

Research article

Eco-sustainable passive treatment for mine waters: Full-scale and long-term demonstration

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ABSTRACT

This paper tries to analyse the technical and economic performance of a full-scale passive Disperse Alkaline Substrate (DAS) treatment plant steadily operating for 28 months (840 days) to treat extremely acidic and metal rich mine waters in the Iberian Pyrite Belt (SW Spain). For the first time, an economic evaluation of this technology and its comparison with other passive treatments is reported. During this period, around 56,000 m³ of mine waters have been treated, without significant clogging or exhaustion of the alkaline substrate. The efficiency of the system is demonstrated by a significant decrease in the average net acidity (from 2005 to −43 mg/L as CaCO₃ equivalent) and the total elimination of Al, Cu, REY, Zn, As, Cr, Mo, V, Cd, Pb, Co and other trace metals. Water quality of the treated output discharge meets the threshold values for irrigation and drinking standards, except for Fe, Mn and sulphate. The accumulation of elements of economic interest in the waste (e.g., 32 t of Fe, 6.1 t of Al, 0.8 t of Cu, 0.8 t of Zn, 39.4 kg of REE, 20 kg of Co or 1 kg of Sc), easily extractable with diluted acids, may turn a hazardous waste into a valuable resource. The benefits associated with the revalorization of this metal-rich waste could reach a total of 27478 USD, but is more reliably estimated to be around 8243 USD due to technologic limitations. This benefit would help to defray the maintenance costs (8428 €) and make DAS an economically self-sustainable treatment. The annual treatment cost for DAS was 0.27 €/m³, being the lowest value found among other reported conventional passive schemes, and from 8 to 12 times lower compared to active technologies. The results obtained prove that the DAS technology is the most technically and economically sustainable way to decontaminate acid and metal-rich mine waters in abandoned mines.

1. Introduction

The huge growth of world mining industry in the last years may inevitably imply that environmental challenges and technical solutions must be adopted to mitigate the impacts. For instance, water resources may be strongly damaged by mine activities, and become a key factor in the viability of a mine project (Pozo et al., 2017) due to the management costs, particularly associated with the acid mine drainage (AMD) treatment. Mine waters are commonly highly-acidic and metal(loid)s-rich, being considered as one of the most environmentally damaging causes derived from the metal and coal mining industry (e.g. Clyde et al., 2016). Moreover, the great and increasing number of abandoned and remote mines also represents a challenge for decision makers on mine water management (Favas et al., 2016). This "orphan site" legal

situation commonly forces the public administration to face the expenses required to comply with the environmental regulations.

A worldwide outstanding example of this situation is the Odiel River Basin (SW Spain), with hundreds of kilometers of streams and reservoirs deeply polluted by AMD (e.g. Sarmiento et al., 2009; Cánovas et al., 2016), discharging to the Atlantic Ocean thousands of tonnes of toxic contaminants (Nieto et al., 2013). The current situation of environmental degradation in the Odiel watershed is due to intense mining activities developed during centuries in the Iberian Pyrite Belt (IPB), with a total absence of environmental control labours. The IPB is considered as one of the most important metallogenic provinces in the world (Sáez et al., 1999). This unique geological unit, with over 4500 years of mining history, makes the IPB one of the oldest mining districts in the world (Nocete et al., 2005).

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This uncontrolled, intensive and continuous mining practice over time has resulted in around 4800 ha of surface occupied by rock piles, pits, tailings impoundments and other mining facilities; and hundreds of kilometers of shafts, tunnels and galleries scattered throughout more than 80 orphan mines (Grande, 2016). The European Water Framework Directive (WFD, Directive 2000/60/EC) has established the main goal of achieving a good ecological and chemical quality status for all European water bodies before 2015 (Buaisha et al., 2020). This deadline, however, can be extended if natural conditions do not allow to reach a good quality status by technical feasibility and/or economic unsustainability in this period. This is the specific case of the Odiel River, where the regional authorities have extended the deadline imposed by the WFD until 2027 (Macías et al., 2017a). Then, extensive remediation measures should be adopted to fulfil the WFD requirements before the new deadline, among them the treatment of the huge volume of AMD generated in the watershed.

Mine waters can be treated by different types of technologies, which can be classified into two different groups: active and passive technologies (Johnson and Hallberg, 2005). The active treatments require energy consumption and continuous chemical dosage, while passive treatments use the sources of energy available in nature such as gravity, energy of microbial metabolism, photosynthesis and simple geochemical reactions (Akciil and Koldas, 2006). Another advantage of passive over active systems is the scarce maintenance requirements. Active treatments are commonly used in operating mines because of the need to treat large volumes of water, whereas passive treatments are more suitable for abandoned mines or during the remediation programs after mine closure (Johnson and Hallberg, 2005).

Different passive schemes have shown high performance in the treatment of AMD with low to medium acidity content (mainly in coal mines) (Younger et al., 2002) and with contaminated neutral drainage (e.g. Neculita and Rosa, 2019). These passive technologies include aerobic (AW) and anaerobic wetlands (AnW), vertical flow wetlands (VFWs), sulphate-reducing Biochemical Reactors (PBRs), Passive Bio-reactors (BioR), Anoxic Limestone Drains (ALD) or Reducing and Alkalinity Producing Systems (RAPs), or different combinations of these techniques. However, as pointed out by Ayora et al. (2013), these conventional passive technologies showed very poor performance when subjected to extremely acid and metal-rich waters.

