Acid Mine Drainage in the Iberian Pyrite Belt: an Overview with Special Emphasis on Generation Mechanisms, Aqueous Composition and Associated Mineral Phases

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INTRODUCTION

A long history of metalliferous mining in the IPB mining district has left a legacy of abandoned mines, mainly in the province of Huelva (SW Spain), and a big number of waste piles (n=57, total volume of 107 Hm³), tailings impoundments (n=10, total volume of 42 Hm³) and flooded pits (n=22, total volume of acidic water of 25 Hm³), which represents one of the World’s largest accumulations of mine wastes and AMD. The mineralogical and textural characteristics of the IPB ores (with a dominantly pyritic, fine-grained, usually brecciated and fractured, and highly reactive mineralization, and a considerable lack of carbonates to neutralize acidity), has favoured the oxidation and dissolution of pyrite, and the subsequent formation of AMD. These acid mine waters have caused severe pollution of acidity and dissolved metals (Fe, Al, Cu and Zn). This acidity and metal pollution has caused the loss of most forms of aquatic life, with the exception of acidophilic microorganisms which inhabit these extreme environments (e.g., López-Archilla and Amils, 1999; López-Archilla et al., 2001; González-Toril et al., 2003; Aguilera et al., 2006).

This work provides a brief overview about the mechanisms of sulphide oxidation and metal leaching that occur in the mining areas, the water chemistry of the resultant AMD discharges and acidic mine pit lakes, and the most relevant mineral phases associated to the acidic mine waters. These acidic solutions vary largely in chemical composition, either spatially (between different mine sites) and seasonally (due to marked hydrologic variations), and include cases with very low pH and very high sulphate and metal contents. The mineralogy and chemistry of the Fe precipitates (e.g., schwertmannite, jarosite, goethite, ferrihydrite), Al phases (e.g., hydrobasaluminite, alunite) and Fe(II)-Fe(III)-Mg-Al efflorescent sulphates (e.g., melanterite, rozenite, epsomite, halotrichite, coquimbite) present in these environments, as well as their solubility and trace metal retention capacity, is also discussed. Finally, some examples of hydrogeochemical evolution and metal transport and precipitation are provided to illustrate the environmental impact of AMD in the IPB.
This paper provides an overview about the AMD problem in the IPB district, mainly from a geochemical and mineralogical perspective. It firstly reports some basic features about the oxidation of pyrite, the main geochemical process responsible for the generation of AMD, and about the microorganisms that catalyze this process in shafts, galleries, piles, tailings and pits. Secondly, the composition of AMD typically found in the IPB, as well as the mineralogy and chemistry of mineral phases associated to the acid mine waters, are also discussed.

**THEORETICAL CONSIDERATIONS**

**Fundamentals of pyrite oxidation**

The oxidative dissolution of pyrite is one of the most extensively studied geochemical processes on the Earth surface, although it is not yet fully understood (e.g., Nordstrom and Alpers, 1999a; Ehrlich, 2002). The reaction which classically describes the oxidation of pyrite in the presence of oxygen and water is (Singer and Stumm, 1970):

\[
\text{FeS}_2(s) + 3.5 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+ \quad (1)
\]

The formed ferrous iron is then usually oxidized to Fe³⁺ by the reaction:

\[
14 \text{Fe}^{2+} + 3.5 \text{O}_2 + 14 \text{H}^+ \rightarrow 14 \text{Fe}^{3+} + 7 \text{H}_2\text{O} \quad (2)
\]

A critical factor in the oxidation of pyrite and the generation of acid mine waters is that Fe³⁺ is able to oxidize pyrite under anoxic subaqueous conditions at a much faster rate than does molecular oxygen, according to the reaction (Garrels and Thompson, 1960; Mckibben and Barnes, 1986):

\[
\text{FeS}_2(s) + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ \quad (3)
\]

Because at pH<3.5, reaction (2) is orders of magnitude slower than reaction (1), the oxidation of Fe²⁺ by oxygen is usually considered the rate-limiting step in pyrite oxidation (Singer and Stumm, 1970). However, the presence of acidiphilic bacteria such as *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* greatly accelerate (by a factor of around 10⁶) the abiotic oxidation rate (Singer and Stumm, 1970; Nordstrom and Alpers, 1999a), thus maintaining a high concentration of ferric iron in the system.

The overall process resulting from the combination of reactions (2) and (3) is traditionally known as the “propagation cycle” (Singer and Stumm, 1970), and along with reaction (1) depicts a model by which pyrite oxidation initially starts by reaction (1) with oxygen as the oxidant at near-neutral pH conditions, and as pH decreases to about 4 the oxidation of pyrite proceeds through reaction (3). Oxygen will always be required to replete the supply of ferric iron according to reaction (2), so that the overall rate of pyrite oxidation in a tailings or waste pile or in a mine will largely depend on the overall rate of oxygen transport by advection and diffusion (Nordstrom and Alpers, 1999a; Ritchie, 2003).

