 14 mg/L Fe, 9 mg/L Cu; in addition to other minor metals as Co, Ni and Cd, with concentrations that varied between 628 μg/L and 104 μg/L) (Fig. 2).

The DAS system was able to effectively treat 14 L of acidic waters, corresponding to 32 days of experiment. During the treatment, the calcite dissolution raised the pH of the AMD up to average values of 7.7. This strong increase in pH caused the total removal of trivalent metals (Fe and Al) and around 89 % of Cu (Fig. 2). Furthermore, around 92 % of Cd and 100 % of Zn were removed from AMD but only during the first 14 and 5 days of experimental run-times, respectively, followed by increasing concentrations during the rest of the experiment (Fig. 2). Except for the first few days, the pH values achieved in the calcite-DAS treatment were not enough for the retention of other divalent metals such as Co or Ni whose solubility minimum is found at higher pH values (Cortina et al., 2003; Fig. 2). These results are similar to those obtained in DAS treatment with commercial limestone sand (Torres et al., 2018). Sulfate concentrations were slightly higher than those found in the input solution, which could be expected as a consequence of gypsum dissolution present in the DAS alkaline reagent (see Section 3.1).

According to the PHREEQC calculations, the significant decrease in the concentrations of dissolved trivalent metals (i.e., Fe and Al) in the AMD during alkaline treatment may be due to the precipitation of oxyhydroxides and oxyhydroxysulfates (i.e., lepidocrocite (FeOOH), goethite (FeOOH), ferryhidrite ($Fe(OH)_3$), schwertmannite ($Fe_8O_8(OH)_5(SO_4)_{1.5}\bullet nH_2O$), diaspore (AlOOH), and/or gibbsite ($Al(OH)_3$); see Table S3). Furthermore, according to the geochemical modeling, the solutions resulting from the DAS treatment also showed a tendency towards oversaturation of Al phases such as basaluminite ($Al_4(OH)_{10}SO_4\bullet 5H_2O$) and boehmite (AlOOH), which could also play a key role in the immobilization of contaminants during the AMD treatment. The precipitation of these Fe and Al mineral phases could also be controlling, at least partially, the depletion of other metals such as Cu, Zn, and Cd, due to co-precipitation and/or adsorption processes (Caraballo et al., 2011). In addition, the decrease in the concentration of Cu and, during almost half of the experiment, of Zn could also be associated with the precipitation of carbonate phases (e.g., malachite ($Cu_2(CO_3)(OH)_2$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$)), respectively, which showed a tendency towards oversaturation according to the geochemical modeling (Table S3). Moreover, solutions after DAS treatment were close to equilibrium or slightly undersaturated with respect to gypsum throughout the experimental period. Thus, this phase, considered as the main constituent of the alkaline reagent, could undergo dissolution, explaining higher SO_4 concentrations in the treated water than in the input solutions.

3.3. Mineralogical characterization

Once the experiment finished, the solids newly-precipitated inside the DAS column and the decantation vessel were analysed. XRD analysis of these solids only revealed the presence of gypsum (Fig. S2b). Even though Al and Fe are the major metals removed during the treatment, no Al and Fe mineral phases were identified by XRD due likely to the low crystallinity of the precipitates found in these environments which makes their identification difficult by XRD, as previously reported by other authors (e.g., Macías et al., 2012c). For this reason, a more detailed mineralogical characterization by FESEM was carried out. The mineralogical study by FESEM revealed that the solid precipitates collected in the DAS column were mainly composed of angular granular aggregates chemically constituted by S, Ca, and O, again indicative of gypsum (Fig. 3a). This gypsum, inherited from the starting alkaline reagent, seems to have suffered a dissolution process since cavities and cracks are observed on its surface, which serves as a nucleation center for the formation and subsequent growth of other solids composed of Al, S, and O, suggesting basaluminite presence (Fig. 3a). Other pollutants (e.g., Cu, and Fe) were detected in the same precipitates, suggesting the co-precipitation and/or adsorption of these metals on the basaluminite. In addition, some grains constituted by Fe, S, and O were observed, suggesting the possible precipitation of schwertmannite (Fig. 3b). These oxyhydroxysulfates were reported by Orden et al. (2021) as the main mineral phases that control the solubility of Fe and Al during the DAS treatment of AMD. On the other hand, the FESEM analysis of newly-formed solids collected from the decantation vessel showed sub-rounded granular aggregates composed mainly of Zn, Cu, and O,

