First Results of a Full Scaled Passive Treatment System for High Metal Concentration AMD at the Iberian Pyrite Belt, SW Spain

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Abstract

Acidity load and clogging are two of the most important design factors that affect the effectiveness of a passive treatment system. These two parameters sometimes limit traditional passive treatment systems to low metal concentration AMD or to a short period of working. To overcome these and other problems, we have developed the Dispersed Alkaline Substrate (DAS), implementing it at a full-scale passive treatment system at Mina Esperanza in SW Spain.

Key words: Acid mine drainage, high metal concentration, passive system treatment, Iberian Pyrite Belt.

Introduction

In many places around the world, acid mine drainage (AMD) is an ancient legacy that impacts not only the environment but also the economy and health of people living in these polluted areas. The progressive change in society's mind concerning nature conservation has encouraged the appearance of many passive treatment systems developed to remediate waters affected by AMD. Many of these systems are focused on treating AMD with low to very low metal concentration as those existing, for instance, at coal mining districts (Barrie Johnson et al. 2005; Gagliano et al 2004; Sapsford et al. 2007; Whitehead et al. 2005).

However, these passive treatment systems (anaerobic wetlands, sulphate reducing bioreactors, anoxic limestone drains, etc.) show severe problems of clogging or reactivity loss when exposed to AMD with high metal concentrations (Rötting et al. 2005). To overcome these problems, we have developed a novel Dispersed Alkaline Substrate (DAS) consisting of a mixture of wood chips (a coarse inert matrix increasing hydraulic conductivity) and an alkaline reactive substrate (fine-grained limestone to raise pH and generate alkalinity). This novel substrate has been successfully tested in laboratory experiments (Rötting et al. 2007) and in a pilot-scale field experiment (Caraballo et al. 2007) at the Monte Romero field site, Iberian Pyrite Belt (IPB), SW Spain. The next step of our investigation has been the development of a full-scale AMD passive treatment system at the Mina Esperanza field site (IPB, SW Spain). This paper provides an overview of the hydrochemistry and metal removal efficiency of the "DAS" passive treatment system constructed at Mina Esperanza.

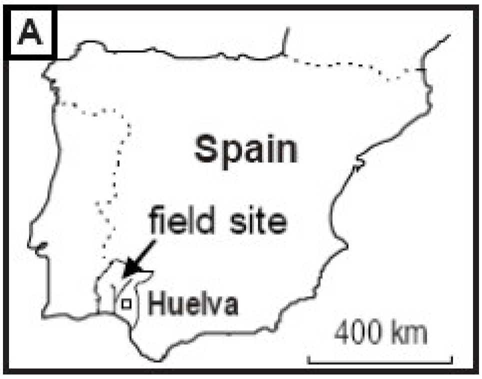
Materials and Methods

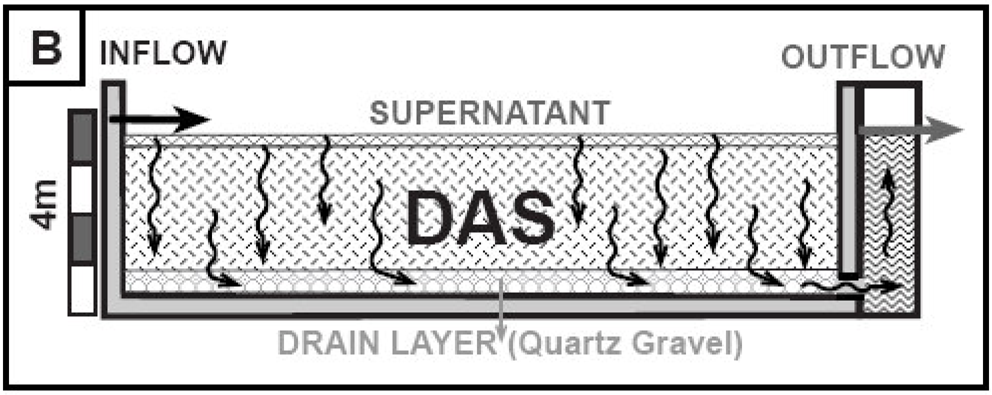
Field Site and Treatment Description

Mina Esperanza is located in the northern part of the IPB (Figure 1A), in southwestern Spain (37º45´34´´N-6º41´00´´O). The Mina Esperanza mineralization is a massive pyrite deposit with minor amounts of chalcopyrite. The enclosing rocks are mainly slates and schist. This underground sulphide mine was operated during the first half of the last century. After closure, the mine was flooded; a polluted creek emerges from the main adit and seriously impacts the water quality of the Odiel River. AMD at the exit of the adit has a pH of 2.66-2.95, net acidity of 2200-2800 mg/L (as $CaCO_3$), 750-950 mg/L Fe (95% Fe^{2+}), 3500-4200 mg/L SO_4^{2-} , 125-160 mg/L Al, 15-20 mg/L Zn, Cu, 0.1-1 mg/L As, Pb, Co, Cd, and V.