**The concept of bioleaching: direct vs. indirect mechanism**

The mechanisms by which acidophilic chemolithotrophic microorganisms obtain energy by oxidizing sulphidic minerals have been controversial for many years (Ehrlich, 2002). Two basic mechanisms, concerning the relative relationship between the mineral substrate and the microbial catalyst, the direct and the indirect attack, have been considered (Sand et al., 2001; Schippers et al., 1996; Schippers and Sand, 1999). In the direct attack, microorganisms solubilize mineral sulphides by attaching to their surface, facilitating an enzymatic oxidation by channelling electrons from the mineral to an appropriate electron acceptor (respiration). In the indirect attack, microorganisms are mainly involved in the regeneration of ferric iron, a strong oxidant, in the solution. This soluble ferric iron is responsible for the oxidation of exposed sulphidic minerals and other reduced compounds. The demonstration that ferric iron present in the cell envelop and/or the exopolymers of bioleaching microorganisms is responsible for the electron transfer from the sulphidic minerals to the electron transport chain (Gehrke et al., 1995), has clarified the situation. Based on this observation, Sand and coworkers proposed that because ferric iron is ultimately responsible for the oxygenation of exposed sulphidic minerals to the microbial function in AMD systems (Singer and Stumm, 1970; Nordstrom and Alpers, 1999a), thus maintaining a high concentration of ferric iron in the system.

Although microbes do attach to sulphide mineral surfaces and can oxidize them (e.g., Edwards et al., 1998), it is generally accepted that the soluble ferric iron produced by microbial oxidation is responsible for the oxidation of other sulphides common in waste piles or tailings.

Thus, this model proposes that the principal microbial function in AMD systems during sulphide bioleaching is to keep the Fe³⁺ ions in an oxidized state and to generate sulphuric acid biologically to supply protons for hydrolysis attack. Based on laboratory experiments, Schippers and Sand (1999) estimated that up to 16% of the total sulphur released during pyrite oxidation was elemental sulphur (the rest being mainly SO₄²⁻, whereas the oxidation of other sulphides like sphalerite, chalcopyrite or galena can result in the production of between a 92% and nearly a 100% of native sulphur, and only trace amounts of sulphate and polythionates (SO₄²⁻, S₈O₂⁵⁻).

Finally, Schippers et al. (1996) have demonstrated that the bacterial species involved in pyrite oxidation is a determining factor as regards to the sulphur species generated during the cyclic (indirect) leaching mechanism. Thus, in the case of pyrite bioleaching by Leptospirillum ferrooxidans, an organism without sulphur-oxidizing capacity, with sulphate as the main product (Schippers and Sand, 1999; Sand et al., 2001):

\[
\text{FeS}_2(s) + 6 \text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow 2 \text{S}_8 + 7 \text{Fe}^{2+} + 6 \text{H}^+ \quad (4)
\]

\[
\text{S}_2\text{O}_3^{2-} + 8 \text{Fe}^{3+} + 5 \text{H}_2\text{O} \rightarrow 2 \text{SO}_4^{2-} + 8 \text{Fe}^{2+} + 10 \text{H}^+ \quad (5)
\]

Most metal sulphides (including ZnS, CuFeS₂ and PbS) are susceptible to a proton acid attack as well as to ferric iron oxidation. They are oxidized through the so-called polysulphide mechanism (Schippers and Sand, 1999; Sand et al., 2001):

\[
\text{MS} + \text{Fe}^{3+} + \text{H}^+ \rightarrow \text{M}^{2+} + 0.5 \text{H}_2\text{Sn} + \text{Fe}^{2+} (n \geq 2) \quad (6)
\]

\[
0.5 \text{H}_2\text{Sn} + \text{Fe}^{3+} \rightarrow 0.125 \text{S}_8 + \text{Fe}^{2+} + \text{H}^+ \quad (7)
\]

The produced elemental sulfur can be further oxidized to sulfuric acid:

\[
0.125 \text{S}_8 + 1.5 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2 \text{H}^+ \quad (8)
\]
Besides the production of tetra- and pentathionate, a detectable accumulation of elemental sulphur may occur, whereas in the case of Acidithiobacillus ferrooxidans, only small amounts of elemental sulphur are detectable because of the microorganism’s capacity to oxidize sulphur compounds.