During the last 15 years, laboratory- and field-scale experiments with Dispersed Alkaline Substrate (DAS) have demonstrated that it is the only passive technology capable to overcome the clogging and armouring problems of the conventional passive treatments. The DAS technology is a multi-step treatment mainly composed by: Natural Fe-Oxidizing Lagoons (NFOL) (Macías et al., 2012a), limestone-DAS reactors (e.g. Rötting et al., 2008) and/or MgO-DAS reactors (e.g. Caraballo et al., 2009). Basically, DAS concept is a mixture of a fine-grained alkaline reagent to provide high reactive surface and complete dissolution before passivation, dispersed in a coarse inert matrix to provide high porosity to delay clogging. Detailed information about DAS technology can be found in Ayora et al. (2013). The DAS technology has been successfully tested at lab-scale in mine waters not only from the IPB but also in other regions of the world (e.g. Rakotonimaro et al., 2016; 2018; Delgado et al., 2019). However, DAS technology upscaling is needed to comply with the technical requirements for AMD remediation measures of the WFD. In this sense, this technology has been successfully tested at pilot scale in the IPB (e.g. Caraballo et al., 2009; 2011a), though the long-term performance of the technology at industrial scale has not been still reported to date. In addition, most of the reported cases of mine water treatments do not sufficiently address their economic performance, which is a critical factor in the implementation of technologies at large-scale. Thus, the main aim of this study is to analyse the performance of the DAS technology at full-scale and long-term periods (i.e. 840 days) during the treatment of acid and metal-rich waters from Mina Esperanza (IPB) and compare its cost-efficiency with respect to other treatment systems. To this end, the spatial and temporal evolution of the

treated water as well as the system efficiency will be presented; a comparative economic evaluation of DAS technology with those of conventional systems will be profusely discussed; and finally, the economic implications for the valorisation of metals retained during the treatment will be addressed.

2. Materials and methods

2.1. Location and treatment plant description

The treatment system was set up at the Mina Esperanza abandoned mine (Fig. 1). From 1906 to 1931 polymetallic sulphide ores composed mainly of massive pyrite with minor amounts of chalcopyrite were mined. The total amount of mineral extracted was around 1.8 millions of tonnes, with a Cu grade oscillating between 1 and 2% (Pinedo Vara, 1963). Following the cessation of the mining and pumping operations, the water table recovered background values and acidic leachates have been flowing from an old gallery ever since. Hydrological and hydrochemical fluctuations of this acid discharge at intra- and inter-annual scale were previously studied by Caraballo et al. (2016).

To remediate contamination from this AMD source and contribute to fulfil the WFD requirements, the first full-scale DAS passive treatment was constructed and run into operation in late 2014. The treatment plant is firstly made of a pre-treatment (NFOL) composed of aeration cascades and a sedimentation lagoon of 100 m² of surface (Fig. 1). Afterwards, the water enters two reactive tanks (RT1 and RT2), both divided into two different vessels, with a dimension of 960 m³ (20 × 12 × 4) and 720 m³ (15 × 12 × 4), respectively. At the exit of each reactive tank there is a 100 m² settling pond to enhance the sedimentation of the mineral precipitates. All the units of the treatment plant are connected by open channels (Fig. 1). The reactive tanks are filled (from bottom to top) with a 0.5 m drain layer of coarse quartz gravel, a 2 m layer of limestone-DAS reactive mixture (80% (v/v) pine wood chips and 20% (v/v) limestone sand), and 1.5 m of free wall for supernatant water. The system was treating an average flow of 0.8 L/s during 28 months continuously. The average residence times of water in RT1 and RT2 were 5 and 4 days, respectively.

2.2. Water sampling and analyses

The research methodology followed in this study can be seen in Figure SM1 of the Supplementary Material. Water samples were taken at least twice a month from December 2014 to April 2017, totalling 44 sampling campaigns in the different components of the plant (see Fig. 1): mine shaft (ME 1), pre-treatment outflow (ME 2), exit of the reactive tanks (RT1 and RT2) in ME 3 and ME 5, and in the outflows of the settling ponds (D1 and D2) in ME 4 and ME 6 sampling points. In total, 269 samples were collected for this study.

Physico-chemical parameters (pH, temperature (T^a), electrical conductivity (EC) and redox potential (ORP)), were measured in the field using a Crison® MM40+ multiparameter equipment previously calibrated with certified solutions. The ORP values were corrected according to the standard hydrogen electrode (Nordstrom and Wilde, 1998). The alkalinity (Alk) was determined using Total Alkalinity evaluation kits of Titrets® CHEMetrics brand, with measurement ranges of 10–100 or 100–1000 mg/L of CaCO₃ equivalents. The accuracy of this measurement is approximately 5%.

Water samples were filtered through 0.1 µm Millipore filters on Millipore syringe filter holders, acidified in the field to pH < 2 with suprapure HNO₃ and stored at 4 °C in 60 mL sterile polypropylene containers to prevent metal precipitates until analysis. Major elements (Al, Ca, Cu, Fe, Mn, S, Si and Zn) were analysed by ICP-OES (Yobin Ivon Ultima2) while trace elements (rare earth elements (REE), Y, Li, Sc, V, Cr, Co, Ni, As, Se, Mo, Cd, Sb, Tl, Pb and U) were analysed by ICP-MS (Agilent 7700). Detection limits were 0.2 mg/L for Al, Cu, Zn and Si; 0.1 mg/L for Fe, Ca and Mn, 0.5 mg/L for S, and 0.2 µg/L for trace