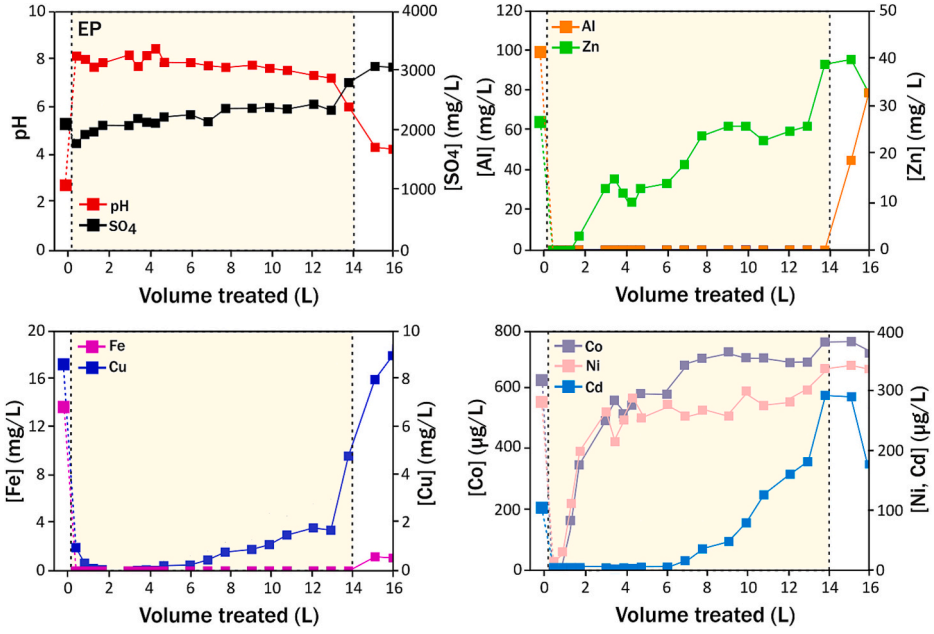

Fig. 2. Evolution of the pH and output concentration of pollutants dissolved in the AMD during its treatment with the calcite-DAS system. EP: effective period of pollutants removal.