"Iberian" microbes involved in pyrite and Fe(II) oxidation

The microbiological findings carried out until now in the acidic mine waters of the Iberian Pyrite Belt (e.g., López-Archilla and Amils, 1999; López-Archilla et al., 2001; González-Toril et al., 2003; Aguilera et al., 2006) have been mainly centered on the microbial (prokaryotic and eukaryotic) communities of the Tinto and (in a lesser extent) the Odil river systems, which are both highly acidic (average pH values of around 2 and 3.5, respectively) and present metal contents in the order of hundreds to a few thousands mg/L. The iron-oxidizing, acidophilic, prokaryotic communities of these waters is dominated by Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans, two microorganisms that have been extensively studied in mine drainage environments, along with a minor presence of Acidiphilium spp. These microorganisms have been also found in pit lakes of the IPB such as San Telmo (Sánchez-España et al., 2007c) or Corta Atalaya (D.B. Johnson, University of Bangor, pers. com.). A study conducted in acidic effluents draining several mines (Sánchez-España et al., 2007) has revealed that these acidophilic microbes oxidize Fe(II) at field rates of about 10^{-7} mol L^{-1} s^{-1}.

Johnson (2006) studied the microbiology of an acidic and thixotropic mine pond in Sao Domingos (Portugal) and reported an ecosystem composed of L. ferrooxidans, Ferrimicrobium spp., and At. Ferrooxidans. Rowe et al. (2007) have studied the microbiology of an acidic effluent (pH 2.5-2.7) draining an old cementation channel in Tharsis mine and found a complex community dominated by Acidithiobacillus ferrooxidans in the mine water, and by the heterotrophic acidophilic bacteria Acidobacteriacae and Acidiphilum spp. in the streamer growths, along with sulfidogenic bacteria in the lowest depths of the streamers.

More recently, Sánchez-España et al. (in press) have described the microbiological composition of an extremely acidic (pH 0.61-0.82) and hypersaline (e.g., 134 g/L SO_{4}^{2-}, 74 g/L Fe, 7.5 g/L Al, 3 g/L Mg, 2 g/L Cu, 1 g/L Zn) leachate which seeps from a pyrite pile in San Telmo mine (Huelva, SW Spain). This ultra-concentrated water accumulated in evaporative pools and formed crystals of Zn-rich malaniterite (Fe+2SO_{4}·7H_{2}O). The microbiological investigation has revealed a surprisingly high biomass (1.4x10^{6} cells mL^{-1}) and an exotic ecosystem composed of acidophilic, Fe-oxidizing archaea (mainly Ferroplasma spp., representing 52% of the microbial population), and minor numbers of acidophilic bacteria (including Leptospirillum spp. (3.2%), Acidithiobacillus spp. (1.6%), and Alfaproteobacteria (2.8%), which is only comparable to those reported in similar waters with pH 0.5-1.0 from Iron Mountain, California (Edwards et al., 1999, 2000; Druschel et al., 2004).

AQUEOUS CHEMISTRY OF ACID MINE DRAINAGE IN THE IBERIAN PYRITE BELT

Effluents from piles, tailings and mine portals

In a previous paper, Sánchez-España et al. (2005a) studied 64 AMD discharges from 25 different mines of the IPB. These AMD-generating mine sites included waste rock piles (50%), mine adits (30%), tailings impoundments (10%), mine holes (7%), and mine pit lakes (3%) located in some of the largest and most important deposits of the IPB (Río Tinto, Tharsis, La Zarza, San Telmo, Sotiel-Almagra) and many others of medium size (Lomero-Poyatos, San Miguel, Cueva de la Mora, Aguas Teñidas, Concepción, San Platón, Poderosa, Tinto-Sta Rosa). Some examples of mine drainage systems of the Iberian Pyrite Belt are illustrated in Figure 1.

The physico-chemical data reported for these acidic effluents suggested a highly variable nature as regards to seasonal continuity (permanent, seasonal or ephemeral drainage), water volume (0.1-220 L/s), acidity (200-30000 mg/L CaCO_{3} eq.), redox conditions (Eh=400-800 mV), electric conductivity (EC=1000-24000 mS/cm), dissolved O_{2} content (anoxic to O_{2}-saturated), or dissolved Fe(II) to total iron ratio (Fe(II)/Fe_{tot}=0.1-1).
The chemical composition of these waters is extremely variable, and may include extreme concentrations of dissolved SO₄ (up to 44 g/L) and metals (up to 7.7 g/L Fe, 2.6 g/L Al, 2.9 g/L Mg, 1.4 g/L Zn, 435 mg/L Cu and 440 mg/L Mn). Trace elements are also found to be significantly enriched in these acid waters (for example, maximum values of 17 mg/L As, 8 mg/L Cd, 48 mg/L Co, 17 mg/L Ni, and 728 µg/L Pb). Also, U and Th, which are usually found in the acid leachates from other sulphides (chalcopyrite, sphalerite, te, galena, arsenopyrite).