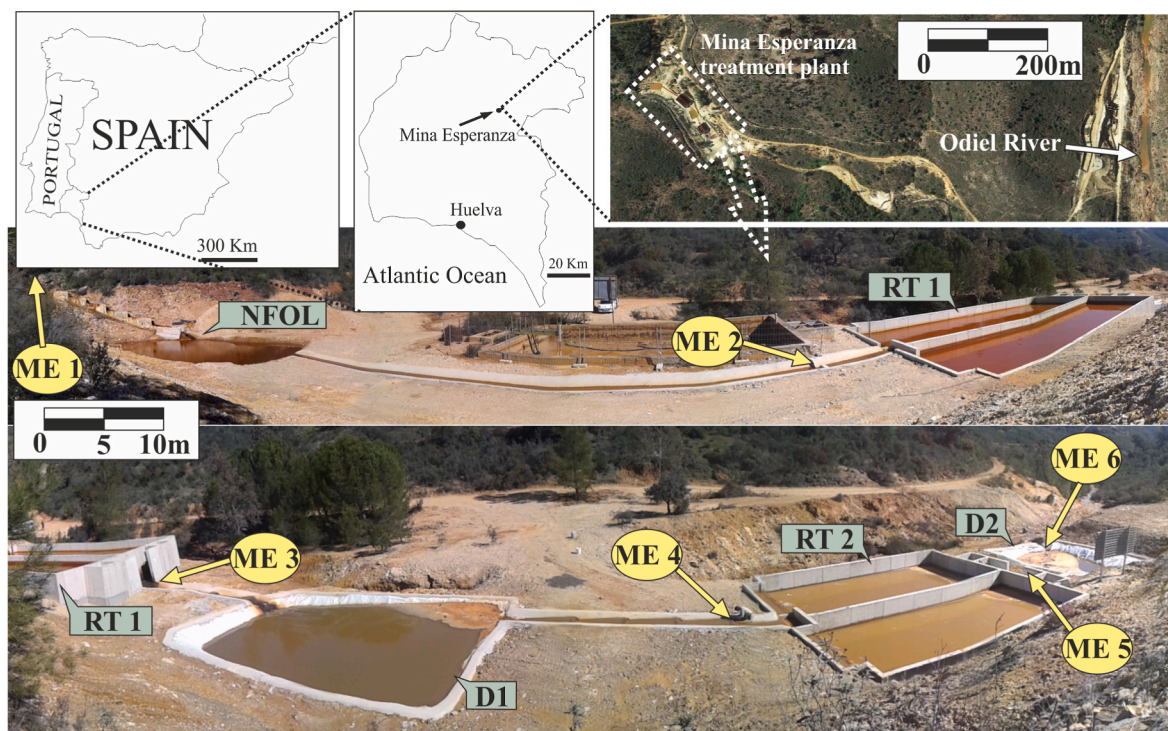


Fig. 1. General and detailed location, and panoramic view of the Mina Esperanza DAS passive treatment plant, showing the different parts and the sampling points. RTx (reactive tanks), NFOL (Natural Fe-oxidizing lagoon) and Dx (decantation ponds). ME1: adit, ME2: NFOL output, ME3: first reactive tank output, ME4: first decantation pond output, ME5: second reactive tank output, and ME6: second decantation pond output.

elements.

Net acidity (N_A) (mg/L of CaCO_3 equivalent) was calculated using the following equation (Kirby and Cravotta, 2005a,b):

$$N_A = 50045 * (3 * C_{Al} + 2 * C_{Fe} + 2 * C_{Mn} + 2 * C_{Zn} + 10 - p^H) - \text{Alk}$$

where 50045 is the conversion factor from mol/L to mg/L as CaCO_3 equivalents, C_x are molar concentrations of the different metals and Alk is the measured alkalinity (mg/L of CaCO_3 equivalents).

In order to contrast the effectiveness of the system in each component of the plant, the relative metals removal (r) (%) has been obtained according to the following equation:

$$r = (C_{in} - C_{out}) / C_{in} * 100$$

where C_{in} and C_{out} are the input and output concentrations (mg/L) in each component of the system.

Acid load reduction (AR; in g/(m²day), normalized by the specific area of the system, was calculated as follows:

$$AR = Q * (N_{A_{in}} - N_{A_{out}}) / A * 100$$

where Q is flow rate (m³/day), $N_{A_{in}}$ and $N_{A_{out}}$ are the net acidity values of the feeding and outflowing waters of the plant, and A is surface area of the treatment system (m²).

A geochemical modelling was carried out using the PHREEQC code v2.12.01 (Parkhurst and Appelo, 2005) with the WATEQ4f thermodynamic database (Ball and Nordstrom, 1991). This modelling tool was used to obtain the saturation indexes of minerals and to determine the aqueous speciation of solutions from the different steps of the treatment plant. The database was modified to include thermodynamic data for schwertmannite and basaluminite from Sánchez-España et al. (2011), and hydronzincite from Schlinder et al. (1969).

2.3. Economic modelling of the DAS treatment plant

With the aim of performing an economic evaluation of the Mina Esperanza DAS treatment plant, construction and maintenance costs have been compared with other passive and active technologies available for the same working conditions. This approach has been made by the use of the AMD-Treat code (Version 5.0.2 Plus), a software developed by the Office of Surface Mining Reclamation and Enforcement (OSMRE) of the US Department of the Interior (<https://amd.osmre.gov/>). The software allows to estimate the costs for a variety of active and passive treatment systems. The model is based on the acidity load of the acid waters to be treated and the neutralizing capacity of the selected alkaline reagent. Thus, input data are divided into two different blocks: Total Capital Cost, including treatment facility construction and ancillary costs (e.g. ponds and ditching), and Annual Cost. For passive treatments, these Annual Costs are referred to the maintenance (calculated as 3.5% of Total Capital Costs) and the cost of sludge removal (0.2 €/m³). In the case of active treatments, the Annual Costs include the maintenance, pumping, and reagents costs (e.g. neutralizing and oxidants).

The cost-effectiveness of Mina Esperanza DAS treatment plant has been compared with the modeled results for different passive treatment systems (ALD, AnW, AW and BioR) and for active treatment systems using caustic soda, hydrated lime, lime and soda ash.

3. Results and discussion

3.1. Spatial and temporal evolution

The treatment system can be divided into three different components: the pre-treatment, the reactive tanks and the decantation ponds. To understand the performance of the different components of the system, this section will show the average spatial evolution of the physico-chemical parameters such as pH, ORP, EC, alkalinity (Fig. 2) and net acidity, as well as the evolution of some selected metals such as Fe, Al,

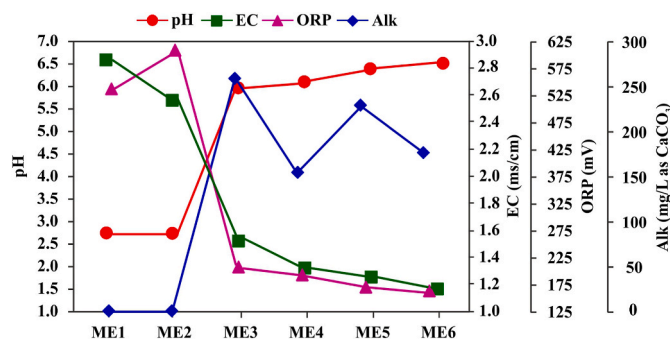


Fig. 2. Average evolution of physical-chemical parameters in the different parts of the treatment plant.

