First time full-scale use of $BaCO_3$-DAS to remove sulphate from acid mine drainage

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INTRODUCTION

Along the Iberian Pyrite Belt (IPB), southwest of the Iberian Peninsula, a hundred of old, abandoned mining districts act as continuous sources of acid mine drainage (AMD), for which suitable remediation measures seems to be unaffordable. One of these mining districts is Mina Concepción which produces AMD whose composition could be considered as representative (in terms of acidity and metal concentration) of the mine waters of the IPB. In this sense, an AMD passive treatment plant was constructed at Mina Concepción with a surface around 20000 m^2. This plant comprises a multi-step system for treating AMD based on Dispersed Alkaline Substrate (DAS) technology, which is one of the few passive treatments that have been successfully applied to treat high acidity and metal-rich AMD (Macías et al., 2012a, 2012b). The performance of this plant was previously evaluated by using a MgO-DAS reactive tank (Martínez et al., 2019). The main aim of this work was to evaluate the removal of sulphate and metals from mine water by using barium carbonate ($BaCO_3$) for the first time at full-scale.

MATERIALS AND METHODS

Treatment plant description

The full-scale treatment plant (Fig. 1) of Mina Concepción is fed by two different AMD inputs: a pit lake overflow (S1) and a partially restored waste dump (S2). The treatment plant, in order of steps, is composed of a natural Fe-oxidizing lagoon (NFOL; Macías et al., 2012b) of around 100 m^2, which enhances iron oxidation and the removal of Fe and As by co-precipitation/or adsorption processes. After this pretreatment, the water runs into the first two alkaline reactive tanks (which are divided into two vessels, RT1 and RT2, of 960 m^3 and 720 m^3, respectively) filled with limestone-DAS, which causes the removal of trivalent metals from the AMD. These tanks are serially connected with two settling ponds (D1 and D2, of 100 m^2 each) that enhance the sedimentation of precipitates.

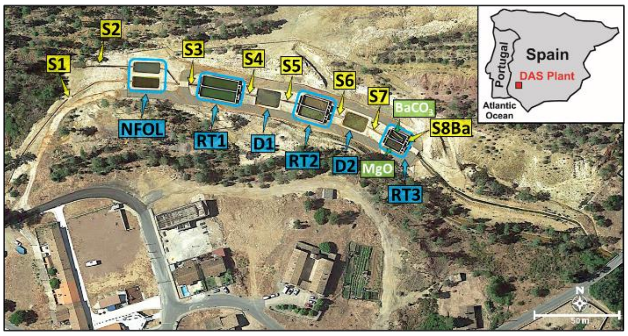

Fig 1. *Aerial view of Mina Concepción DAS passive treatment plant showing the different parts (blue) and the sampling points (yellow). NFOL (Natural Fe-oxidizing lagoon), RTx (reactive tanks), and Dx (decantation ponds).*

The outflows then reach the third DAS reactive tank (RT3, 400 m^3), which is also divided into two vessels: one filled with MgO and the other one filled with whiterite ($BaCO_3$). At these tanks the pH increases above 7 and the concentration of divalent metals is reduced. Finally, the treated water is released into the fluvial system.

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Water sampling and analyses

Water samples in the different components of the plant were collected during 12 sampling campaigns from the end of December 2019 to the end of May 2020 (see Fig. 1). Physico-chemical parameters (pH, temperature, electrical conductivity (EC) and oxidation reduction potential (ORP), were measured *in situ* using a Crison® MM40^{+} multiparameter previously calibrated. Water samples were filtered through 0.1 µm Millipore filters, acidified in the field to pH < 2 with suprapure HNO_3 and stored at 4 ◦C in 60 mL sterile polypropylene containers to prevent metal precipitates until analysis. Major, minor and trace elements were analysed by ICP-OES and ICP-MS.

RESULTS AND DISCUSSION

The S1 discharge is characterized by a low pH (mean pH = 3.1), SO_4 (mean = 2300 mg/L) and metal concentration (mean concentration of Fe = 1000 mg/L, Al = 130 mg/L or Co = 1370 µg/L) while S2 AMD shows a slightly higher pH (mean pH = 4.2) and content of SO_4 (mean = 590 mg/L) and metals (mean concentration of Fe = 70 mg/L and Co = 350 µg/L) except for Al (mean = 100 mg/L). The average flow for S1 and S2 during the samplings was 1.6 and 2.6 L/s, respectively, although these points dried out during the dry season.

The pH values and the concentration of some elements at different parts of the treatment are displayed as box plots in the Fig. 2. As can be observe the pH increases (Fig. 2A) from around 3 up to alkaline values (pH > 7). The concentration of metals such as Fe, Al and Co decreased drastically to values below the detection limit in most cases. In addition, the SO_4 concentration also decreased significantly to a mean value below 500 mg/L. Throughout the entire system, close to 100% removal for metals such as Al, Cu, Fe, Zn, Cd, Co, Ni, V and As, 85% for Pb, 79% for Mn and up to 76% for SO_4 were obtained.

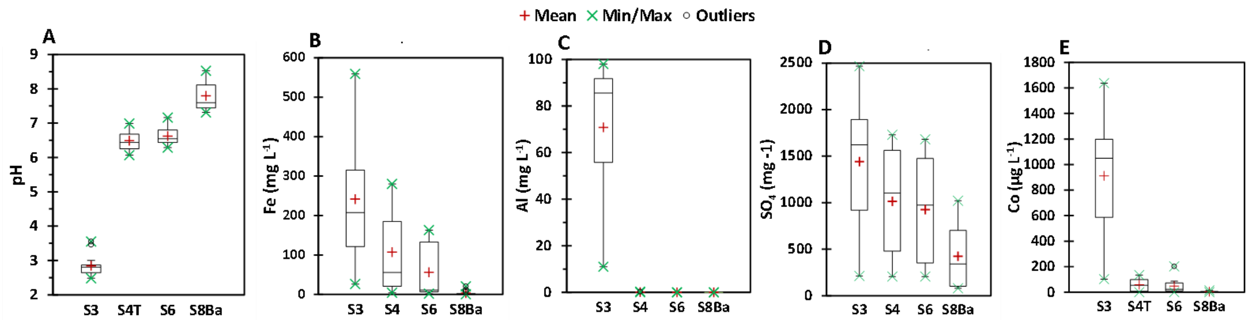

***Fig 2**. Box plots of the pH and some elements in the samples collected after the NFOL (S3), after the limestone-DAS tanks (S4 and S6) and after the $BaCO_3$-DAS tank (S8Ba). Central line: median; box limits: first and third quartiles; whiskers: minimum and maximum non-outliers.*

CONCLUSIONS

A full-scale $BaCO_3$-DAS passive treatment plant for highly polluted AMD was running for the first time in Mina Concepción (SW Spain). As a result, an alkaline effluent is obtained with a low metal content. An almost total removal of most metals and a very high removal for Pb (≈ 85%) and Mn (≈ 80%) was observed. It also highlights the significant removal (≈ 75%) obtained for SO_4, decreasing the concentration from values above 2000 mg/L in the acidic inflow to values below 500 in the alkaline outflow.

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