Some anomalous exceptions to the reported sulphate and metal concentrations can be eventually found in evaporative pools of ultra-concentrated water seeping from pyrite piles, as described recently in San Telmo mine (Sánchez-España et al., 2009). A liquor found in this mine site showed a pH of 0.6 and extremely sulphate (134 g/L) and metal concentrations (e.g., 74 g/L Fe, 7.5 g/L Al, 3 g/L Mg, 1.9 g/L Cu, 1 g/L Zn; Table 1).

Pit lakes

The water chemistry of twenty-two pit lakes of the IPB has been recently reported in Sánchez-España et al. (2008). These pit lakes show surface areas ranging from less than 1 ha (e.g., Angostura, Herrerías) up to 28 ha (e.g., Angostura, Herrerías) up to 28 ha (e.g., San Telmo, Los Frailes). The pit lakes of the IPB show a large variety of water compositions, ranging from circumneutral and relatively low metal contents (e.g., Los Frailes pit lake, with pH 7.2, 0.07 mg/L Fe, 1 mg/L Al, 0.01 mg/L Cu, and 30 mg/L Zn) to extremely acidic and metal-enriched solutions (e.g., Corta Atalaya pit lake, with pH 1.2, 36.7 g/L Fe, 1.9 g/L Al, 3 g/L Cu and 6.7 g/L Zn; Table 1), with a general pattern of increasing dissolved solids content at decreasing pH. However, with the cited exceptions of Corta Atalaya and Los Frailes, a typical pit lake of the IPB shows a pH value around 2.6 (2.2-4.7), total Fe chiefly composed of Fe(III), average values of dissolved SO₄²⁻ around 4 g/L, and metal contents (average values) in the order of 265 mg/L Fe, 123 mg/L Al, 34 mg/L Mn, 20 mg/L Cu, and 31 mg/L Zn, in addition to around 90 µg/L As, 100 µg/L Cd, 1100 µg/L Co, 650 µg/L Ni, and 120 µg/L Pb (Table 1).

The lithology of the rock substrate, with abundance of massive sulphide (especially pyrite) and aluminosilicates, and scarcity of carbonates, is undoubtedly determining the water chemistry of the IPB mine pit lakes. The high contents of Fe and SO₄²⁻ dissolved in the waters result from the oxidative dissolution of pyrite, whereas the rest of metals are thought to be the result of the subsequent dissolution of sphalerite (source of Zn, and minor Cd), chalcopyrite (source of Cu and Fe), galena (Pb), arsenopyrite (As, Fe), tetrahedrite-tennantite (Fe, Cu, Zn, As, Sb), rhodocrosite (Ca, Mn) and gangue aluminosilicates like feldspars (Al, K, Na, Ca), chalcostite (Al, Fe, Mg, Co, Ni) and sericite-muscovite (Al, Na, K). In addition to these primary sources, the dissolution of secondary sulphate salts (see below) must have been another control of the pit lake water chemistry, especially during the initial flooding phases.

MINERAL PHASES ASSOCIATED TO AMD: ENVIRONMENTAL SIGNIFICANCE

As can be deduced from the above stated chemical compositions, iron, aluminium, magnesium, calcium and silicic acid are involved, the most abundant metals dissolved in AMD (with Fe>Mg>Al>Ca>>Zn>Cu>Mn), so that the minerals that are commonly formed in these AMD environments are chiefly Fe(II), Fe(III), Al, Mg and Ca sulphates and (oxy)hydroxy sulphates. Some

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Acidic mine drainage</th>
<th>Average a</th>
<th>Acidic mine pit lakes</th>
<th>Average c</th>
<th>Extreme case d</th>
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<td>pH</td>
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<td>Co</td>
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<tr>
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<td>52</td>
<td>38</td>
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<tr>
<td>Ni</td>
<td>µg/L</td>
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<td>3.220</td>
<td>656</td>
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<tr>
<td>Zn</td>
<td>µg/L</td>
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<td>122</td>
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<td>µg/L</td>
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<td>V</td>
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<td>µg/L</td>
<td>65</td>
<td>6.756</td>
<td>27</td>
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</tbody>
</table>