The passive system treatment developed at Mina Esperanza comprises a stepped open channel connecting the adit to the DAS reactive pool (15 m in length, 8 m in width, and 4 m deep) followed by aeration cascades and a sedimentation pond (10 m by 3 m and 2 m deep).

Figure 1A and 1B. *Respectively, localization of Mina Esperanza passive treatment system and schematic cross section of the Mina Esperanza "DAS" reactive pool.*





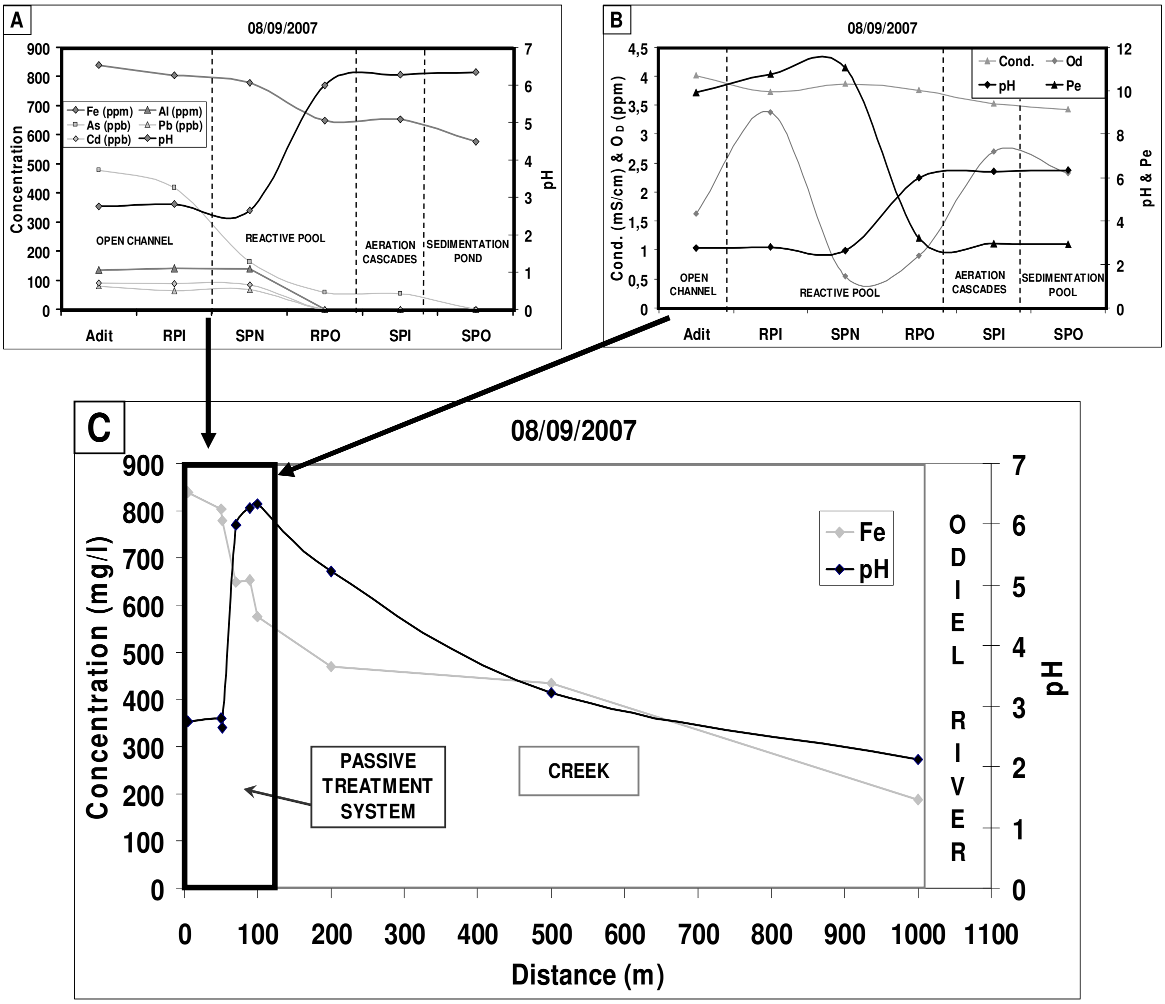
The reactive pool comprises (bottom to top): a 40 cm drainage layer of quartz coarse gravel (10-20 cm) and a second 10 cm drainage layer of quartz fine gravel (1-2cm), overlain by a 2.5 m layer of calcite-DAS reactive material (20% (v/v) of fine-grained calcite and 80% (v/v) of pine wood chips). Due to the system configuration, there is a 25 cm supernatant and 1 m of free wall (Figure 1B). As can be observed in Figure 1B, inflow water comes directly from the adit by an open channel, and feeds the tank by gravity flow.
With porosity around 50% and a mean inflow of 0.5L/s, the AMD residence time at the reactive pool can be estimated as 5 days.

