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Metal and acidity fluxes controlled by precipitation/dissolution cycles of sulfate salts in an anthropogenic mine aquifer

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Underground mine drainages are extremely difficult to study due to the lack of information about the flow path and source proximity in relation to the outflow adit. Geochemical processes controlling metals and acidity fluxes in a complex anthropogenic mine aquifer in SW Spain during the dry and rainy season were investigated by geochemical and statistical tools. High concentrations of acidity, sulfate, metals and metalloids (e.g. Fe, Cu, Zn, As, Cd, Ni, Co) were observed due to intense sulfide oxidation processes. The high residence time inside the anthropogenic aquifer, around 40 days, caused the release of significant quantities of metals linked to host rocks (e.g. Al, Ca, Ge, Li, Mg, REE). The most outstanding characteristic of the acid mine drainage (AMD) outflows is the existence of higher Fe/SO_4 molar ratios than those theoretical of pyrite (0.50) during most of the monitored period, due to a fire which occurred in 1949 and remained active for decades. Permanent and temporal retention mechanisms of acidity and metals were observed in the galleries. Once released from sulfide oxidation, Pb and As are sorbed on Fe oxyhydroxysulfate or precipitated as low solubility minerals (i.e. anglesite) inside the galleries. The precipitation of evaporitic sulfate salts during the dry season and the subsequent re-dissolution after rainfall control the fluxes of acidity and main metals (i.e. Fe, Mg, Al) from this anthropogenic aquifer. Some elements, such as Cd, Cu, Ni, REE and Zn, are retained in highly soluble sulfate salts while other elements, such as Ge, Pb and Sc, have a lower response to washout processes due to its incorporation in less soluble sulfate salts. In this way, metal concentration during the washout processes would be controlled by the proportion and solubility of each type of evaporitic sulfate salt stored during the dry season. The recovery of metals of economic interest contained in the AMD could help to self-finance the remediation of these waters in derelict mines worldwide.

1. Introduction

The Water Framework Directive (WFD) establishes a community framework of action in the scope of water policy. Its main objectives are to achieve a good ecological and chemical quality of all European waters by 2015 and to demand that EU members adopt the necessary measures to reach this goal. Nevertheless, the WFD allows the extension of the deadline for reasons of technical feasibility, when improvements within the timescale would be disproportionately expensive and if natural conditions do not allow timely improvement. These conditions are met in the Iberian Pyrite Belt (IPB) in SW of the Iberian Peninsula, which hosts one of the largest concentrations of massive sulfide deposits in the world (Tornos, 2006). This mineral richness has caused intense mining activities in the region dating back since prehistoric times (Nocete et al., 2005). The IPB is drained by the Tinto and Odiel river basins and is famous worldwide for its Acid Mine Drainage (AMD) pollution (e.g. Sánchez-España et al., 2005; Olías et al., 2006; Cánovas et al., 2007; Sarmiento et al., 2009; Nieto et al., 2013). The natural geologic conditions of these basins, with an absence of

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carbonate rocks, do not promote acidity neutralization. These acidic waters are characterized by high to extreme metal and metalloid loads, which inevitably damage the chemical and ecological quality of the surrounding fluvial systems.

Most of the AMD pollution within the IPB comes from abandoned mining sites; almost 70 AMD sources from around 30 abandoned mines have been cataloged, of which almost 40% of AMD discharges come from outflows of underground mining labors (Sánchez-España et al., 2005; Olías et al., 2016). Once sulfate and metals are mobilized by sulfide oxidation and dissolution of host rocks, they are transported into the receiving water bodies by hydrological drivers. However, underground mine drainages are extremely difficult to study since geochemical processes governing the metal release and transport can be only inferred from adit outflows. The complexity is due to the lack of information about the flow path and source proximity in relation to the outflow adit; AMD sources originate from a complex "anthropogenic aquifer" with extensions of hundreds to thousands m^2 of surface area, through which the water flows in the natural porous media and by a complex system of interconnected shafts, galleries and tunnels. In addition, underground systems have a more complex hydrological response than surface systems, which exhibit a relatively faster response. In underground systems the response is strongly linked to hydrogeological parameters that are usually unknown especially in derelict mines, thereby it is difficult to predict and obtain a complete monitoring. In these underground systems, metals and acidity mobilized by sulfide oxidation can be temporally retained as secondary minerals (mainly efflorescent sulfate salts and oxyhydroxysulfates) (Gzyl and Banks, 2007). The release of these pollutants fluctuates depending on weather conditions over a short and a long term (Caraballo et al., 2016).