The lithology of the rock substrate, with abundance of massive sulphide (especially pyrite) and aluminosilicates, and scarcity of carbonates, is undoubtedly determining the water chemistry of the IPB mine pit lakes. The high contents of Fe and SO₄²⁻ dissolved in the waters result from the oxidative dissolution of pyrite, whereas the rest of metals are thought to be the result of the subsequent dissolution of sphalerite (source of Zn, and minor Cd), chalcopyrite (source of Cu and Fe), galena (Pb), arsenopyrite (As, Fe), tetrahedrite-tennantite (Fe, Cu, Zn, As, Sb), rhodocrosite (Ca, Mn) and gangue aluminosilicates like feldspars (Al, K, Na, Ca), chalcostite (Al, Fe, Mg, Co, Ni) and sericite-muscovite (Al, Na, K). In addition to these primary sources, the dissolution of secondary sulphate salts (see below) must have been another control of the pit lake water chemistry, especially during the initial flooding phases.
common Fe, Al, Mg and Ca minerals associated to, and precipitating from AMD of the IPB, along with their respective formulae and usual pH ranges of occurrence, are given in Table 2. This table includes highly crystalline sulphate salts (e.g., melanterite, rozenite, copiapite, halotrichite) formed by evaporative processes from very acridic brines in small pools or in the margins of AMD-impacted streams, as well as nearly amorphous compounds of Fe(III) (schwertmannite, streams, as well as nearly amorphous pools or in the margins of AMD-impacted halotrichite) formed by evaporative processes. The formation of efflorescent sulphates by AMD, where iron has been partially oxidized and the pH is slightly higher (typically between 1.5 and 3). These sulphates are usually found as botryoidal (colliform-like) efflorescences of variable colour (turquoise blue to emerald green in the case of melanterite, white in the case of szomolnokite, orange to yellow in the case of the epsomite-hexahydrite series; Figure 3a-c), being normally zoned from the inner to the outer zones, and suggesting a paragenetic sequence of sulphates with distinct solubilities and degrees of dehydration. They are rarely found as monomineralleric phases, and most commonly consist in mixtures of Fe(II)-Fe(III)-Al-Mg hydrated sulphates. Gypsum is also very frequent as accicular crystals and efflorescences in mine adits and waste piles (Figure 3d). Stalactites composed of gypsum/copiapite-jarosite are observed in AMD discharge points. Chemical analyses of mixtures of these sulphates have revealed very high metal contents (e.g., average values of 2,800 ppm Cu and 9,000 ppm Zn, with Zn values eventually reaching percent units; Sánchez-España et al., 2005a). On the other hand, As contents of the sulphates are very low (195 ppm on average), whereas Co, Ni and Cd show average values of 240, 155 and 30 ppm, respectively. Because these sulphates are highly soluble, the first rainstorm events taking place in the early autumn usually imply the re-dissolution of large amounts of these salts accumulated during the spring-summer, and the subsequent incorporation of toxic metals to the rivers. Therefore, seasonal cycles of