Zn, Ca and Cu (Fig. SM2); and As, Cr, Co, Cd, Pb and REE (Fig. SM3). During the pre-treatment, a rise in ORP values (from 541 to 613 mV) is observed, coinciding with a decrease in Fe concentration (from 683 to 566 mg/L). There are no pH changes (it remains at around 2.8) while the EC values decrease from 2.8 to 2.5 mS/cm. An average of 17% of Fe is removed during the pre-treatment due to the oxidation and subsequent precipitation of schwertmannite (Caraballo et al., 2011b). After this pre-treatment, the water shows equilibrium or oversaturation with respect to schwertmannite (Fig. SM4). The absence of pH variations between input and output waters seems to indicate that the protons released during Fe(III) precipitation are counterbalanced by both Fe(II) oxidation and dissolution of the Portland cement paste used in the aeration cascades and channels (visually observed during the treatment performance).

The precipitation of these mineral phases during the pre-treatment leads to the removal of other pollutants; for example, an average decrease in sulphate concentration (main component of schwertmannite) of around 8% is observed. Additionally, the concentrations of other metal(loid)s are also significantly reduced: from 301 to 122 µg/L of As, from 6 to 1 µg/L of Mo and from 71 to 33 µg/L of V.

After this step, the water enters the first reactive tank (RT1; Fig. 1), where dramatic chemical changes occur. These highly-acidic waters interact with the reagent mixture dissolving a large amount of limestone (50 tons during the study period). Indeed, calcite remains sub-saturated in T1 over the entire period (Fig. SM4). Consequently, a sharp rise of pH is observed (from 2.7 to 6.0) at the output of the first tank (ME3; Figs. 1 and 2), which proves the limestone-DAS effectiveness. On the contrary, the ORP and EC values suffer a strong drop from 613 to 211 mV and from 2.5 to 1.5 mS/cm, respectively (Fig. 2). The limestone dissolution in the tank led to a significant increase in Ca concentration (from 123 to 553 mg/L; Fig. SM2) and alkalinity (from 0 to 260 mg/L of CaCO₃; Fig. 2). These changes entail the retention of trivalent metals and a general decrease in the concentration of the rest of the elements, i.e. Fe concentration falls from 566 to 227 mg/L (50% of removal) and Al concentration from 106 to 0.5 mg/L (close to 100% of removal) due to the precipitation of Fe and Al oxy-hydroxy-sulphates such as schwertmannite and basaluminite, respectively (Fig. SM4). This difference in removal efficiency between Fe and Al is mainly due to the existence of considerable amounts of Fe(II), which unlike Fe(III), is mobile at this pH value. Moreover, the precipitation of Fe and Al minerals caused the removal of around 15% of dissolved sulphate, while other metals such as Cu (Fig. SM2), REE, Pb, Cr, As, V and Mo were completely removed from the solution (Fig. SM3, V and Mo not shown), probably by processes of adsorption and/or co-precipitation onto these minerals (Caraballo et al., 2011a; Lozano et al., 2019, 2020a). Other divalent metals were also significantly reduced by the same sorption processes described above: from 14 to 2 mg/L of Zn, from 358 to 108 µg/L of Co, from 120 to 24 µg/L of Ni or from 52 to 2 µg/L of Cd.

Once the water flows out the first reactive tank, it reaches an oxidation cascade and the first settling pond (ME4; Fig. 1), where Fe

oxidation and precipitation are enhanced due to the near-neutral pH and the increasing residence times. Consequently, a decrease of alkalinity (from 258 to 155 mg/L of CaCO₃; Fig. 2) is observed in response to its consumption by the precipitation of Fe, which in turn decreases its concentration from 227 to 163 mg/L (Fig. SM2). Simultaneously, a slight increase in pH (from 6.0 to 6.1) can be observed (Fig. 2), which can be explained by the degassing of CO₂ until achieving equilibrium. After the settling pond, the water flows through the second reactive tank (ME5; Fig. 1), where the dissolution of limestone causes a new increase in pH values (from 6.1 to 6.4; Fig. 2) and alkalinity (from 176 to 228 mg/L of CaCO₃) (Fig. 2), less abrupt than that observed in T1 due to the lower acidity of waters, leading to a lower dissolution of limestone (7 tons). The EC and ORP values decrease slightly (from 1.3 to 1.2 mS/cm and from 197 to 174 mV, respectively; Fig. 2). In this step the remaining divalent metals (i.e. Zn, Co and Cd) are removed from the water below the detection limit (Figs. SM2 and SM3), with a withdrawal of Fe from 163.4 to 81.8 mg/L; only 10% Fe(II) remains dissolved.

The drop in ORP values observed at the exit of the tanks (RT1 and RT2) may be due to the achievement of partial reducing conditions within each tank by the presence of labile organic matter in wood shavings. The additional alkalinity supplied by the second reactive tank allows eliminating the remaining divalent metals such as Cd, Zn, Ni, or Co from waters (Figs. SM2 and SM3) as well as decreasing the sulphate concentration (from 2225 to 2077 mg/L in T2; Fig. SM2). The calculated saturation indexes (Fig. SM4) suggest that the main minerals controlling the solubility of sulphate in the reactive tanks may be basaluminite and schwertmannite, which showed oversaturation; whereas gypsum appears to be in equilibrium. Sorption processes may also play an important role in metal removal. In this sense, Caraballo et al. (2009) reported that the removal of Cd in this system may be caused by pH-dependent adsorption. The high specific surface of the mineral precipitates and the pH-dependence observed in the behaviour of Cd, Zn, Co and Ni along the different components of the plant suggest the importance of adsorption in the removal of divalent metals from water. Finally, the residence time of waters in the second settling pond D2 (ME6, Fig. 1) causes a slight decrease in Fe concentration (from 81.8 to 64.8 mg/L; Fig. SM2) and water alkalinity (from 228 to 175 mg/L; Fig. 2). The removal percentages of sulphate in the settling ponds (D1 and D2) are not significant compared with previous components of the plant.