On the other hand, the intensity of AMD pollution in the IPB requires the implementation of remediation measures that are unreasonably expensive and particularly ineffective when hydrogeochemical processes of contaminant mobilization are not well known (Nordstrom, 2011). The application of passive treatment systems for highly metal-rich waters in some AMD sources of the IPB has proved to be very effective in reducing metal and acidity fluxes (Macías et al., 2012; Ayora et al., 2013); however, a greater effort is required mainly in underground adits. A detailed knowledge of geochemical mechanisms governing metals and acidity fluxes in these "hidden" systems is essential to face the challenge of decontamination in derelict mines. Thus, these sorts of studies are essential to optimize future treatment systems in such complex areas. For these reasons, the main objectives of this work are to geochemically characterize a selected AMD adit outflow of the IPB and to identify the main geochemical processes controlling metal release and solubility along the flow path. The execution of these goals will be performed by the application of geochemical and statistical tools to the results obtained under different hydrological conditions (i.e. dry and rainy periods) in a selected AMD underground effluent of the IPB.

2. Materials and methods

2.1. Site description

The study area is the abandoned sulfide underground mine of Perrunal in the central sector of the IPB (UTM29: 688236X, 4175342Y). The zone is characterized by a dry Mediterranean climate with average rainfall around 700 mm, mainly accumulated between autumn and winter. The sulfide deposit is hosted by volcanic and volcanoclastic felsic rocks (mainly rhyolites), in contact with sedimentary rocks (black and gray shales, and minor sandstones) and jaspers to the south (Fig. 1A and B). Although mining activity in the Perrunal mine dates back to Tartessian and Roman times, intense exploitation of this deposit began around 1900, with a total sulfide production of 7.5 Mt. until 1960 (Pinedo Vara, 1963). Underground workings were developed at 5 different galleries (Fig. 1B) interconnected by shafts. The sulfide obtained in Perrunal had a content of 48–51 wt.% of S, 45 wt.% of Fe, 0.5–1.0 wt.% of Cu, 0.20–0.42 wt.% of Zn, 0.30 wt.% of As, 0.1 wt.% of Pb and 0.02 wt.% of Co (Pinedo Vara, 1963). A fire took place in 1949 due to spontaneous heating of the sulfide deposit comprising levels 4 and 5. Firefighting measures put into practice by the company were unsuccessful and the affected area had to be isolated to continue the activity in the adjacent sulfide body placed at the same depth of the mine. As a result, around 600,000 tons of sulfides were confined in levels 4 and 5, being exposed to combustion. Finally, mining activity ceased at the end of 1968 and underground galleries were progressively flooded after water table recovery, promoting AMD generation that is active nowadays, and expected to continue for hundreds or thousands of years (Younger, 1997). At present, AMD discharge emerges from a cooling/ventilation tunnel of the underground mine, being the only discharge detected in the area (Fig. 1C).

2.2. Data, sampling and analysis

Rainfall data from the meteorological station of La Zarza (1 km from Perrunal Mine; Fig. 1A) were provided by the Regional Environmental Authorities and the Spanish Meteorological Service. Water samples were collected just at the AMD outlet (Fig. 1C) at least twice a month from May 2012 to February 2013. Flow rate was measured at the outlet of the mine gallery by emplacing a V-notch weir. Samples were collected in 60 mL sterile polypropylene containers and filtered immediately after collection through 0.1 μm Millipore filters. The use of 0.1 μm filters instead of 0.45 μm prevents the incorporation of Cr and As-rich Fe colloids in this type of water (Cánovas et al., 2012). Then, samples were acidified in the field to $pH < 1$ with suprapur HNO_3 and stored at 4 °C in the dark until analysis.

Temperature, electrical conductivity (EC), pH and redox potential (ORP) were measured using a portable multiparameter Crison® MM40+. A 3-point calibration was performed for both EC and pH (147, 1413 μS/cm and 12.88 mS/cm; and 4.01, 7.00 and 9.21, respectively). ORP was controlled using 2 points (240 and 470 mV). The calibration and control standards used were Crison® standard solutions. ORP measurements were corrected to the Standard Hydrogen Electrode to calculate pE (Nordstrom and Wilde, 1998). Dissolved O_2 was measured with the auto-calibrating Hanna® portable meter HI9143. Ferrous and total Fe were determined in the field by colorimetry at 510 nm after complexation by the addition of 0.5% (*w*/w) 1.10-phenanthroline chloride solution to the filtered sample (Rodier et al., 1996) using a DR/890 portable colorimeter (HACH®). The detection limit was 0.3 mg/L and precision was better than 5%; Fe(III) was calculated as the difference between total Fe and Fe(II).