

# Geochemical Controls in an AMD Outflow by Strong Water-Rock Interactions

/ CARLOS RUIZ CÁNOVAS (1\*), FRANCISCO MACÍAS (1) AND RAFAEL PÉREZ-LÓPEZ (1)

(1) Departamento de Geología. Universidad de Huelva, Fuerzas Armadas s/n, 21007 Huelva, (España)

## INTRODUCTION

The Water Framework Directive (WFD) requires achieving a good ecological and chemical quality of all European waters by 2015, and demand EU members to 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 the timely improvement. These conditions are met in the Iberian Pyrite Belt (IPB) in SW of Iberian Peninsula, mined since prehistoric times, which is deeply affected by acid mine drainage (AMD) processes (e.g. Sarmiento et al., 2009).

The implementation of remediation measures is unreasonably expensive and particularly ineffective when hydrogeochemical processes of contaminant mobilization are not well known. A detailed knowledge of geochemical mechanisms of source and release of metals and acidity in these systems would provide management tools to regional and local authorities to face the challenge of metal pollution in areas affected by derelict mines. Thus, the main objectives of this work are to characterize geochemically a selected AMD discharge and identify the main geochemical processes governing metal mobilization and transport.

## STUDY SITE

The studied area is the abandoned sulfide mine of Perrunal in the central sector of the IPB (UTM29: 688236X, 4175342Y). The area is characterized by a dry Mediterranean climate with average rainfalls around 700 mm, mainly accumulated between autumn and winter. The Perrunal mine is enclosed in materials belonging to the

Culm Group; the sulfide deposit is hosted in igneous rocks in contact with Carboniferous shales by the south (Pinedo-Vara 1963).



Fig 1 Mine adit releasing AMD waters from the Perrunal Mine.

Although mining activity in Perrunal dates back to Tartessian and Roman times, intense exploitation of this deposit began around 1900, with a total pyrite production of 7.5 Mt until 1960. Mining activity finally ceased at the end of 1968 and underground galleries were progressively flooded promoting AMD generation that flows outside the gallery (Fig. 1) with an average flow of 0.5-1 L/s. The longevity of AMD will remain these processes to continue during hundreds or thousands years.

## METHODS

Rainfall data from the meteorological station of La Zarza (1 km from Perrunal Mine) were used to study the hydrological response of the AMD outflows. Water samples were collected just at the gallery outlet (Fig. 1) at least twice a month from May 2012 to February 2013, obtaining a total of 22

samples. Discharge was monitored by the settlement of a V-notch weir. Samples were filtered immediately after collection through 0.1 µm Millipore filters, acidified to pH < 1 and stored at 4°C until analysis. Temperature, electrical conductivity (EC), pH and redox potential (Eh) were measured using a portable multiparameter Crison® MM40+. Both ferrous and total Fe were determined in the field by colorimetry at 510 nm after complexation with 0.5% (w/w) 1.10-phenanthroline chloride solution to the filtered sample.

Concentrations of sulfur and dissolved metals were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES; Jobin-Yvon Ultima2). Geochemical speciation and saturation indices (SI) calculations were performed by the PHREEQC code v.3.1 (Parkhurst and Apello, 1999).

## RESULTS AND DISCUSSION

The rainfall observed in the studied period was 812 mm, accumulated between autumn and winter (Fig. 2) and had a direct response in the AMD flow rate. The flow is quite stable during the dry period (0.3 to 0.6 L/s) but almost is duplicated after the first rainy events (0.8 to 1.1 L/s) with a delay of around  $40.5 \pm 1.5$  days between the rainfall and AMD flow peaks. This may be the residence time of the meteoric waters inside the galleries, which implies a high interaction of the water with fresh sulfide and enclosing host rocks.

The pH values of AMD flowing out the gallery remain almost constant (3.24-3.31) through the whole period with a slight decrease with the first rainfalls (Fig. 2) concomitant to an increase in EC values. The adit outflows showed high metal and sulfate concentrations (e.g. average of 2220 mg/L Fe, 6900 mg/L of sulfate, 239 mg/L of Al) due to strong

**palabras clave:** Sales solubles Evaporíticas, Procesos de lavado, Movilización de metales, Retención de metales.

**key words:** Evaporitic sulfate salts, Washout processes, Metal mobilization, Metal retention.

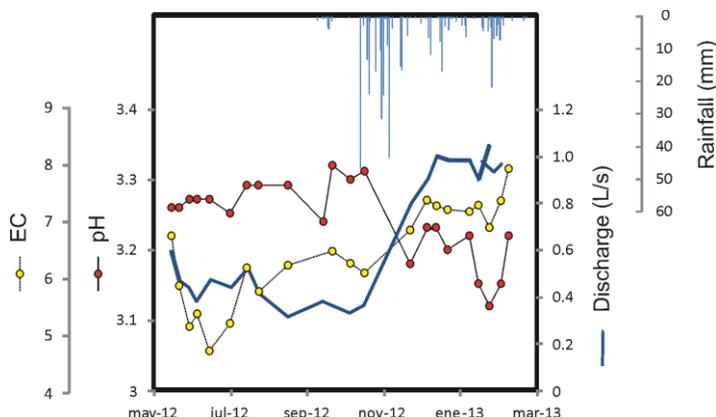


fig 2. Distribution of rainfalls and evolution of discharge, pH, EC during the monitored period.

interactions between infiltrating water, sulfides and enclosing rocks. Higher Fe/SO<sub>4</sub> ratios in the outflow than those theoretical of pyrite may be due to the existence of acidic leaching of Fe from silicates or Fe oxides or intense precipitation of non-Fe sulfate salts inside the gallery. Iron is mainly found as Fe(II) (97-99%) due to the low Eh/pH conditions observed in the galleries.