The performance of the treatment plant through the time can be seen in Figure SM5, where the evolution of different physico-chemical parameters and the concentration of some metals are plotted. As can be seen, the EC values and the content of metals in mine shaft waters before and after the pre-treatment (ME1 and ME2) vary seasonally, with maximum values observed during the dry season due to the decrease in flow and increase in evaporation and minimum in winter due to greater runoff contribution. The factors controlling metal variability in these mine shaft waters are explained in detail by Caraballo et al. (2016). The good performance of the plant is confirmed by the high pH values (above 6) of output waters and the near complete removal of Al, Cu, Zn, Cd, Co, Ni, As and Pb (the latter not shown in Fig. SM5) throughout the period. However, a lower efficiency of RT1 for Zn removal can be seen at the end of the period. This loss of efficiency may be related to limestone exhaustion within the tank, as evidenced by the progressive decrease in alkalinity and Ca concentrations since 2016 in the output waters from the reactive tanks, especially from the first one (Fig. SM5); e.g. around 50% of alkalinity decreases at ME 6; from 257 mg/L as CaCO₃ in 2016 to 126 mg/L as CaCO₃ onwards. In the case of Fe, it can be observed the occurrence of periods with different efficiency (ranging from 80 to 90% of removal), probably due to variable rates of Fe(II) oxidation.

3.2. Metal removal and system efficiency

During the entire operation time of the treatment plant (840 days), up to 99% of the total Al, Cu, REE, V, Cr, As, Mo, Cd, Zn, Co, Sb, Tl and Pb contained in mine waters was removed. In addition, up to 97% of Ni,

U and Se, 90% of Fe or 86% of Sc were also eliminated (Table 1). The efficiency of the treatment plant can be also evaluated considering the individual components. Specifically, only in the pre-treatment 100% of Sb, 83% of Mo, 60% of As, 53% of V, 17% of Fe, and 11% of Cr were removed from the water. However, the greatest metal removal occurred inside the first tank, where up to 90% of Al, Cu, Pb, Cd, Tl and REE was retained. Other pollutants such as U (81%), Zn (80%), Co (65%) and Ni (75%), among others, were also removed although to a lesser extent than the first group. Additionally, after the second tank, 100% of Zn and Cd, above 90% of Co and Ni, and approximately 90% of Fe were removed. With regard to the settling ponds, these components enhance the settlement of particulate metals and the precipitation of Fe(III) (around 9% in D1 and 2% in D2), but the metals removal is not very significant when compared to the reactive tanks (Table 1).

The acid load reduction (AR) is a parameter commonly used to characterize the surface efficiency of a passive treatment system, and as a system design criterion. In this case, the DAS treatment plant achieved a median AR of 647 g/(m²day), which is higher than the value of 400 g/(m²day) obtained in the previous pilot-scale DAS treatment (Caraballo et al., 2011a) where NFOL pre-treatment was not implemented. In addition, the high efficiency of DAS technology is demonstrated by comparing with average ARs of different passive schemes. Data obtained from 32 VFW, 6 AW, 28 AnW, 37 ALD and 11 settling ponds (Ziemkiewicz et al., 2003; Skousen and Ziemkiewicz, 2005) showed average ARs of 74.9, 16.3, 20.5, 70.8 and 1.7 g/(m²day), respectively, which are one or two orders of magnitude lower than that obtained at Mina Esperanza DAS treatment plant.

The reduction of the net acidity in waters could be considered as one of the best ways to determine the effectiveness of a treatment system. This parameter considers not only the proton acidity of waters but also the mineral acidity, provided by hydrolysable metals such as Fe, Al, Mn and Zn. Thus, positive values would imply net acidic waters, and on the contrary, negative values would indicate net alkaline waters. The evolution of this parameter through the different components of the plant shows a sharp decrease of average net acidity values from the input waters (2005 mg/L of CaCO₃ equivalent) to the final treated waters (−43 mg/L). This change from acidic to alkaline conditions in water proves, once more, the efficiency of the treatment system (Fig. 3A).

To evaluate the changes in water quality, a modified Ficklin diagram has been also performed (Ficklin et al., 1992). This diagram is commonly used to classify the AMD waters based on the pH and the concentration of dissolved metals. According to this diagram, a remarkable improvement of the chemical water quality along the different components of the plant can be observed (Fig. 3B). Thus, highly acidic and extremely metal-rich waters (in ME1 and ME 2) evolve into waters close to the neutrality and highly metallic (ME 3 to ME 6), with a metal content two orders of magnitude lower than that of the input waters. The main reason for such a high metal content despite the circumneutral pH values reached is the high concentration of Fe(II) (64.8 mg/L) and Mn (3.7 mg/L), whose removal was less effective than for other metals.

Table 2 compares the concentration of metal(loid)s of the output waters with the limit values recommended by the Food and Agriculture Organization of the United Nations (FAO) for irrigation waters (Ayers and Westcot, 1985), by the World Health Organization (WHO) for drinking water, as well as the Canadian Environmental Quality Guidelines (CEQGs) for Canadian Environment Council. It is observed that with the exception of the concentration of Fe, Mn and sulphate obtained, none of the elements considered exceeded the limits established for such regulations. The average concentration of Fe at the end of the treatment is 65 mg/L, noticeably higher than the limit value (5 mg/L) established by FAO, WHO and CEQGs. It is expected that for the near neutral pH values of the final outflow, the remaining Fe (II) oxidizes and precipitates as ferrihydrite at expenses of the residual alkalinity. Additional and more expensive treatments would be required to abate Mn and SO₄ below the regulated values (Macías et al., 2012b; Torres et al., 2018).

