

Geochemical processes in an acidic mine lake in the Iberian Pyrite Belt: San Telmo pit lake (SW Spain)

Procesos geoquímicos en un lago de origen minero en la Faja Pirítica Ibérica: la Corta de San Telmo (SO España)

Carlos Ruiz Cánovas^{1, 2}, Manuel Olías Alvarez³ and Jose M. Nieto Liñán⁴

¹ Instituto de Diagnóstico Ambiental y Estudios del Agua (IDAEA-CSIC). c/ Jordi Girona 18-26, 080034, Barcelona, Spain. carlos.ruiz@dgeo.uhu.es

² Departamento de Geodinámica y Paleontología, Facultad CC. Experimentales, Universidad de Huelva, Avenida 3 de Marzo s/n, 21071, Huelva, Spain. carlos.ruiz@dgeo.uhu.es

³ Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide. Ctra. Utrera, km. 1, 41013, Sevilla, Spain. molialv@upo.es

⁴ Departamento de Geología, Facultad CC. Experimentales, Universidad de Huelva, Avenida 3 de Marzo s/n, 21071 Huelva, Spain. jmnieto@uhu.es

ABSTRACT

This study provides information on the physicochemical processes of water and sediments from San Telmo pit lake. It is a valuable tool to evaluate best treatment remediation options in the long term. This lake has a meromictic nature, is highly acidic (pH of 2.8) and pH- buffered by Fe(III) precipitation. In San Telmo sediments, iron reduction and sulphide oxidation may be thermodynamically favoured due to low pH values in pore waters and the abundance of schwertmannite. The transformation of schwertmannite into goethite may limit sulphate reduction. As far as the Acid Mine Drainage pressure on the lake remains, the pH buffering exerted by schwertmannite in sediments will limit natural attenuation processes by sulphate reduction.

Key-words: Acidic mining lakes, sulphur species, reactive Fe, schwertmannite transformation.

RESUMEN

Este trabajo estudia los procesos físico-químicos en las aguas y sedimentos de la corta minera de San Telmo, que supone una información valiosa para adoptar las medidas óptimas de remediación a largo plazo. Este lago de origen minero presenta meromixis, una elevada acidez (pH 2.8) y sus aguas están tamponadas por la precipitación de Fe(III). Los bajos valores de pH y la abundancia de schwertmannita en los sedimentos favorecen termodinámicamente los procesos de reducción de Fe y oxidación de sulfuros. La transformación de schwertmannita en fases minerales más cristalinas, como la goethita, parece tamponar el pH en el agua de poro, limitando los procesos de reducción de sulfatos. La neutralización de la acidez en los sedimentos por reducción de sulfatos no será posible en tanto no disminuya el aporte actual de AMD a la corta.

Palabras clave: Lago ácido de origen minero, especies de S, Fe reactivo, transformación de schwertmannita.

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Introduction

The Iberian Pyrite Belt (IPB) is one of the most important sulphide-mining regions in the world. Mining activity in the IPB dates back to prehistoric times and developed in such a magnitude that provoked the deterioration of water courses by acid mine drainage (AMD) (Cánovas *et al.*, 2007; Sarmiento *et al.*, 2009). In the second half of the 1800's, underground workings gave way to open mining in the IPB in order to exploit more efficiently the mineral deposit. This activity has provoked the existence of a high number of mine pits in the IPB. During exploitation, the suppression of the water table is required to avoid the flooding of the

mining labours. When the mining activity ceases, the water table recovers its original condition, flooding the open pits and giving rise to mine pit lakes. In the IPB, it has been recorded the existence of more than 30 mine pit lakes, many of them flooded during the 1960-1990's (Sánchez-España *et al.*, 2008) concomitant to the decline of mining activities. The rise of the water table promotes the oxidative dissolution of sulphides contained on the pit banks, interconnected underground galleries and shafts, etc., which may cause water acidification. As a consequence, pit lakes may contain large volumes of acidic and metal-rich waters.

The EC Water Framework Directive (WFD; EC 2000) defines mining lakes as ar-

tificial surface water bodies which have to be monitored and managed in order to reach a good water quality status. The consecution of this goal requires the adoption of remediation strategies, supported on a deep knowledge of physicochemical processes and interactions between water column and lake sediments. In this sense, it has been widely reported the neutralization processes of acidity in mining lakes by sulphate reduction (e.g. Blodau and Peiffer, 2003, Blodau, 2007).