### Table 2

<table>
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<tr>
<th>Mineral</th>
<th>Formula</th>
<th>pH range</th>
<th>Occurrence</th>
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<td>Melanterite</td>
<td>Fe³⁺SO₄²⁻·3H₂O</td>
<td>&lt;1.5</td>
<td>Efflorescences</td>
<td>Near pyrite sources</td>
<td>Very common</td>
</tr>
<tr>
<td>Roselite</td>
<td>Fe³⁺SO₄²⁻·4H₂O</td>
<td>-</td>
<td>Efflorescences</td>
<td>Near pyrite sources</td>
<td>Very common</td>
</tr>
<tr>
<td>Szomolnokite</td>
<td>Fe³⁺SO₄²⁻·H₂O</td>
<td>-</td>
<td>Efflorescences</td>
<td>Near pyrite sources</td>
<td>Very common</td>
</tr>
<tr>
<td>Copiapite</td>
<td>Fe²⁺Fe³⁺(SO₄)₂(CH₃OH)·2H₂O</td>
<td>1-2.5</td>
<td>Efflorescences</td>
<td>Mining areas of streams</td>
<td>Common</td>
</tr>
<tr>
<td>Coquimbite</td>
<td>Fe³⁺(SO₄)₂·9H₂O</td>
<td>-</td>
<td>Efflorescences</td>
<td>Mining areas of streams</td>
<td>Common</td>
</tr>
<tr>
<td>Rhomboclase</td>
<td>(H₃O)Fe⁺³(SO₄)₂·3H₂O</td>
<td>&lt;1</td>
<td>Efflorescences</td>
<td>Mining areas, evaporative pools</td>
<td>Rare</td>
</tr>
<tr>
<td>Basaluminite</td>
<td>Al₄(SO₄)(OH)₁₀·5H₂O</td>
<td>3.5-5.5</td>
<td>Efflorescences, precipitates</td>
<td>Highly acidic effluents, pools and pit lakes</td>
<td>Common</td>
</tr>
<tr>
<td>Alunogen</td>
<td>Al₂(SO₄)₃·17H₂O</td>
<td>&lt;1</td>
<td>Efflorescences, precipitates</td>
<td>Mining areas and margins of streams</td>
<td>Rare</td>
</tr>
<tr>
<td>Jurbaniite</td>
<td>Al(SO₄)(OH)·5H₂O</td>
<td>&lt;4</td>
<td>Efflorescences, precipitates</td>
<td>Mining areas and margins of streams</td>
<td>Rare</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>1-5</td>
<td>Efflorescences</td>
<td>Mining areas, margins of streams, pools</td>
<td>Ubiquitous</td>
</tr>
<tr>
<td>Ichthyocollicite</td>
<td>CaSO₄·2H₂O</td>
<td>-</td>
<td>Efflorescences</td>
<td>Mining areas, margins of streams</td>
<td>Rare</td>
</tr>
<tr>
<td>Coquimbite</td>
<td>Fe³⁺(SO₄)₂·9H₂O</td>
<td>1.5-2.5</td>
<td>Efflorescences</td>
<td>Mining areas of streams</td>
<td>Common</td>
</tr>
<tr>
<td>Halotrichite</td>
<td>Fe⁺²Al₂(SO₄)₄·22H₂O</td>
<td>1.5-2.5</td>
<td>Efflorescences</td>
<td>Mining areas and margins of streams</td>
<td>Very common</td>
</tr>
<tr>
<td>Goethite</td>
<td>Fe⁺³(OH)₂</td>
<td>-</td>
<td>Efflorescences, precipitates</td>
<td>Mining areas of streams</td>
<td>Very common</td>
</tr>
<tr>
<td>Ferrhydrite</td>
<td>Fe⁺³5HO₈·4H₂O</td>
<td>5-8</td>
<td>Efflorescences</td>
<td>Mining areas of streams</td>
<td>Very common</td>
</tr>
<tr>
<td>Ferruthoite</td>
<td>Fe⁺²2(SO₄)³·9H₂O</td>
<td>1.5-2.5</td>
<td>Efflorescences</td>
<td>Mining areas and margins of streams</td>
<td>Common</td>
</tr>
<tr>
<td>Rozenite</td>
<td>Fe⁺²SO₄·4H₂O</td>
<td>1.5-2.5</td>
<td>Efflorescences</td>
<td>Mining areas and margins of streams</td>
<td>Very common</td>
</tr>
<tr>
<td>Xanthosiderite</td>
<td>Fe⁺²5HO₈·4H₂O</td>
<td>5-8</td>
<td>Efflorescences</td>
<td>Mining areas and margins of streams</td>
<td>Very common</td>
</tr>
</tbody>
</table>

* Common pH range of the acidic waters associated with these mineral phases

### Formation of evaporative sulphate salts near the pyrite sources

The formation of efflorescent sulphates from AMD waters occurs throughout all the year, although it is especially abundant during spring and summer. The mineralogy of these soluble sulphates is closely associated with their spatial distribution and the pH of the brines from which these salts are precipitated (Nordstrom and Alpers, 1999a,b; Nordstrom et al., 2000; Jambor et al., 2000; Buckby et al., 2003; Velasco et al., 2005; Sánchez-España et al., 2005a; Romero et al., 2006). Thus, the Fe(II)-sulphates like melanterite, rozenite or szomolnokite are dominant in isolated and highly concentrated pools near the pyrite sources, under conditions typical of green, ferrous AMD with pH below 1, whereas rozenite and szomolnokite form by partial dehydration and the pH is slightly higher (typically between 1.5 and 3). These sulphates have been observed to follow a paragenetic sequence of dehydration and mineralogical maturation, with melanterite > rozenite > szomolnokite > copiapite > coquimbite > rhomboclase > halotrichite (Nordstrom and Alpers, 1999a,b; Jambor et al., 2000; Nordstrom et al., 2000; Buckby et al., 2003; Velasco et al., 2005). In the Iberian Pyrite Belt mining district, many evaporative sulphate salts have been reported from mine sites and from the margins of rivers severely affected by AMD pollution such as the Tinto and Odiel rivers (e.g., García García, 1996; Hudson-Edwards et al., 1999; Buckby et al., 2003; Velasco et al., 2005; Romero et al., 2005; Sánchez-España et al., 2005a, and in press). In the margins of acidic effluents, these soluble metal sulphates are usually found as botryoidal (colliform-like) efflorescences of variable colour (turquoise blue to emerald green in the case of melanterite, white in the case of szomolnokite, orange to yellow in the case of the epsomite-hexahydrite series; Figure 3a-c), being normally zoned from the inner to the outer zones, and suggesting a paragenetic sequence of sulphates with distinct solubilities and degrees of dehydration. They are rarely found as monominerallic phases, and most commonly consist in mixtures of Fe(II)-Fe(III)-Al-Mg hydrated sulphates. Gypsum is also very frequent as accicular crystals and efflorescences in mine adits and waste piles (Figure 3d). Stalactites composed of gypsum/copiapite-jarosite are observed in some AMD discharge points.
precipitation/re-dissolution of salts can seriously determine the water quality of AMD-impacted rivers. As an example, a seasonal pattern of background Cu and Zn values during the summer, followed by sharp increases in their concentrations during the first rainfalls in autumn, has been reported in rivers draining the IPB province (e.g., Tinto and Odiel rivers; Olías et al., 2004) and in many other mine districts (e.g., Alpers et al., 1994).