Table 1
Average relative metal removal (r, %) in the different steps of the treatment plant.

	Fe	Al	Cu	Zn	As	Cr	Mo	V	Cd	Pb	REE	Co	Ni	U	Se	Sc	Sb	Tl	Li
NFOL	17.3	4.0	7.1	5.8	59.5	10.6	82.8	53.2	2.1	2.7	0.4	7.1	6.3	7.0	16.0	7.5	100.0	5.8	6.5
RT1	49.5	95.6	92.6	80.4	39.7	87.4	17.2	46.0	93.8	96.8	97.3	64.9	75.1	81.1	74.3	72.2	0.0	91.3	1.9
D1	9.3	0.3	0.2	2.1	0.6	1.0	0.0	0.1	0.9	0.5	1.5	2.0	2.1	5.5	2.1	3.1	0.0	1.9	0.0
RT2	11.9	0.0	0.0	11.6	0.0	0.3	0.0	0.1	3.2	0.0	0.4	23.5	12.9	0.0	5.6	2.9	0.0	0.9	0.0
D2	2.5	0.0	0.0	0.0	0.3	0.2	0.0	0.1	0.0	0.0	0.0	1.7	0.7	4.3	0.4	0.5	0.0	0.0	0.0
Total	90.5	99.9	100.0	100.0	99.6	99.5	100.0	99.5	100.0	99.1	99.6	99.2	97.1	97.9	98.4	86.2	100.0	99.9	8.4

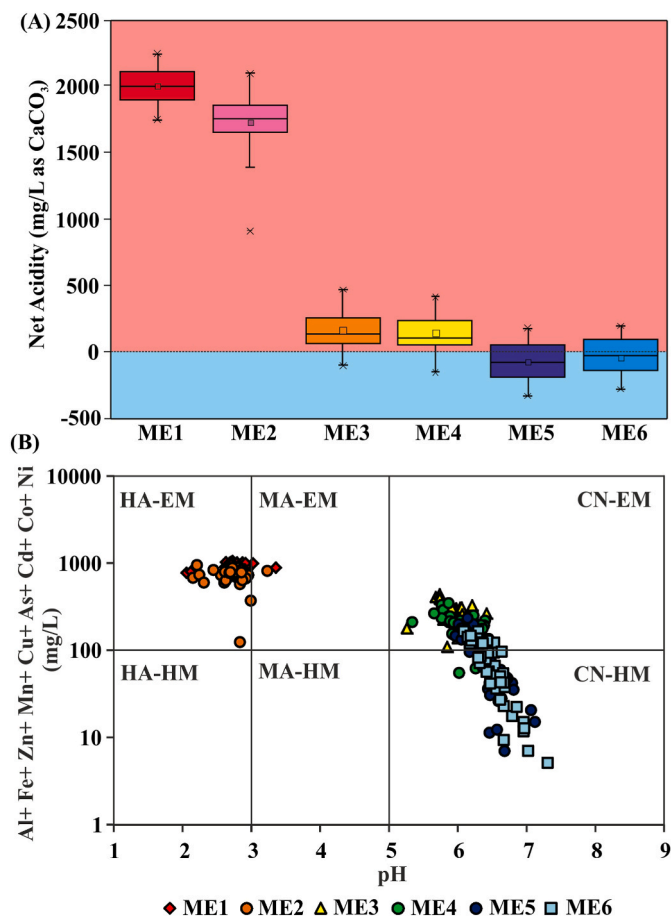


Fig. 3. Box and whiskers plots of net acidity (A) and Modified Ficklin diagram (B) in the different parts of the treatment plant. HA: high acidity, MA: moderate acidity, CN: circum-neutral, EM: extreme metallic, and HM: high metallic.

Table 2

Chemical composition of the inflow and outflow AMD water of Mina Esperanza treatment plant, and comparison with quality standards. Data obtained from 47 sampling campaigns.

	Inflow	Outflow	Water quality			
			FAO	WHO	CEQGs	
					Irrigation	Livestock
Major elements (mg/L)						
Fe	683.4	64.8	5	5	5	n.r.
Al	116.7	0.1	5	0.2	5	5
Cu	14.1	0.1	0.2	2	1	5
Zn	15.1	0.1	2	3	n.r.	50
Mn	3.6	3.7	0.4	0.2	0.2	n.r.
SO ₄	2871.7	2061.1	n.r.	250	n.r.	1000
Ca	133	551	n.r.	n.r.	n.r.	1000
Minor elements (µg/L)						
As	301.1	1.3	100	10	100	25
Cr	21.8	0.1	100	50	n.r.	n.r.
Co	385.8	3.1	50	n.r.	50	1000
Mo	6.3	0.2	n.r.	n.r.	n.r.	100
Cd	52.9	0.2	10	3	5.1	0.8
V	70.8	0.4	n.r.	n.r.	100	100
Pb	18.1	0.2	5000	10	200	100
U	10.6	0.5	n.r.	n.r.	10	200
Ni	128.2	3.7	200	70	200	1000
Se	5.1	0.1	n.r.	n.r.	n.r.	50

FAO = irrigation water recommendations of the Food and Agriculture Organization of the United Nations. WHO = drinking water limits according to the World Health Organization. CEQGs = Canadian Environmental Quality Guidelines. n.r. = no references.

The positive impact of the treatment plant on the receiving water bodies is significant; the amount of metal(loid)s retained in the treatment system accounted for a total of 100 tons, avoiding its discharge into the Odiel River. It is especially remarkable the accumulation of 58.9 t of SO₄, 32.3 t of Fe, 6.1 t of Al, 0.8 ton of Cu, 0.8 ton of Zn, 39 kg of REE, 20 kg of Co, 16 kg of As, 6.4 kg of Ni, among others (Table 3).