San Telmo Pit Lake can be considered as a reference example to study these processes and interactions due to its size and the magnitude of pollution. Therefore, this study is aimed to provide valuable in-



Fig. 1.- Panoramic view of San Telmo pit lake.

Fig. 1.- Vista panorámica de la corta minera de San Telmo.

formation on physicochemical processes in water and sediments from San Telmo pit lake as a tool to evaluate best treatment remediation options in the long term.

Site Description

San Telmo mine is located in the municipal district of Cortegana (Huelva, SW Spain). Although mining activity in San Telmo has been developing since ancient times, the more intense period of mining activity took place between 1859 and 1960, when around 2 million tonnes of mineral were obtained (Pinedo Vara, 1963). From 1960 on, approximately other 2 million tonnes were produced, ending finally in 1989 when the mine was closed. Intense opencast mining activities originated a pit of more than 100 m depth, which was progressively flooded after mining cessation. The water got to the overflow level in 1995, reaching the pit lake its actual configuration (Fig. 1). A bathymetric study performed in 2005 by Morales *et al.* (data not published) shows a maximum depth of 130 m in the pelagical zone, accounting for a total dimension of 580 m x 375 m x 130 m, which represented until recently, the biggest volume of acidic waters stored in the IPB, after the flooding of the Riotinto open pit.

The rapid flooding of San Telmo pit lake is due to its location, placed within the drainage area of the Fresnera Stream. This

is not the only AMD input received by San Telmo; it is also fed by mining lixiviates coming from the intersecting galleries, runoff generated from rainfall episodes, and lixiviates originated by the washout of mining wastes placed in the vicinity of the pit lake.

Methods

Sediment and water sampling was performed during June 2006 in the San Telmo

pit lake (Fig. 1). A vertical profile was also carried out to measure temperature (T^a), pH, redox potential (Eh), dissolved oxygen (DO), electrical conductivity (EC) and turbidity by means of a SEBA HYDROMETRIE KLL-Q multi-probe. Three water samples (0, 40 and 123 m) were collected along the water column according to changes in water mineralization. Water samples were filtered (0.20 μ m), acidified with HNO_3 to pH below 2, cooled at 4°C and stored in dark until analysis. Samples were analyzed in the Central Research Services of the University of Huelva by using a Jobin Yvon (JY ULTIMA 2) optical spectrometer (ICP-OES).

A sediment core was taken by an UWITEC™ gravity corer from the pelagical zone at around 123 m. This core was sealed and cooled to avoid oxidation processes before analysis. After slicing, pore water was collected from different layers of sediment by centrifugation, and pH, Eh and T^a were immediately measured. Ferrous and total iron concentrations were analyzed following the phenantroline method.

Reactive Fe was determined in sediments after digesting the samples with HCl 1 N and shaking for 24 h. Total Fe was also measured using HCl 6 N as digestion solution. Total Reduced Inorganic Sulphur (TRIS) was analyzed photometrically by the methylene blue method after hot acid digestion and subsequent reduction with $Cr(II)Cl_2$ to H_2S . Elemental Sulphur (S^0) was analyzed by high pressure chromatography and UV-detector after extraction with methanol. Total

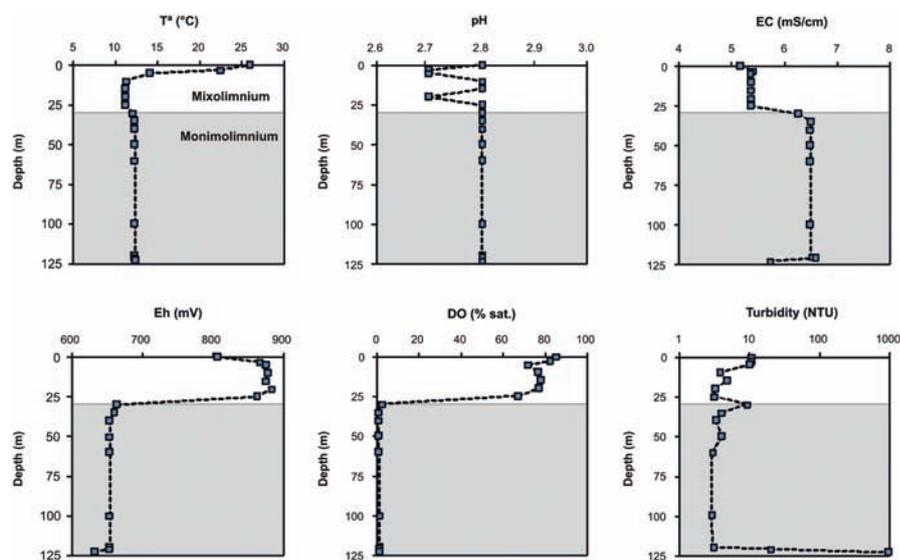


Fig. 2.- Physico-chemical profile in the San Telmo pit Lake.