The formation-dissolution-precipitation cycle of melanterite in pyrite piles

The formation-dissolution-precipitation cycle of melanterite represents an important control of the aqueous composition of the acidic leachates draining pyrite piles. When oxygen and moisture are available, melanterite can be directly formed on the pyrite grain surfaces by the reaction:

$$\text{FeS}_2(s) + 3.5 \, \text{Fe}^2+ + 8\text{H}_2\text{O} \rightarrow \text{FeSO}_4\cdot7\text{H}_2\text{O}(s) + \text{H}_2\text{SO}_4$$  (9)

This mineral can either persist if the ambient humidity conditions are appropriate, or be transformed to less hydrated forms of ferrous sulphate such as rozenite (FeSO$_4$·4H$_2$O) or szomolnokite (FeSO$_4$·H$_2$O) or even mixed Fe$^2+$-Fe$^3+$ salts like copiapite (Fe$^2+$-Fe$^3+$SO$_4$·7H$_2$O$\cdot$OH$_2$·2H$_2$O) (Nordstrom and Alpers, 1999a,b; Frau, 2000), but regardless of the final mineral phase considered, these solids always store large amounts of Fe$^{2+}$ and SO$_4^{2-}$ in the piles.

Apparently, the simple dissolution of melanterite through reaction (10) does not produce acid, unless coupled with oxidation of Fe(II) and hydrolysis/precipitation of a ferric iron hydroxide (11):

$$\text{FeSO}_4\cdot7\text{H}_2\text{O}(s) \rightarrow \text{Fe}^2+ + \text{SO}_4^{2-} + 7\text{H}_2\text{O}$$  (10)

$$\text{FeSO}_4\cdot7\text{H}_2\text{O}(s) + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe(OH)}_3(s) + \text{SO}_4^{2-} + 2\text{H}^+ + 4.5\, \text{H}_2\text{O}$$  (11)

However, laboratory experiments carried out by Frau (2000) have demonstrated that the simple dissolution of melanterite is a fast acidity-producing mechanism without the participation of Fe$^{2+}$ oxidation. This author explained the production of acidity by the coupled reactions of Fe$^{2+}$ hydrolysis (12) and the SO$_4^{2-}$/HSO$_4^-$ buffer system (13):

$$\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(s) + \frac{1}{2} \text{O}_2 \leftrightarrow \text{Fe}^2+ + \text{SO}_4^{2-} + 7\text{H}_2\text{O}$$  (10)

$$\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(s) + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe(OH)}_3(s) + \text{SO}_4^{2-} + 2\text{H}^+ + 4.5\, \text{H}_2\text{O}$$  (11)

The acid Fe(H$_2$O)$_6$$^{2+}$ (Ka=10$^{-9.5}$) is stronger than the base SO$_4^{2-}$ (Kb=10$^{-12.1}$; Stumm and Morgan, 1996), so that the dissociation of melanterite is an acidity-generating process.

Once the acidic solutions emerge from the piles to the surface, flow downstream and accumulate in pools, the water is partly evaporated and therefore all solutes (including H$^+$) are re-concentrated. If the Fe$^{2+}$ and SO$_4^{2-}$ concentrations reach the solubility product constant for melanterite, this mineral may precipitate from the solution through reaction (14) until chemical equilibrium is attained:

$$\text{Fe}^2+ + \text{SO}_4^{2-} + 7\text{H}_2\text{O} \rightarrow \text{FeSO}_4\cdot7\text{H}_2\text{O}(s)$$  (14)

The presence and environmental significance of melanterite has been widely reported in the IPB mining district. For example, Buckby et al. (2003) reported the presence of melanterite in the banks of the Tinto river which had apparently precipitated from a highly acidic water (pH=0.4) draining a pyritic waste pile. Velasco et al. (2005) have also reported melanterite and rozenite forming directly from pyrite oxidation in a dried pool adjacent to a pyrite pile in the San Miguel mine, although these authors did not include water analyses in their study. The role of these sulphate efflorescences in the storage and transport of trace elements in stream waters polluted by acid mine drainage in Peña del Hierro mine, has been also reported by Romero et al. (2006). More recently, Sánchez-España et al. (in press) have reported the occurrence of melanterite crystals directly formed in green pools of extremely acidic water (pH=0.6) in San Telmo mine (Figure 3b; Table 1). This acidic liquor was close to saturation with respect to melanterite, and its composition was found to be influenced by dissolution of this mineral.