Most metals followed a similar trend than EC, with decreasing concentrations during the dry season and increasing during the first rainfalls (Fig. 3A). The concentration of Ca remains almost constant (Fig. 3A) due to its proximity to gypsum equilibrium (SI of -0.2). However, the use of metal ratios allows inferring a geochemical control inside the galleries. Considering the SI values provided by PHREEQC, no mineral phase was found to be in equilibrium with Mg. In the case of Fe and Al, waters were close to equilibrium with jarosite and alunite. However, the scarcity of Fe(III) present in waters and the similar trend followed by both elements dismiss a geochemical control exerted by these mineral phases.

We hypothesize that the metal solubility in the galleries is controlled by cycles of precipitation and redissolution of evaporitic sulfate-salts (Fig. 3B). During the first stage of the dry season, AMD outflows are impoverished in Mg in relation to Ca, Al and Fe (Fig. 3C-E-F) due to the predominant Mg efflorescent salts (e.g. epsomite) precipitation. As long as the dry season runs, the water table drops and evaporative conditions in the galleries became more extreme, enhancing the precipitation of Fe and Al sulfate salts over Mg and Ca (Fig. 3D-E-F).

The inverse tendency is observed with the first rainfalls which caused the redissolution of evaporitic salts formed during the dry season, commonly observed in AMD systems (e.g. Cánovas et al. 2008).

A higher increase of Al in relation to Fe was initially observed, due to the higher solubility of alunogen, the main Al-storing sulfate salt. Once the water table continues rising, metal ratios in AMD outflows are strongly linked to the different amount of evaporitic salts

previously precipitated. In this case an increase in Fe with respect the rest of metals (Fig. 3F) is observed, suggesting melanterite as the main precipitating efflorescent salt in the gallery.

REFERENCES

Cánovas C.R, Hubbard C.G, Olías M, Nieto J.M., Black S., M.L. Coleman (2008). Hydrochemical variations and contaminant load in the Rio Tinto (Spain) during flood events. *J. Hydrol.*, **350** (1-2), 24-40.  
 Parkhurst D.L. and C.A.J. Appelo (1999). User's guide to PHREEQC (Version 2). A computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. USGS water-resources investigations report 99-4259. Denver, Colorado.  
 Pinedo Vara I. (1963). *Piritas de Huelva. Su historia, minería y aprovechamiento. Summa. Madrid, Spain.* 1003 pp  
 Sarmiento A.M, Nieto J.M, Olías M., Cánovas C.R (2009). Hydrochemical characteristics and seasonal influence on the pollution by acid mine drainage in the Odiel river basin (SW Spain). *Appl. Geochem.* **24**, 697-714.

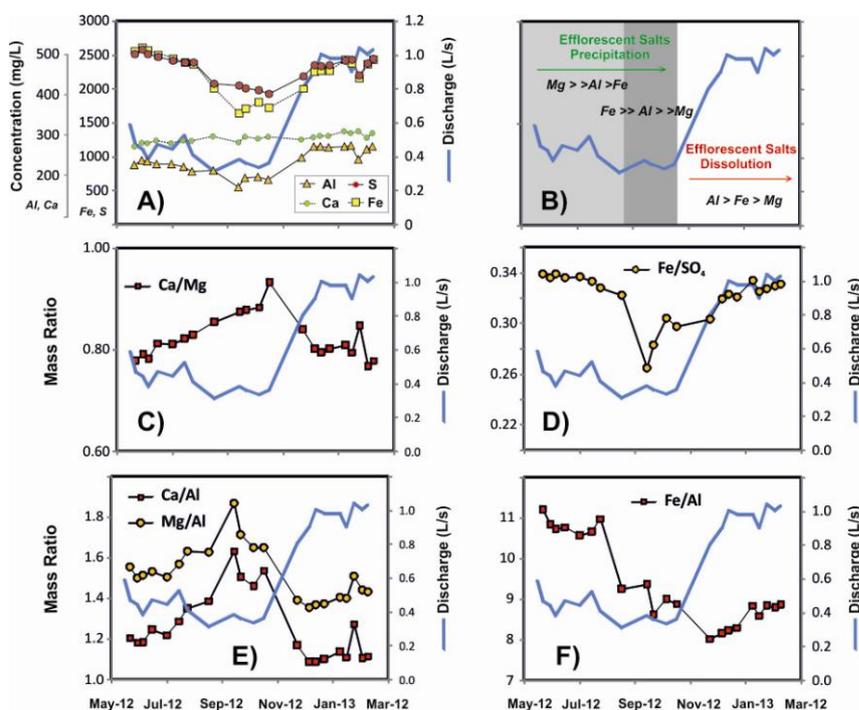


fig 3. A) Concentration of sulfate and main metals in the AMD outflow, B) Diagram showing the predominance of geochemical processes controlling main metal solubility, C-F) sulfate and metal ratios in the AMD outflow.