3.3. Treatment costs and economic evaluation of the DAS treatment plant

In addition to technically suitable, a treatment system must be cost effective. The costs associated with the construction and operation of Mina Esperanza DAS treatment plant are shown in Table 4. The total capital cost accounted for 196100 €, with 166000 € in facility construction and 30100 € in the DAS-reactive mixture filling (RT1 and RT2, Fig. 1). The reactive material must be replaced every 3 and 5 years for RT1 and RT2, respectively. In this sense, the replacement of this material can be considered as the only maintenance cost in the DAS technology treatment plants, accounting for around 18060 € for RT1 and 12040 € for RT2. This implies an annual maintenance cost for Mina Esperanza DAS plant of 8428 €/yr (Table 4). Taking into account the mean flow rate of AMD treated during the monitoring period, an annual treatment cost of 0.27 €/m³ can be estimated (Table 4).

The comparison between the total capital costs of Mina Esperanza DAS plant and other conventional passive technologies showed a higher cost for treatments based on bacterial activity (AnW and BioR), and slightly lower costs for ALD and AW (Table 4). The high construction costs of the facilities for AnW and BioR are related to the large land surface required, because the bacterial activity needs a high residence time for a proper functioning. However, the maintenance costs are higher for other conventional passive treatments (ranging from 0.30 to 0.52 €/m³) compared to DAS (0.27 €/m³) (Table 4). Unsurprisingly, due to the low flow rate of Mina Esperanza discharge, the capital costs for active treatments are very low compared to DAS (and other passive technologies); from 8897 to 40587 € depending on the alkaline materials used (i.e. soda ash or hydrated lime, Table 4). However, the maintenance and operation costs of active technologies are unsustainable; in the best case, the annual costs would double those of the facility construction. This implies that the active technologies would require annual treatment costs between 8 and 12 times higher (from 2.27 to 3.13 €/m³) than those needed for the DAS treatment.

This economic evaluation clearly shows that the DAS technology is the best option to successfully treat highly acid and metal-rich waters at orphan sites not only from a technical but also from an economic point of view. Considering the long-term efficiency of the treatment plant as

Table 3

Metal accumulation in the different steps of the treatment plant after 840 days.

(Ton)	Al	Cu	Fe	Mn	SO ₄	Si	Zn
NFOL	0.56	0.07	6.47	0.01	11.83	0.15	0.1
RT1	5.51	0.70	17.10	0.00	23.29	1.23	0.6
D1	0.01	0.00	3.51	0.01	5.08	0.20	0.03
RT2	0.00	0.00	3.92	0.00	7.94	0.10	0.1
D2	0.00	0.00	1.31	0.01	10.75	0.05	0.0
TOTAL	6.08	0.77	32.31	0.03	58.89	1.73	0.8
(Kg)	REE	Sc	V	Cr	Co	Ni	As
NFOL	2.45	0.08	2.11	0.13	1.43	0.42	10.32
RT1	35.54	0.88	1.82	1.06	13.19	5.07	6.27
D1	0.32	0.04	0.00	0.01	0.73	0.13	0.06
RT2	0.11	0.03	0.00	0.00	4.82	0.83	0.00
D2	0.00	0.01	0.00	0.00	0.00	0.00	0.0
TOTAL	38.42	1.04	3.93	1.20	20.17	6.45	16.65
(Kg)	Se	Mo	Cd	Sb	Tl	Pb	Li
NFOL	0.04	0.30	0.18	0.14	0.06	0.02	0.37
RT1	0.22	0.05	2.53	0.00	1.13	0.97	0.12
D1	0.00	0.00	0.03	0.00	0.02	0.00	0.28
RT2	0.01	0.00	0.09	0.00	0.01	0.00	0.01
D2	0.00	0.00	0.00	0.00	0.00	0.00	0.12
TOTAL	0.27	0.35	2.83	0.14	1.22	0.99	0.90

Table 4

Modeled costs for a variety of passive and active technologies using AMD-Treat, and real costs for Esperanza DAS.

	Passive				Active				Esperanza DAS
	ALD	AnW	AW	BioR	Caustic Soda	Hydrated Lime	Lime	Soda Ash	
Total Capital Cost (facility construction)	115,796 €	269,822 €	151,946 €	346,165 €	12,197 €	40,587 €	36,390 €	8,897 €	196,100 €
Annual Cost (maintenance and operation)	10,936 €	16,327 €	12,203 €	9,350 €	98,273 €	77,587 €	71,551 €	94,709 €	8,428 €
Annual Treatment Cost (€/m³ of AMD treated)	0.35	0.52	0.39	0.3	3.13	2.46	2.27	3.01	0.27

ALD (Anoxic Limestone Drain), AnW (Anaerobic Wetland), AW (Aerobic Wetland), BioR (Sulphate-reducing bioreactor).

well as its cost effectiveness, the DAS technology represents the most economic and environmentally friendly treatment to date for this type of waters.

The DAS technology is eco-friendly since it neither requires energy nor maintenance, uses recycled or low-cost materials, and has a long-lasting efficiency. In addition, the impact of construction is negligible compared to those associated with the operation phase. The global warming potential (GWP) of the DAS plant was estimated to be around 1.86 kg CO₂ eq/m³ of treated AMD, primarily associated with limestone dissolution (94% of the total value). However, this value is lower than other AMD treatments (Martinez et al., 2019).

3.4. Potential metal ores and economic implications

In recent years, the growing technological advances have led to an overall increase in demand for raw materials known as “technological metals”, being scandium, lanthanides and yttrium (here considered as REE) the most valued. Most REE deposits are carbonatites or intrusive igneous rocks, which are commonly concentrated in specific areas of the world. Currently, China remains the most influential country in terms of global supply, with the large deposit of Bayan Obo, the main deposit of REE in the world (Fan et al., 2016). Only the last year, the mine and separation production quotas were 132000 tons. China’s monopoly and the growing demand for these metals due to technological development in recent years have led to the worldwide deficit of these critical raw materials.