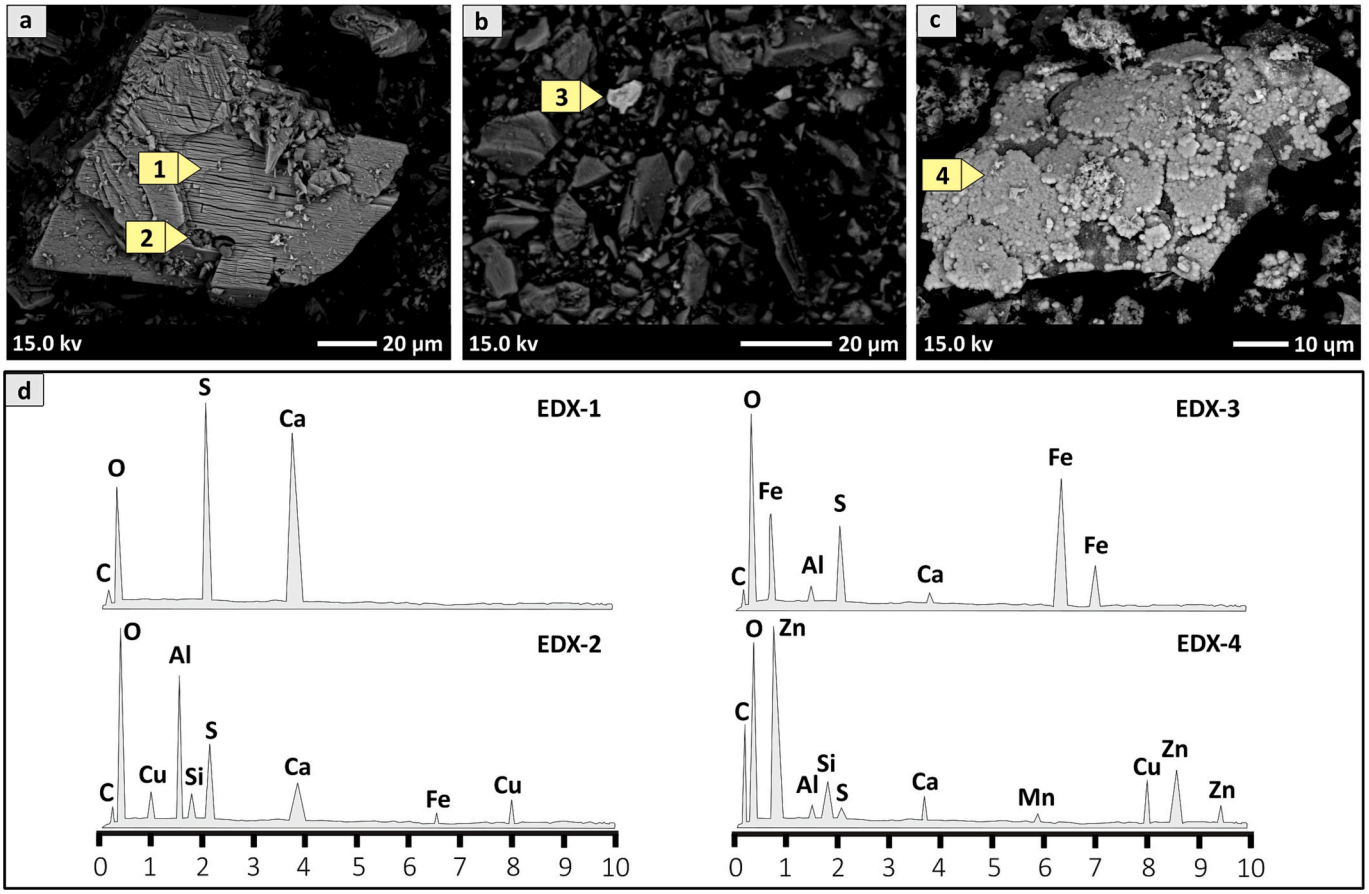

Fig. 3. Representative FESEM images of newly-formed precipitates during DAS treatment: (a) gypsum and basaluminite, (b) schwertmannite, (c) hydrozincite and malachite and (d) some EDS spectra of points of interest.

which could be hydrozincite and malachite (Fig. 3c, d) assuming that C in EDS derives not only from the sample preparation by FESEM but also from calcite dissolution and diffusion of atmospheric CO_2 into solution, and on the other hand, aggregates constituted by a mixture of gypsum and basaluminite crystals. The presence of these sulfate, oxy-hydroxysulfate and carbonate phases would be consistent with the result of the geochemical calculations performed with the PHREEQC code (Table S3). The non-identification of calcite, one of the main constituents of the starting reactive material (Fig. 3 and Fig. S2a, b), in the solids collected from the DAS treatment could be due to its total dissolution and exhaustion during the experiment, which would explain the loss of effectiveness of the system after 32 days.

3.4. Water quality assessment

To assess the improvement in the chemical quality of the water achieved by the passive DAS treatment during the effective period, a modified Ficklin diagram has been used (Fig. 4). This type of diagram is commonly used to classify AMD based on metal concentrations and pH (Ficklin et al., 1992; Ríos et al., 2008). The diagram classifies the waters from highly acidic (HA) to moderately alkaline (MAlk) in relation to pH and from extremely metallic (EM) to low metallic (LM) in relation to the total metallic concentration of the leachates. The untreated AMD solution was classified as highly acidic and extremely metallic (HA-EM). Once the acid leachate flowed through the DAS treatment system, there was an improvement in its chemical quality, reaching the near neutral field, although with high metallic content as average values due to the still presence of dissolved divalent metals. Average concentrations of the main pollutants found in the output of the DAS system during the effective period were compared with the limit values established for these elements in irrigation (Food and Agriculture Organization of the United Nations (FAO); Ayers and Westcot, 1985) and drinking waters (WHO, 2011) to assess the improvement in the water quality. The treated water showed concentrations of Fe, Al and Cd below the threshold levels recommended by the FAO for irrigation water (Table 1). However, additional treatments are required to reduce the