Fig. 2.- Perfil de parámetros físico-químicos en la Corta de San Telmo.

and organic carbon was analyzed by a C-S Leco Analyser.

Results and Discussion

The San Telmo Pit Lake is highly acidic, with pH values almost constant to around 2.8 (Fig. 2), suggesting a pH buffering by Fe(III). The San Telmo pit lake seems to have a meromictic nature, with a 29m shallower oxygenated and lower density layer called mixolimnion and a 100 m deeper anoxic and higher density layer called monimolimnion (Fig. 2). The mixolimnetic waters show more oxidative conditions and lower mineralization (807-883 mV; 5.3 mS/cm) than monimolimnetic (650 mV; 6.6 mS/cm). This coincides with that found by Sánchez-España *et al.* (2008), which suggest the permanent stratification throughout the year

The turbidity in the water column ranged from 3 to 5 NTU (Fig. 2). Higher values were reached in the upper 5 m (11 NTU), at the halocline (9.3 NTU) and close to the bottom lake (20 NTU). The highest values were observed at the water-sediment interface, close to 1000 NTU. This increase may be linked to Fe(III) precipitation processes (increasing colloidal Fe) and microbiological activity. At this respect, the geochemical code PHREEQC (Parkhurst and Appelo, 1999) predicts supersaturation of mixolimnetic waters with respect jarosite and schwertmannite. The precipitation of the latter mineral is supposed to be the cause of pH buffering between 2.8 and 3.2 in most acidic mine lakes (Sánchez-España *et al.* 2008). High concentrations of sulphate (3963-4227 mg/L) and metals (e.g. 139-163 mg/L of Fe, 81-90 mg/L of Cu, 223-237 µg/L of Cd) were recorded through the water column, reaching their highest values in the monimolimnion.

Regarding sediment pore waters, increasing pH values can be observed; from 3.3 at the water-sediment interface to 3.8 at the bottom sediment (Fig. 3). The opposite tendency was observed for Eh values (from 375 to 224 mV). Higher Fe concentrations were found in sediment pore waters (963-2024 mg/L) than that recorded in the water column (Fig. 3). This sharp increase in Fe concentration may be caused by reductive processes of Fe in sediments. These processes consume acidity, which provokes the increase in pH values observed in pore waters in respect to the water column.

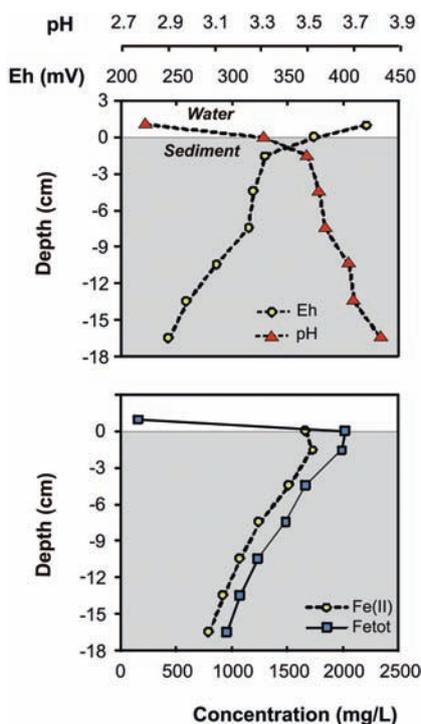


Fig. 3.- Profile of pH, Eh, Fe(II) and Total Fe in sediment pore waters of San Telmo.

Fig. 3.- Evolución del pH, Eh y del contenido en Fe(II) y Fe total en las aguas de poro de los sedimentos de la Corta de San Telmo.

Visually, the sediment core could be divided into two different zones. The first upper 10 cm contained brownish orange sediments with a dry weight of around 40%. Downwards, the sediment had a yellowish brown color with decreasing water content due to compaction as suspended matter is progressively settled down. A decrease in total and organic carbon in depth was also observed in the sediments (Table I). Organic carbon takes part in reductive processes in sediments as electron donor; however its use may be limited by the formation of Fe coatings. The highest content in reactive iron was found in the upper centimeters of the sediment (25 g/kg; Table I).

