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The oxidation of ferrous iron in acidic mine effluents from the Iberian Pyrite Belt (Odiel Basin, Huelva, Spain): Field and laboratory rates ☆

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Abstract

The oxidation of Fe(II) in acidic mine waters emerging from the portals of abandoned mines (Lomero, Esperanza, Tharsis and Poderosa) of the Iberian Pyrite Belt (IPB) massive sulphide province, has been investigated. Field and laboratory studies have been performed in mine effluents with different iron concentrations (290 to 1940 mg/L Fe(II)) and pH (1.9–3.1) to calculate: (1) the reaction rates at which dissolved Fe(II) is oxidised to Fe(III) in the mine portals, (2) the hourly variations of these oxidation rates, and (3) the rate at which Fe(III) is subsequently hydrolyzed and precipitated as schwertmannite. The calculated field rates, between 5.5×10^{-6} and 4×10^{-7} mol L^{-1} s^{-1}, are characteristic of bacterial oxidation. A marked difference has been recognized between the different mine sites depending on the biomass density. The oxidation rates measured in the mine portals with dense biofilms of acidic slime streamers (Tharsis and Esperanza), are notably faster than those measured in the mine sites where streamers are not present (Lomero mine portal). Among the sites with the highest density of biofilms, pH also appears to control the oxidation rate, with the effluents of lowest pH (Poderosa mine, pH 1.9) showing slower rates than those with higher pH (Tharsis and Esperanza, pH 2.7–3.0). The oxidation kinetics of Fe(II) appears to be zero-order and highly dependent on the water temperature (T). Consequently, iron-oxidation rates vary significantly along the day, being minimum at the early morning and sunset (with $T\sim$ 15–25 °C), and maximum at midday (with $T\sim$ 25–35 °C). Laboratory oxidation studies performed with samples of these mine effluents have confirmed the influence of T, pH, dissolved oxygen content and biofilm presence/absence on the oxidation rate of Fe(II). Precipitation of Fe(III) takes place at pH 2.7–3.1 and rates ranging from 1.7×10^{-6} to 10^{-7} mol L^{-1} s^{-1}, also showing a daily cycle.

Keywords: Acid mine waters; Ferrous iron oxidation; Acidophilic bacteria; Iberian Pyrite Belt

1. Introduction and scope

Acid mine drainage (AMD) represents a major environmental problem in the region of Huelva (SW Spain), as it causes a strong impact on the water quality of the Odiel and Tinto fluvial systems. These solutions transport large quantities of acidity, dissolved sulphate and metals, including Fe, Al, Mn, Cu, Zn, Cd and, in minor quantities, As, Pb, Co and Ni. The geochemistry and environmental implications of the acid mine waters

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of the Odiel basin have been recently discussed in Sánchez España et al. (2005).

As these acidic waters evolve downstream, Fe(II) is oxidised to Fe(III), and Fe(III) is subsequently hydrolyzed and precipitated at pH ~ 2.5–3.5 in the form of hydrous iron oxides and/or oxyhydroxysulphate minerals.

The general, simplified reactions commonly cited to account for the iron oxidation and hydrolysis are (Stumm and Morgan, 1996):

$$Fe^{2+} + 1/4O_2 + H^+ \Leftrightarrow Fe^{3+} + 1/2H_2O \qquad (1)$$

$$Fe^{3+} + 3H_2O \Leftrightarrow Fe(OH)_3(s) + 3H^+ \qquad (2)$$

In mine drainage settings, Eq. (1) is catalyzed by iron-oxidising bacteria (Nordstrom and Alpers, 1999) and Eq. (2) is usually replaced by Eq. (3), leading to the formation of schwertmannite, a poorly crystallized iron oxyhydroxysulphate (Bigham et al., 1996):

$$8Fe^{3+} + SO_4^{2-} + 14H_2O \Leftrightarrow Fe_8O_8(SO_4)(OH)_6 + 22H^+ \qquad (3)$$

