Long term remediation of highly polluted acid mine drainage: A sustainable approach to restore the environmental quality of the Odiel river basin

Manuel A. Caraballo [a],[*], Francisco Macías [a], Tobias S. Rötting [b], José Miguel Nieto [a], Carlos Ayora [c]

[a] Geology Department, University of Huelva, Avenida 3 de Marzo s/n, Campus "El Carmen", E-21071 Huelva, Spain
[b] Technical University of Catalonia (UPC), Hydrogeology Group, E-08034 Barcelona, Spain
[c] Institute of Environmental Assessment and Water Research, IDÆA − CSIC, Jordi Girona 18, 08034 Barcelona, Spain

ABSTRACT

During 20 months of proper operation the full scale passive treatment in Mina Esperanza (SW Spain) produced around 100 mg/L of ferric iron in the aeration cascades, removing an average net acidity up to 1500 mg/L as $CaCO_3$ and not having any significant clogging problem. Complete Al, As, Cd, Cr, Cu, Ti and V removal from the water was accomplished through almost the entire operation time while Fe removal ranged between 170 and 620 mg/L. The system operated at a mean inflow rate of 43 m^3/day achieving an acid load reduction of 597 $g \cdot (m^2 \ day)^{-1}$, more than 10 times higher than the generally accepted 40 $g \cdot (m^2 \ day)^{-1}$ value commonly used as a passive treatment system designing criteria. The high performance achieved by the passive treatment system at Mina Esperanza demonstrates that this innovative treatment design is a simple, efficient and long lasting remediation option to treat highly polluted acid mine drainage.

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1. Introduction

Acid mine drainage (AMD) generation has been thoroughly described in many previous studies related with inorganic water pollution (Bigham and Nordstrom, 2000; Younger et al., 2002). It is sufficient here to state that it arises from the oxidative dissolution of sulfide minerals, mainly pyrite, ordinarily present as main ore-forming minerals in sulfide mining districts (Akcil and Koldas, 2006) or as minor constituents in coal deposits (Younger et al., 2002).

About 19,300 km of rivers and streams and more than 72,000 ha of lakes and reservoirs in the continental USA have been damaged by AMD (Kleinmann, 1989). In England and Wales, it is estimated that some 1800 km of surface streams and rivers are currently impacted by AMD (Jarvis et al., 2006), whereas in SW Spain, from a total of 1149 km of the river network examined at the Odiel basin, 427 km were affected by AMD (Sarmiento et al., 2009b). These studies clearly present AMD water pollution as a widespread and intense environmental problem that, taking into account only three countries in the world, implies more than 21,500 km of rivers and streams affected.

The Iberian Pyrite Belt (IPB), located in the south-west of the Iberian Peninsula, can be considered one of the biggest massive sulfide deposits in the world with a length of over 200 km, a width of about 40 km and original estimated reserves in the order of 1700 Mt of sulfide ore (Sáez et al., 1999). The result of the intense mining during almost 5000 years (Leblanc et al., 2000) is a region where abandoned sulfide-rich wastes in spoil heaps and tailings and flooded underground mines and opened pits generate an ubiquitous problem of AMD pollution (Achterberg et al., 2003; Sarmiento et al., 2009a).

As the main economic activity in the Huelva province (IPB) has changed from mining to agriculture, the current pollution and possible remediation of inland water resources in the Odiel river basin has become an issue of great concern.

AMD can be remediated by two generic approaches: active or passive treatment. While the former is more appropriate to be used in mines under operation where fast remediation of enormous amounts of water is needed, the latter is a more realistic solution when AMD remediation has to be achieved in abandoned mine sites (like the ones at the IPB) where the absence of any accountable entity and the remote location require the use of a long lasting, low cost and environmentally sustainable treatment option with no artificial energy requirements (PIRAMID-Consortium, 2003).