Reactive iron is the fraction of iron that easily undergoes chemical or microbial dissolution and therefore can be regarded as potentially available for microbial reduction (Canfield, 1989). The accumulation of reactive Fe in sediments is the result of oxidation of Fe(II) in the mixolimnion and subsequent precipitation of Fe hydroxysulphates (according to PHREEQC). This involves a constant input of reactive Fe in sediments, as far as the pit lake receives AMD inputs.

Total iron concentrations ranged from 120 g/kg at the top to 25 g/kg at the sediment bottom. This iron fraction includes (apart from reactive Fe) other more crystallized minerals such as goethite or detrital pyrite. Reactive Fe tends to be transformed with burial into more crystallized minerals such as goethite or jarosite, releasing acidity into the pore waters. For this reason, the ratio Fe_r/Fe_t decreased in depth from 21% to 10%. The acidity released during this transformation counteracts the consumption of protons during the reductive dissolution of Fe, avoiding the rise of pH values above 4 in pore waters (Fig. 2). The low content in Corg could also explain the low pH values in sediments.

The content of total sulphur ranged from 27 to 78 g/kg (Table I); reaching the highest values at the sediment bottom. Concerning sulphur species, AVS (FeS) was not analyzed in samples owing to the lack of black coloured bands indicative of this sulphur species in sediments, supported by the low pH values recorded (<4) in the sediments. In the presence of schwertmannite and at low pH, iron reduction is thermodynamically favored over sulphate reduction, because acidification impedes sulphate reducing bacteria but promotes Fe reducing bacteria (Blodau and Peiffer, 2003). If Fe reduction is the predominant electron accepting process in the sediments, Fe(II) is mobilized as shows the higher Fe(II) values in

Depth cm	H ₂ O %	C tot %	C org %	Fe _r gr/kg	Fe _t gr/kg	TRIS gr/kg	S° mg/kg	S tot gr/kg
0-3	63	0.56	0.27	25	120	1.9	0.167	44
3-6	59	0.43	0.22	18	99	2.9	0.007	27
6-9	60	0.45	0.24	15	100	0.90	0.018	42
9-12	49	0.30	0.14	9.1	71	3.7	0.006	38
12-15	42	0.14	0.05	4.8	48	7.1	0.027	45
15-18	34	0.12	0.04	3.9	25	9.0	0.016	78

Table I.- Content of water, carbon, reactive and total Fe and main S species in San Telmo sediments.

Tabla I.- Contenido de agua, carbono, Fe reactivo y total, y las principales especies de S en los sedimentos de la corta de San Telmo.

pore waters (Fig. 2). The subsequent reoxidation of ferrous pore waters to Fe(III) released from the sediments and precipitation as schwertmannite may cause further acidification in the water column.

The concentrations of S^0 were generally low (from 6 to 27 $\mu\text{g}/\text{kg}$; Table I) except in the upper centimeters of the sediments (167 $\mu\text{g}/\text{kg}$) due probably to oxidation of detrital pyrite by Fe(III). Elemental sulphur is an intermediate product during sulphide oxidation. Another possibility would be the oxidation by Fe(III) of S from organic matter in the sediments. The content of TRIS (FeS_2 , FeS and S^0) in the sediments ranged from 0.90 to 9.0 g/kg, with the highest values found at the sediment bottom. These figures can be attributable to detrital pyrite accumulated in the sediments by erosive processes.

Conclusions

The San Telmo pit lake is highly acidic due to the intense sulphide oxidation processes occurred during its flooding. This lake seems to have a meromictic nature, with a 29 m shallower oxygenated and lower density layer called mixolimnion and a 100 m deep anoxic and higher density layer called monimolimnion.

In the mixolimnion, the ferrous iron is oxidized to ferric iron, which then precipi-

tates, releasing acidity which provokes a pH buffering. These newly formed minerals (mainly schwertmannite) settle down in the sediment, where may be converted with burial to more stable minerals such as goethite or jarosite, releasing H^+ . This process seems to inhibit sulphate reduction in these sediments as indicates the absence of AVS. The content of TRIS in sediments was limited to detrital pyrite accumulated in the sediment and S^0 formed by pyrite oxidation and/or oxidation of S organic compounds by Fe(III).

Instead, the low pH values and the presence of low crystallized minerals such as schwertmannite favour iron reduction. This reaction consumes acidity and release Fe(II) to pore waters which may cause further acidification in the mixolimnion after oxidation and precipitation.

As far as the supply of ferrous and ferric waters to the pit lake remains at similar rates, the sulphide reduction will be inhibited through schwertmannite transformation and reduction processes.

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