Minerals Engineering 26 (2012) 86–98

Contents lists available at SciVerse ScienceDirect

Minerals Engineering

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

Heavy metal removal of intermittent acid mine drainage with an open limestone channel

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ARTICLE INFO

Article history:
Received 7 September 2011
Accepted 8 November 2011
Available online 3 December 2011

Keywords:
Acid rock drainage
Tailings
pH control
Environmental
Pollution

ABSTRACT

This study is focused on the influence of a particular open limestone channel (OLC) on the quality of the surface water drained from an intermittent watercourse. The OLC was constructed along a creek surrounded by upstream tailings deposits, in an extensive, abandoned sulfide-mining site, which generates acidic and heavy metals-rich drainage water during the occasional precipitation that occurs. The overall length of the OLC is 1986 m, it has an average slope of 4.6%, and consists of two main segments. The effectiveness of this channel was evaluated through different physico-chemical parameters: pH, electrical conductivity (EC), total solids (TS), and heavy metal concentrations (Al, Fe, Zn, Ni, Cu, As, Cd, and Pb), measured in surface water. A total of 47 water samples were collected in 12 rainfall events, in the period 2005–2009. Moreover, for three different precipitation events, depletion curves of these parameters were constructed. The values of pH and Ca were increased downstream of the channel, related to the alkalinity and calcium release of the OLC and carbonates present in the watershed, whereas the EC, TS, K, Mg, SO_4^{2-}, Al, Mn, Fe, Ni, Cu, Zn, As, Cd, and Sb decreased towards the mouth of the creek. The OLC reduced the input of heavy metals into the Mar Menor lagoon by one order of magnitude. According to the results, this kind of constructive solution is effective with regard to mitigating the effects of intermittent acid mine drainage in Mediterranean and semi-arid regions.

1. Introduction

Sierra de Cartagena-La Unión (Southeast Spain) contains one of the most important Pb–Zn accumulations in the Iberian Peninsula. This region has been mined from the Phoenician and Carthaginian times until 1991, using underground and open-pit mining techniques. The most frequent metallurgical process to recover valuable minerals from sulfide ores has been froth flotation, followed in importance by gravity separation. Mining activities have generated more than 200 Mm^3 of mine wastes, spread over an area of 9 km^2. According to the type of mining activity, mineral processing and disposal methods, nine types of mining and metallurgical wastes can be distinguished: open-pit spoils, post-flotation wastes, gravity concentration spoils, “false” gossan dumps, molten slag, pre-concentration wastes, mine spoils, well borings, and post-flotation sludge (Robles-Arenas et al., 2006). Oxidation and hydrolysis of metal sulfides generate an intermittent acid mine drainage every rainfall event. In order to neutralize surface water acidity, reducing its pollution charge, a passive treatment system of almost 2 km has been implemented over certain watercourse. This paper reports the effectiveness of this system from the point of view of the pollution reduction that enters the Mar Menor lagoon, a wetland included on the list of the Ramsar Convention (Duran et al., 2003) and in the Coastal Area Management Programme by the UN Environment Programme (Da Cruz and Murcia regional working group, 2003) for its ecological importance.

Acid mine drainage (AMD) water originates from the oxidation and weathering of sulfide deposits. These geological materials are, in most cases, multi-mineral aggregates, because they include a variety of minerals, such as aluminosilicates, oxides, hydroxides, phosphates, halides, and carbonates, apart from sulfides.

As far as generation of H^+ is concerned, the weathering process of each single mineral can be classified as acid-producing (sulfide minerals, iron and aluminum hydroxides, and secondary sulfate minerals), acid-buffering (carbonates and certain aluminosilicates), or neutral (oxides, such as quartz, rutile, and zircon). The balance of all the chemical reactions occurring in a particular waste at a certain time will determine the final pH of the acidic, metal-rich pore water solution that drains into the watercourse (Lottermoser, 2007).

Rate of acid generation is determined by pH, temperature, oxygen concentration in gas and water phases, chemical activity

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doi:10.1016/j.mineng.2011.11.006

of Fe^{3+}, surface area of exposed metal sulfide, chemical activation energy, and bacterial activity (Akcil and Koldas, 2006). It is known that, above pH 3.5, oxidation of iron in mine drainage is not due to microbial activity (Hallberg, 2010). Therefore, a slight increasing of pH directly restricts one of the primary factors of acid generation.

Mining activities usually have a strong influence on natural waters. In particular, pollution of surface water due to leaching from tailings deposits demands close attention, due to the fact that some of its consequences can endure for many years after the abandonment of mining. Different types of mining impact on the water environment can be distinguished: mining *per se*, mineral processing and disposal of mine wastes, and post-mining flooding and uncontrolled discharge of polluted waters (Younger and Wolkersdorfer, 2004). In the particular creek and landscape that are the object of this study, the impact related to the disposal of mine wastes is the most significant. These products, with different particle sizes, ranging from coarse to fine-grained mineral processing wastes, are usually combined in extensive areas. The precipitation pattern – with occasional, heavy rainfall typical of a Mediterranean climate – leads to the physical and chemical instability of these tailings areas, producing intermittent, acidic, and metalliferous leachates, even when these zones have been revegetated.