In the AMD systems of the Iberian Pyrite Belt (IPB), the solid formed after hydrolysis of Fe(III) is usually schwertmannite (Sánchez España et al., 2005). The mineralogy of the mine drainage precipitates presents a close relation with the water pH, with schwertmannite (±jarosite±goethite) precipitating in the vicinity of the discharge points at pH 2.5–3.5, Al-oxyhydroxysulphates (e.g., hydrobasaluminite) at pH 4–5, and ferrihydrite at pH>6 (Sánchez España et al., 2005). Schwertmannite plays a major role not only in the control of the iron solubility, but also in the retention (by sorption) of metal ions such as As, Cu, Zn, Cd, Co and Ni.

Recently, several microbiological studies (López-Archilla and Amils, 1999; López-Archilla et al., 2000; González-Toril et al., 2003) have successfully identified and described some chemolithotrophic microorganisms in the Tinto and Odiel rivers. This microscopic fauna includes iron- and sulphur-oxidising bacteria (e.g., *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Acidithiobacillus thiooxidans*), fungi (e.g., *Penicillium*, *Trichoderma*, *Aspergillus*) and algae (e.g., genus *Klebsormidium*, *Euglena mutabilis* Euglenophyte). These microbiological studies report that most of the biomass is accumulated in the biofilms which are commonly present in the streams and anchored to the sediments. However, these studies have not described

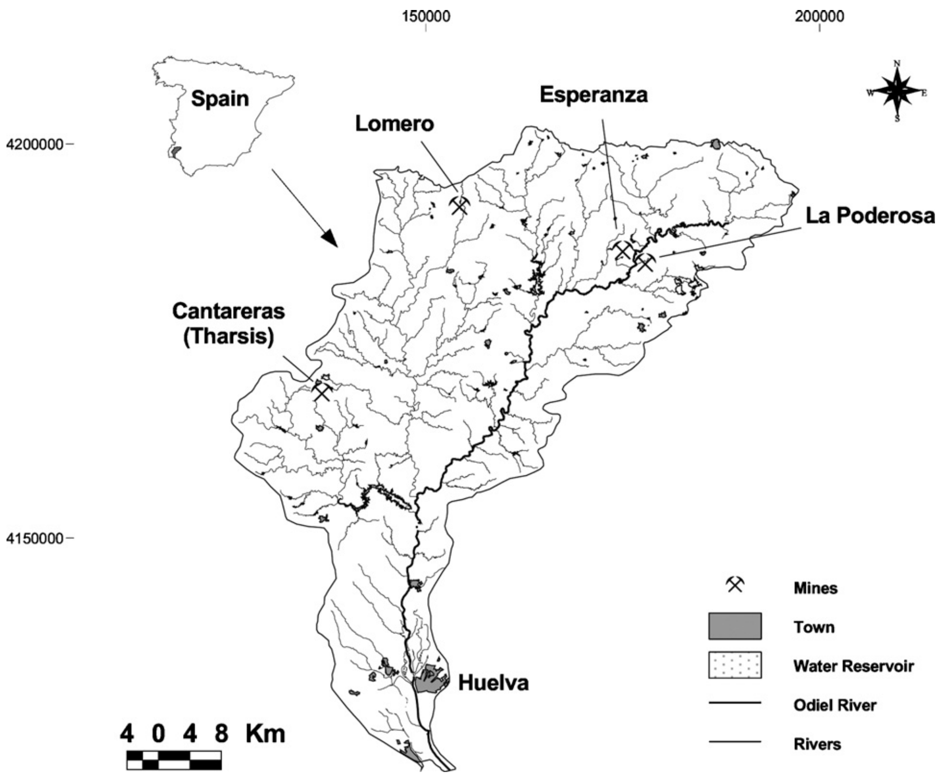

Fig. 1. Location of the studied mine sites and hydrology of the Odiel river watershed (modified from Sánchez España et al., 2005). Map scales are 1:800.000 for the Odiel basin, and 1:40.000.000 for the small Spain map.