Traditional sulfate reducing bacteria (SRB) based treatments, like anaerobic wetlands (Kröpfelová et al., 2009; Marchand et al., 2010) or reactive permeable barriers (Jarvis et al., 2006; Caraballo et al., 2010), have shown encouraging results treating AMD at coal mining districts, however they are not very useful to treat

highly polluted AMD in areas with limited available space because SRB have maximum tolerance levels for certain metals and need a high residence time, up to six days (Neculita et al., 2008), to achieve an optimal bacterial growth. Limestone based treatments like anoxic limestone drainages (Santomartino and Webb, 2007) or limestone sand reactors (Watten et al., 2005) although efficient at treating AMD with low to moderate metal concentrations, commonly exhibit serious problems of clogging and passivation when exposed to AMD with high metal concentrations.

To overcome all the problems shown by the typical passive treatment systems treating highly polluted AMD and design a treatment to be implemented in the IPB, Rötting et al. (2008b) developed the dispersed alkaline substrate (DAS), consisting of a reactive mixture of pine wood shavings and limestone sand. The high metal removal performance of this reactive mixture has been broadly tested both in laboratory columns (Rötting et al., 2008b) and field-scale experiments (Rötting et al., 2008a; Caraballo et al., 2009a) for the highly polluted AMD at the IPB.

The main scope of the present study is to show the encouraging results obtained after 20 months of continuous operation of the full scale DAS passive treatment system implemented at Mina Esperanza and offer this technology as a environmentally and economically sustainable treatment option for a future complete remediation of river basins affected by highly polluted AMD. Water chemistry, precipitate mineralogy and metal removal efficiency of the different sections comprising the treatment will be presented to gain a better understanding of the different hydrochemical, mineralogical and operational processes involved in AMD remediation.

2. Methods and sampling procedure

2.1. Site location

Mina Esperanza is located in the northern part of the IPB (Fig. 1A), in Southwestern Spain (37°45′34″N–6°41′00″O). The mineralization at Mina Esperanza consists of a massive pyrite deposit with minor amounts of chalcopyrite (Pinedo-Vara, 1963). The country rocks are slates and low grade metamorphic phyllites. The AMD emerging from the adit is channeled by a creek, known as Esperanza creek, for 1 km to the Odiel River and can be considered one of the first important pollution sources to this river in the upper section of its basin (Sarmiento et al., 2009b).

AMD composition at the exit of the adit and the main hydrochemical parameters are shown in Table 1.

2.2. Water sampling

Water samples were taken at least twice a month from March 2007 to October 2008, a total of 42 sampling campaigns along the 20 months of the system operation time. Six sampling points were selected as representative of the different sections of the treatment system (Fig. 1A) and called: Adit, T-in (reactive tank input), T-sup (reactive tank supernatant), T-out (reactive tank output), D-in (decantation pond input) and D-out (decantation pond output). Water samples were filtered immediately after collection through 0.1 μm Millipore filters on Millipore syringe filter holders, acidified in the field to pH < 1 with suprapur HNO₃ and stored at 4 °C in 60 mL sterile polypropylene containers until analyzed.

2.3. Field in-situ measurements

Temperature and electrical conductivity were measured using a portable CM35 meter (Crison®) with 3 point calibration (147 and 1413 μS/cm and 12.88 mS/cm). The pH and redox potential were measured using a PH25 meter (Crison®) with Crison electrodes. Redox potential and pH were controlled and calibrated using 2 points (240–470 mV) and 3 points (pH 4.01–7.00–9.21), respectively, with Crison standard solutions. Redox potential measurements were corrected to the Standard Hydrogen Electrode to calculate pe. Dissolved O₂ was measured with an auto-calibrating Hanna® portable meter and gross alkalinity was determined using CHEMetrics® Total Titrets® (range 10–100 or 100–1000 mg/L as CaCO₃ equivalents, accuracy approximately 5%).