An alternative solution to this problem is the extraction from secondary sources. In this sense, it has been previously reported the high concentrations of critical raw materials in AMD due to strong interactions between AMD and rocks (e.g. Cánovas et al., 2020). Extrapolating 21 representative samples of AMD within the IPB, a total of 70–100 tons of REY₂O₃ were estimated to be released annually in the IPB, equivalent to 0.05% of annual world production (Ayora et al., 2016).

A potential way for REE accumulation and recovery can be the neutralization of acid leachates. Laboratory column experiments using DAS technology showed that Fe(III)-precipitates do not scavenge REE in AMD passive treatment, being conservative at pH values below 4 (Verplanck et al., 2004). The same behaviour has been observed during the AMD transit in main streams of the IPB (commonly at pH < 4) (Lozano et al., 2020b), which implies that all REE would remain dissolved before the remediation system. Therefore, REE content from AMD can be entirely recovered with the DAS technology (Ayora et al., 2016). The waste material obtained in the laboratory confirms that REE is selectively retained in the basaluminite precipitated in the limestone-DAS passive remediation systems. Indeed, the basaluminite waste from the previous DAS treatment in Mina Esperanza contained 0.17% REY₂O₃, being this AMD in the lowest range of REE concentrations in the IPB (Ayora et al., 2016).

The REE recovery from residues generated in active treatment plants of AMD is also highly promising from a technical point of view (Macías et al., 2017b; Zhang and Honacker, 2018). For example, Macías et al. (2017b) reported that, adding dilute acids of common industrial usage

(e.g. 1 M HCl), approximately 90% of REE and Yttrium can be extracted from these residues. On the other hand, Zhang and Honacker (2018) reported a recovery of up to 80% of REE contained originally in solution by the step-wise addition of NaOH and subsequent concentration with oxalic acid. As a result, a final product containing 94% of REE was obtained. Taking into account the growing generation of this type of sludge worldwide, these wastes can be considered as promising secondary metal resources. This finding is especially encouraging for mining and mineral processing industries, since recovering critical raw materials from these wastes would convert a commodity what previously had to be managed as a waste.

Although the technical feasibility to recover metals of economic interest such as REE from these wastes has been previously reported, it is also necessary to assess the economic suitability. For this purpose, prices of metals have been consulted in the London Metal Exchange (LME) and in Argus Rare Earths. These values refer to high purity products, a grade which is far from reality in the case of the metal concentrates obtained in the treatment plant. Thus, these values were corrected by a factor of 30% due to economic and technologic limitations described by Smith et al. (2013), based on a real case of metal recovery from AMD treatment plant sludge in the Berkeley Pit and Wellington-Oro mine (USA). Considering these estimations, around 32 tons of Fe, 6 tons of Al, and approximately 1 ton of Cu and Zn (Table 3) could be extracted from these wastes. In the waste, approximately 64 kg are critical raw materials, 39 of which are REE (Table 3). This amount of REE can be easily extracted using commercial dilute acid (Macías et al., 2017b; Zhang and Honacker, 2018). Thus, the potential value of commodities contained in these wastes would be 8243.5 USD (Table SM1), which could help to offset the cost associated with the AMD treatment. Considering the longevity of AMD processes and the “renewable” source of valuable elements in AMD, the recovery of these commodities during passive treatment of AMD turns to be a promising sustainable upcycling solution for metal pollution in AMD orphan sites worldwide.

4. Conclusions

A full-scale DAS passive treatment plant for highly polluted AMD (average flow of 0.8 L/s) was running in Mina Esperanza (SW Spain) during an uninterrupted period of 28 months. This is the first reported case of successful long-term operation of DAS technology worldwide. The NFOL pre-treatment removed 17% of total Fe by Fe(II) oxidation and precipitation of Fe(III) as schwertmannite, as well as 100% of Sb, 83% of Mo, 60% of As, and 53% of V by sorption processes. In the first DAS-limestone tank, removal values close to 100% of Al, Cu, REE, As, Cr, Mo, V and Pb, and more than 70% of Zn, Cd, Co and Ni were achieved. Schwertmannite and basaluminite precipitation, as well as sorption and/or co-precipitation processes, were the main removal mechanisms for these metal(loid)s. The settlement of decantation ponds contributed to eliminate both dissolved and particulate Fe (around 12%) by Fe oxidation and precipitation processes. The second reactive tank mainly promotes divalent metals removal; around 12% of Fe(II) and Zn, 23% of Co and 13% of Ni were retained. Throughout the entire system, around 30% of initial sulphate is removed mainly by schwertmannite,

basaluminite and gypsum precipitation.

The high efficiency attained by the treatment plant is evidenced by the alkaline nature of the final water and the fulfilment of water quality standard limits for most contaminants (except for Fe, Mn and sulphate). It is estimated that around 100 tonnes of metal(loid)s were accumulated in the treatment wastes, some of them considered as critical raw materials (e.g. REE). The potential valorisation of these metals could offset the construction and maintenance costs of this treatment plant, representing in turn a promising sustainable upcycling solution for AMD pollution. The better cost effectiveness of DAS technology (0.27 €/m³ of treated water) compared to other passive (0.30–0.52 €/m³) or active (2.27–3.13 €/m³) technologies, coupled with the long-term performance, confirm the DAS-technology as the best eco-friendly system to treat highly acid and metal-rich AMD at orphan sites worldwide. Despite the good performance exhibited by the plant, additional efforts need to be undertaken to increase the removal of Fe(II), sulphate and Mn.

Credit author statement

Salud Orden: Writing – original draft, Formal analysis. Francisco Macías: Funding acquisition, Conceptualization, Investigation, Writing – review & editing. Carlos R. Cánovas: Investigation, Writing – review & editing. José Miguel Nieto: Funding acquisition, Writing – review & editing. Rafael Pérez-López: Writing – review & editing. Carlos Ayora: Funding acquisition, 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.

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Appendix A. Supplementary data

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