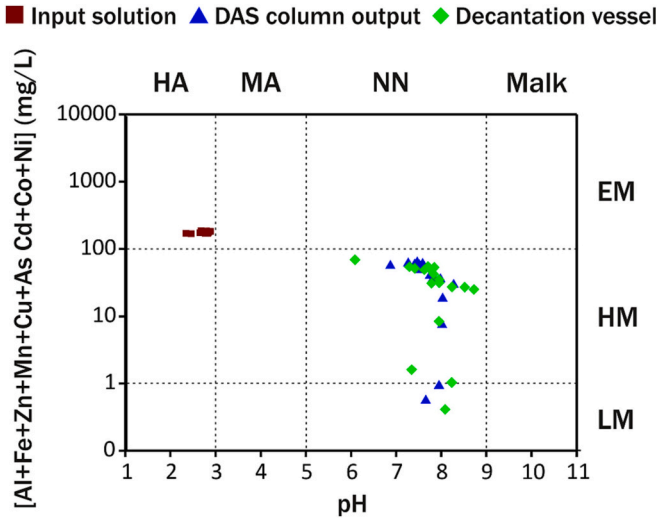

Fig. 4. Modified Ficklin diagram for the DAS treatment system. HA: high acidity, MA: moderate acidity, NN: near neutral, Malk: moderate alkalinity, EM: extreme metallic, HM: high metallic, LM: low metallic.

Table 1
Chemical composition of the initial acid leachate and the solution sampled at the output of the DAS system (average values for the effective period of the treatment), and comparison with the limit values established for metal concentration in irrigation and drinking waters.

	Initial leachate	DAS system output	FAO	WHO
Major elements (mg/L)				
SO_4	2090	2235	n.r.l.	250
Al	100	<l.d.	5	5
Zn	26.3	15.9	5	0.2
Fe	14.3	<l.d.	2	3
Cu	8.73	0.89	0.2	2
Minor elements (μg/L)				
Co	628	557	50	n.r.l.
Ni	283	234	10	3
Cd	104	63.3	200	70

<l.d.: below detection limit, n.r.l.: no referenced limit.

concentrations of divalent metals such as Zn, Cu, Co, and Ni below regulated levels. In this same sense, it is noteworthy that the output solutions fulfilled the WHO requirements for trivalent metals (i.e., Fe and Al), as well as for some divalent metals (i.e., Cu and Cd). These results are similar to those achieved in full scale DAS treatment plant (Macías et al., 2012c). These last authors highlighted the need to use a magnesia (MgO)-DAS treatment after limestone-DAS system for the effective removal of the divalent metals contained in the AMD. Magnesia is able to raise the pH to values of 8.5–10, reaching the minimum solubility of divalent metals and, consequently, achieving their precipitation (Cortina et al., 2003).

3.5. Risk and management assessment of solid wastes generated in the DAS treatment system

The alkaline passive treatment described in this study showed high effectiveness in removing dissolved pollutants (mainly Al, Fe and Cu and to a lesser extent Cd and Zn) in waters affected by AMD. However, this treatment system generates significant volumes of metal-rich wastes, whose hazardousness must be evaluated before its safe disposal to prevent potential environmental impacts. For this reason, these solid wastes were subject to two standardized leaching tests (i.e., EN-12457-2 from the EU and TCLP from the US).