2.4. Laboratory analytical techniques

Concentrations of dissolved Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, S, Si, Sr, Ti, V and Zn were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES Jobin- Ybon Ultima2) using a protocol especially designed for AMD samples (Tyler et al., 2004). Analysis was performed at the Central
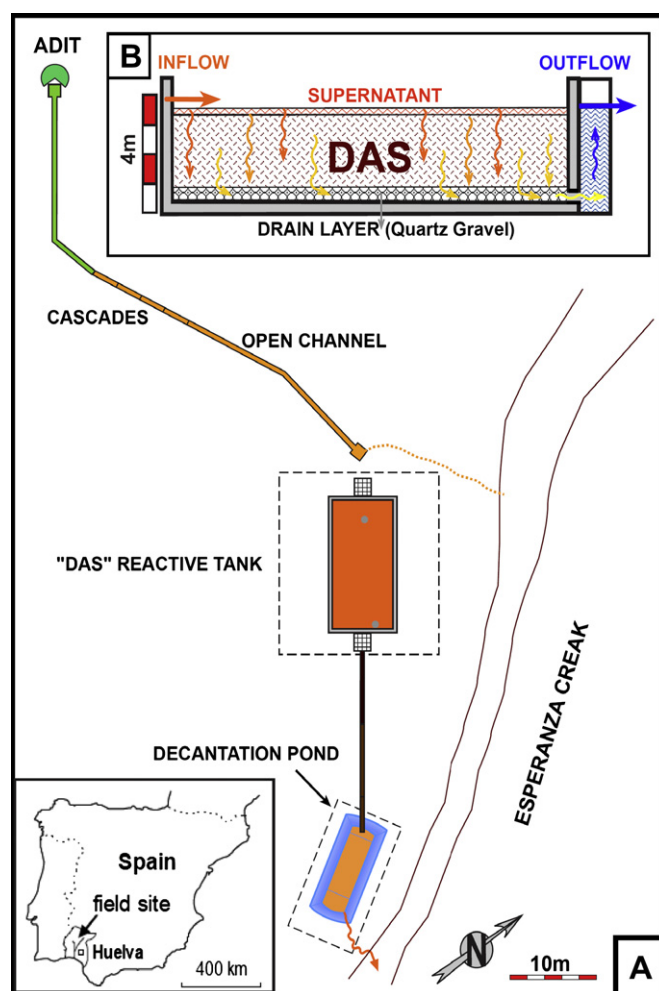

Fig. 1. A) Location and schematic plan view of the passive treatment at Mina Esperanza. 1 = Adit, 2 = reactive tank input, 3 = reactive tank supernatant, 4 = reactive tank output, 5 = decantation pond input and 6 = decantation pond output. B) Schematic cross section of the reactive tank.

Research Services of the University of Huelva. Multielement standard solutions prepared from single certified standards supplied by SCP SCIENCE were used for calibration. They were run at the beginning and at the end of each analytical series. Certified Reference Material SRM-1640 NIST fresh-water-type and inter-laboratory standard IRMM-N3 wastewater test material (European Commission Institute for Reference Materials and Measurements) were also analyzed. Detection limits were calculated by average and standard deviations from 10 blanks. Detection limits were: 200 μg/L for Al, Fe, Mn, Mg, Na, K, Si and S; 500 μg/L for Ca; 50 μg/L for Zn; 5 μg/L for Cu; 2 μg/L for As and 1 μg/L for the other trace elements.

Net acidity (Ac) (mg/L as CaCO₃ equivalents) was calculated using the following equation after Rötting et al., 2008a:

$$Ac = 50,045 \cdot \left(3 \cdot c_{Al} + 2 \cdot c_{Fe} + 2 \cdot c_{Mn} + 2 \cdot c_{Zn} + 10^{-pH}\right) - alk \tag{1}$$

where, c_x are molar concentrations of the different metals (mol/L) and alk is measured gross alkalinity (mg/L as CaCO₃ equivalents).

Relative metal removal r (%) at the output of the system was calculated as:

$$r = \frac{(c_{in} - c_{out})}{c_{in}} \cdot 100 \tag{2}$$

where, c_{in} is the adit concentration (mg/L) and c_{out} is the concentration at the output (D-out) of the system (mg/L).

Acid load reduction RA (g/(m² day)), normalized by system area was calculated as:

$$RA = Q \cdot \frac{Ac_{in} - Ac_{out}}{1,000 \cdot A} \tag{3}$$

where, Q is flow rate (m³/day), Ac_{in} and Ac_{out} are adit and system's outflow net acidity (mg/L as CaCO₃ equivalents), respectively, and A is horizontal area of the treatment system (m²).