Open limestone channels (OLCs) are passive treatment systems that achieve remediation mostly through chemical means (Kalin et al., 2006). They consist of a limestone bed rock and optimal performance is attained on slopes exceeding 12%, where the flow speed and turbulence keep precipitates in suspension (Skousen and Ziemkiewicz, 2005). Other passive systems are anoxic limestone drains, aerobic and anaerobic wetlands, and biological and abiotic permeable, reactive barriers (Johnson and Hallberg, 2005). Very often, an OLC is preferred due to its low building and maintenance costs. Carbonates from limestones and dolostones contribute to increasing the alkalinity and pH of AMD water, causing heavy metals to precipitate on them. Regrettably, this precipitation is accompanied with the formation of an armor of iron hydroxide, aluminum hydroxide, and gypsum that may decrease the permeability and reactivity of the calcareous rock (Ziemkiewicz et al., 1997; Hammarstrom et al., 2003). Furthermore, the rate of the neutralization reaction was observed to decrease dramatically with increasing pH, so that carbonate rocks are not very useful above pH of 5. Although attractive economically, a fresh reactive surface must continually be presented to the acidic mine drainage for neutralization to occur (Egiebor and Oni, 2007). Armoring processes can be represented by the following reactions:

$$CaCO_3(s) + SO_4^{2-} + 2H^+ + H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) + CO_2 \quad (1)$$

$$3CaCO_3(s) + Fe^{3+} + 3H^+ \rightarrow 3Ca^{2+} + Fe(OH)_3(s) + 3CO_2 \quad (2)$$

$$3CaCO_3(s) + Al^{3+} + 3H^+ \rightarrow 3Ca^{2+} + Al(OH)_3(s) + 3CO_2 \quad (3)$$

Generally, OLCs are used to treat AMD under conditions of very-high flow, because continually-moving water may erode any armoring from the limestone (Pavlick et al., 2005). However, their usage with intermittent AMD water is very limited. This paper evaluates the effectiveness of this passive treatment, with regard to its use in other mining areas having semi-arid or Mediterranean climates.

2. Materials and methods

2.1. Location

The OLC that is the object of this study was built onto El Beal creek, an ephemeral watercourse located in the municipality of Cartagena (Region of Murcia, Southeast Spain), between the villages of Llano del Beal (to the east) and El Beal (to the west), and upstream of them. This creek is the main waterway that flows into the southern side of the Mar Menor lagoon, because it channels water coming from the El Llano and San Ginés mountains. These elevations belong to the Sierra de Cartagena-La Unión, a 2500-year-old mining district extended over an area of 100 km^2. The wadi drains a wide watershed, which helps to carry a high volume of fine-grained materials (sand, silt, and clay) to the hypersaline lagoon. The El Beal creek is surrounded upstream by a wide variety of sulfide mine wastes, such as open-pit spoils, gravity concentration spoils, mine spoils, and post-flotation wastes (Fig. 1).

Table 1 shows some annual meteorological variables, averaged from 2000 to 2009, at Roche, the closest station to the creek. This station belongs to the SIAM network (SIAM, 2010, agrometeorological reports). Although these values are typical for a dry-summer, sub-tropical climate, 2009 was an extraordinarily ‘rainy’ year, with an overall precipitation of 543 mm.

When this study was initiated, three sampling points were chosen to monitor the effect of the channel on the surface waters: B1–B3. In December 2009, due to the unexpectedly-fast building of the second section of the channel, three new sampling locations were added, namely A–C (CARM, 2011, cartographic visor): see Fig. 2.

2.2. Timeline

The OLC was visited in the period December 2004 to December 2009, from the initial construction of the first section to the completion of the second section. From February 2005 through December 2009, the surface water running over it was monitored in the main rainwater events. Furthermore, in the period November 2006 to October 2007, two points were sampled repeatedly in the same event, in order to plot depletion curves of certain parameters. The flow patterns were often ephemeral, such that in the space of a few hours the flow ceased, regardless of the amount of precipitation that day. This explains why sometimes there was no surface water flowing at the time of sampling, even after a heavy rainfall. See the timeline of events below:

December 9, 2004: Building labors of the first section. It will measure 1184 m long.
February 9, 2005: Mouth of El Beal creek (B3). With 24 mm of rainfall that day there was surface water running.
February 10, 2005: In B3, after 2 days of rainfall (25 mm altogether), there was no surface water running.
November 15, 2005: After 6 days of rainfall (56 mm altogether), there was surface water running in B2, but not in B1 or B3.
January 7, 2006: After 2 days of rainfall (7 mm altogether), there was no surface water running in B1, B2, or B3.
January 28, 2006: After 2 days of rainfall (32 mm altogether), there was surface water running in B2 and B3, not in B1.
April 17, 2006: After 2 days of rainfall (23 mm altogether), there was surface water running in B1and B2, not in B3.
May 4, 2006: After 3 days of rainfall (20 mm altogether), there was surface water running in B2, but not in B1 or B3.
September 14, 2006: After 3 days of intermittent precipitation (25 mm altogether), there was no surface water running in B1, B2, or B3.
November 3, 2006: Depletion study in El Beal creek. B1 was sampled four times and B2 five times. A total precipitation of 61 mm was recorded in 2 days. In B3, there was no surface water running.
March 27, 2007: Depletion study in El Beal creek. B1 and B2 were sampled five times. In B3, there was no surface water running. A total precipitation of 18 mm was recorded in 2 days of constant, weak rain.
October 18, 2007: Depletion study in El Beal creek. B1 and B2 were sampled five times, and B3 was sampled once. A total precipitation of 63 mm was recorded in 3 days of constant and weak rain.