According to European legislation, the solids generated in the reactive column at depths <5 cm should be considered as hazardous waste, since the concentrations of Zn and SO_4 leached (70.2 mg/kg and 21,022 mg/kg, respectively) exceeded the threshold values for its classification as non-hazardous waste (Table S1). At depths deeper than 5 cm, the solids should also be classified as hazardous waste taking into account the high concentrations of Cu released (i.e., between 58.8 and 143 mg/kg). On the other hand, the newly-formed solids in the decantation vessel should be considered as non-hazardous waste because SO_4 concentration (15,595 mg/kg) exceed the limit threshold value for its classification as inert waste.

According to the US environmental legislation, all the solid samples collected from the calcite-DAS treatment system should be classified as non-hazardous wastes since they did not exceed the TCLP limit values (Table S2). However, the precipitated solids in the decantation vessel should be subjected to a universal standard treatment (UTS), before being deposited in a landfill for non-hazardous waste, because Zn concentration released after the leaching test (30.5 mg/L) exceeded the UTS value for this metal (Table S2).

There are discrepancies between the EU and the US environmental legislations for the classification of solid wastes generated in the calcite-DAS column. According to the European regulation, these wastes should be classified as a hazardous material, while the environmental legislation of the US classifies this waste as non-hazardous. In addition, these solid wastes do not need a universal standard treatment to comply with land disposal restrictions prior to deposit in US landfills. The discrepancies between both environmental legislations have already been previously observed during the hazardousness identification of solid wastes derived from both passive and active treatments of AMD (Macías et al., 2012a, 2017b). The conflicts between both environmental legislations arise from the different extractant solutions and threshold levels established by each legislation. In this sense, the extractant solution employed in the TCLP test (i.e., CH_3COOH) has a higher leaching capacity of the pollutants contained in the DAS solids than the solution used in the EN-12457-2 test (i.e., distilled water) (Table S4). However, the threshold values proposed by the United States environmental legislation are less restrictive than those established by the European regulation. Therefore, the use of complementary protocols for risk assessment of these DAS wastes would be highly recommended. In this sense, this work proposes to assess the possible adverse effects on aquatic life according to the regulations of the US EPA (US EPA, 2023b). For this reason, the results obtained from the different leaching tests reproducing weathering after rainfall events (i.e., EN 12457-2) and under reducing conditions (i.e., TCLP) were compared with the limit values of the Criterion Continuous Concentration (CCC) and the Criterion Maximum Concentration (CMC) issued by the aquatic life criteria of the US EPA (US EPA, 2023b). The CCC is the threshold concentration above which a certain pollutant causes an unacceptable effect on most aquatic organisms at chronic exposure. On the other hand, the CMC indicates the acute exposure to an element (highest 1 h average concentration) that should not be exceeded to avoid unacceptable effects on aquatic organisms. As seen in Table S5, the concentrations of most pollutant (Al, Cu, Fe, Zn, Cd, Ni, Pb or Se) exceeded the CCC and CMC limits after the interaction of the solids from the DAS treatment with rainwater. Similarly, most of the pollutant concentrations (Al, Cu, Fe, Zn, Pb or Se) exceeded the CCC and CMC limits after the interaction of the solid wastes with organic acids (Table S6). Therefore, wastes from the DAS treatment described in this manuscript should not be disposed of in an uncovered landfill, co-disposed with municipal wastes, or covered with vegetation or organic-rich amendments due to its low chemical stability upon rainwater weathering and under reducing conditions.