Sampling and Water Analyses
The main physico-chemical parameters were measured in the field. All the portable meters were properly calibrated on site against supplied calibration standards. Temperature and electrical conductivity were measured using a portable CM35 meter (Crison®) with 3 point calibration (147, 1413, and 12.88 mS/cm). The pH and redox potential were measured using a PH25 meter (Crison®) with Crison Pt and Ag/AgCl electrodes (one different and specific for each parameter). Redox potential and pH were respectively calibrated using 2 points (240-470 mV) and 3 points (pH 4.01-7.00-9.21) Crison standard solutions. The redox potential was corrected in order to obtain the potential referred to the hydrogen electrode. Dissolved oxygen was measured with an auto-calibrating Hanna® portable meter and alkalinity was determined using CHEMetrics® Total Titrets® (range 10-100 or 100-1000 $mg.L^{-1}$ as CaCO3, accuracy approximately 5%).
Water samples were filtered immediately after collection through 0.1 µm Millipore filters on Millipore syringe filter holders and were acidified in the field to pH <1 with HNO_3 suprapur and stored at 4°C in 60 ml sterile polypropylene containers until analysis. Analyses were carried out in the Central Research Services of the University of Huelva. Dissolved concentrations of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Li, Pb, S, Si, Sr, and Zn were determined by Inductively Coupled

Plasma Atomic Emission Spectrometry (ICP-AES Yobin-Ybon Ultima2) using a protocol especially designed for AMD samples (Tyler et al. 2004).

Once a week, six different points were sampled during the year of working. As shown in Figure 2A, the six sampling points were: adit outflow, reactive pool inflow (RPI), supernatant (SPN), reactive pool outflow (RPO), sedimentation pond inflow (SPI), and sedimentation pond outflow (SPO).

***Figure 2A**, **2B and 2C.**Respectively, selected metal and pH distribution, physico-chemical parameters and induced Fe and pH decrease by the system on Esperanza creek.*



Results and Discussion

Figure 2 synthesizes the general hydrochemical behaviour of the Mina Esperanza passive treatment system, including the pH- and Fe-induced attenuation in Esperanza Creek before its confluence with the Odiel River. As can be observed in Figure 2C, most of the Fe removal was achieved at the passive treatment system (250-300 ppm) but important induced attenuation was produced in the creek (100-150 ppm). The detailed removal of some selected metals by the passive treatment system is shown in Figure 2A, where one can see, for instance, 100% Al, As, Pb, and Cd removal by the reactive material. The pH and Pe show (Figure 2B) the typical antisymmetric paths of AMD systems control by the Fe^{2+}/Fe^{3+} redox pair. Electrical conductivity (Cond.) was slightly lowered across the system and dissolved oxygen (O_D) increased quickly at the opened channel, decreased nearly to 0 ppm inside the reactive pool, and finally increased at the end of the system.

Compared to the adit AMD, the system decreased net acidity by 1500 mg/L (as $CaCO_3$) and acidity load by 900 g/m^2•day (as $CaCO_3$). This loading rate is much higher than that recommended for conventional passive treatment systems such as Reducing and Alkalinity Producing Systems (RAPS).

Conclusions

After one year of operation, the Mina Esperanza passive treatment system has demonstrated that calcite DAS-reactive material is an efficient option to treat high metal and high acidity AMD in a relatively small area. The behaviour of the system points gives hope that high metal concentration AMD can be treated in this manner. This would make it feasible to remediate some sub-basins of the Odiel basin by the implementation of passive treatment systems (with one or two DAS-steps) at some strategic points.

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