4. Environmental implications

AMD generated in abandoned mining districts exhibit high acidity and pollutant concentrations, and in some cases like the IPB, these leachates are an important vector of pollution for water bodies (i.e., reservoirs, rivers, estuaries, and even oceans and seas) (Nieto et al., 2013; Cánovas et al., 2016; Pérez-López et al., 2023). In this sense, the Odiel River basin is a worldwide example of fluvial basin strongly affected by AMD. However, Macías et al. (2017c) pointed out that the chemical quality of the waters in the Odiel River basin could be significantly improved with the implementation of around a dozen DAS treatment systems in different strategic locations throughout the watershed. As mentioned above, limestone is the main alkaline reagent used in DAS treatment systems for AMD remediation. Nevertheless, Martínez et al. (2019) pointed out that the use of limestone extracted from a quarry in a DAS system had a significant impact on its ecological footprint due to the reactive material transportation, as well as all the operations carried out for its extraction. For this reason, this work proposes to replace marketable limestone with a low-cost alkaline waste from the treatment of effluents from the fertilizer industry in order to promote a circular economy, as well as to contribute to improving both the economic and environmental sustainability of DAS technology for AMD. According to Orden et al. (2021), 57 t of marketable limestone were used to effectively treat highly acidic and polluted AMD from the Esperanza Mine (SW Spain) for a period of 840 days. In this sense, the results reported in this research work indicate that the potential treatment of the total annual volume of leachates emerging from the Huelva phosphogypsum stack (i.e., approximately 500,000 m^3) by $Ca(OH)_2$-

DAS technology would generate around 3200 t of solid wastes with a 44 % calcite content, which may supply the alkaline reagent necessity for around 25 DAS treatment plants of AMD leachates, tackling both severe environmental concerns of the Huelva region.

5. Conclusions

The main goal of this work has been to evaluate the effectiveness of a calcite-rich waste, generated during the treatment of leachates from phosphate fertilizer industry, for the treatment of acid mine drainage polluted waters. The alkaline treatment proposed in this study achieved average removal rates of 100 % for Fe and Al, and close to 90 % for Cu. In addition, this treatment showed a high capacity to remove Zn and Cd during the first 14 days of treatment, achieving elimination percentages of around 76–92 %. However, the treatment was not effective for the depletion of other divalent metals present in mine drainages such as Co and Ni. These results obtained during the DAS treatment of the AMD leachates with the calcite-rich waste are comparable to those achieved during the treatment with marketable limestone.

This AMD treatment generated solid wastes that could represent an environmental concern. The mineralogical information indicates that the precipitation of oxyhydroxysulfates (i.e., schwertmannite and basaluminite) and carbonates (i.e., malachite and hydrozincite) phases could be controlling the pollutants solubility during the treatment. The hazardousness of the DAS wastes was evaluated for proper management based on EU and US environmental legislations. According to EU environmental regulation, the high mobility of Cu, Zn and SO_4 confers some of these solids the hazardous waste classification. On the contrary, these same solids are considered non-hazardous according to the environmental legislation of the US.

Overall, the DAS treatment proposed for the remediation of the Odiel River waters, strongly affected by AMD, could have a positive environmental impact since it produces an improvement in the chemical quality of extremely acidic and polluted waters. In addition, mechanisms of acidity neutralization and metal retention using this calcite-rich waste are similar to those observed with marketable limestone. Consequently, this research could promote a circular economy by contributing to improve both the economic and environmental sustainability of AMD treatment with DAS technology, proposing the replacement of the limestone, a mined raw material, with an alkaline waste with no previously thought use. The proposed methodology could be extended to other areas around the world affected by similar environmental concerns, given the common generation of acid mine drainage and phosphogypsum leachates worldwide.

CRediT authorship contribution statement

Ricardo Millán-Becerro: Investigation, Data curation, Writing – original draft, Visualization. **Rafael León:** Investigation, Conceptualization, Writing – review & editing. **Jonatan Romero-Matos:** Writing – review & editing. **Raul Moreno-González:** Writing – review & editing. **Rafael Pérez-López:** Project administration, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the Spanish Ministry of Science and Innovation under the research project TRAMPA (PID2020-119196RB-C21). Jonatan Romero is financed by a FPU program of the Spanish Ministry of Education of Vocational Training (FPU20/04441). Raúl Moreno-González also thanks the Spanish Ministry of Science and Innovation, the Spanish Research Agency and the European Union "nextGenerationEU" for the Postdoctoral Fellowship granted under application references FJC2021-047600-I. Ricardo Millán Becerro also acknowledges the Spanish Ministry of Universities for the Margarita Salas Research Grant. We would also like to thank Dr. Damià Barceló (Co-Editor-in-Chief) and two anonymous reviewers for the support and comments that significantly improved the quality of the original paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.168078.

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