Mineral phases controlling the solubility of Fe(III) and Al

Although magnesium and calcium are
usually very abundant in most acidic effluents and pit lakes of the IPB, these elements are highly soluble and commonly behave conservatively, only precipitating as efflorescent sulphates (mostly as epsomite and gypsum, respectively) in evaporative pools or margins of acidic effluents and AMD-impacted rivers. Conversely, iron and aluminium are much less soluble and precipitate as the pH of the acidic discharges is increased. At pH values below 2, both iron and aluminium are chiefly dissolved, and these metals may only precipitate from highly concentrated brines from evaporative pools, where oversaturation of secondary sulphates (e.g., melaniterite, copiapite, halotrichite, jarosite, alunogen) is eventually reached. As pH increases (for example, by partial neutralization during mixing with pristine streams), iron is hydrolyzed and precipitates at pH~2.2, whereas Al tends to be hydrolyzed at pH~4.5-5.0 (Nordstrom and Alpers, 1999a; Bigham and Nordstrom, 2000; Figure 3f-h). The formation of these mineral phases plays an important role in the geochemical evolution of the AMD and pit lakes, as discussed below.

Iron (oxy)hydroxysulphates

The solid formed by precipitation of Fe(III) at pH 2.5-3.5 during mixing and neutralization of the AMD solutions of the IPB is usually schwertmannite (Sánchez-España et al., 2005a, 2006a,b, 2007b, 2008). This mineral is a poorly crystallized iron oxohydroxysulphate whose formation from acid-sulphate waters is described as follows (Bigham et al., 1994, 1996; Bigham and Nordstrom, 2000):

$$8 \text{Fe}^{3+} + \text{SO}_4^{2-} + 14 \text{H}_2\text{O} \rightarrow \text{Fe}_9\text{O}_4(\text{SO}_4)(\text{OH})_4 + 22\text{H}^+$$ (15)

In addition to schwertmannite, some other minerals of Fe(III) have been recognized, with a close relation between their occurrence and the water pH (Table 2). Jarosite is usually favoured to precipitate from very acidic solutions (Figure 3f), normally at pH<2. Schwertmannite precipitates near the discharge points at pH 2.5-3.5 (Figure 3g), whereas ferrihydrite usually forms in fluvial environments (as in the confluences between AMD and unpolluted rivers) at pH~5. These three minerals are meta-stable with respect to goethite, which is the most stable form of Fe(III) at low temperature (Bigham et al., 1996; Bigham and Nordstrom, 2000). Goethite can also precipitate from AMD, although its presence in the particulate fraction of AMD-impacted waters is very minor in relation to schwertmannite or ferrihydrite.

The chemical composition of schwertmannites analyzed in the IPB district includes minor amounts of SiO₂ (0.4-3.8 wt.% and Al₂O₃ (0.7-3.0 wt.%), which suggests either (1) some silicate (clay) contamination of samples, and/or (2) some degree of sorption/coprecipitation of Si and Al onto the schwertmannite particles. Samples formed by titration of acid solutions in the laboratory have shown SiO₂ contents of 0.4-1.5%, which strengthens the second possibility. Average compositions of the analyzed Fe minerals also include significant trace element contents (e.g., 23-12770 ppm As, 80-4800 ppm Cu, 5-6230 ppm Zn, Sánchez-España et al., 2005a, 2006b). This suggests variable sorption of dissolved trace metals onto the schwertmannite, ferrihydrite and jarosite mineral surfaces.

Iron terraces forming in AMD effluents

An outstanding example of iron precipitation in AMD systems is the case of the iron terraces, which are unique geomicrobiological systems which can provide highly relevant information about the interaction between microbes and their surrounding aqueous environments (Figure 4). These singular systems can represent, additionally, potential models for the study of ancient geological formations (e.g., banded iron formations, stromatolites; Brake et al., 2002, 2004), having been also proposed as models for the cycling of iron on Mars (e.g., Fernández-Remolar et al., 2004). Geochemical, mineralogical, morphological and microbiological evidences obtained in the highly acidic and Fer-Rich Tintillo river (Riotinto mines, Huelva; Sánchez-España et al., 2007b; Figures 1d and 4a) suggest that a number of organic and inorganic processes appear to control the formation and internal arrangement of these iron terraces (Figure 4a). The photosynthetically produced dissolved oxygen by eukaryotic microorganisms (green algae, euglenophites and diatoms), and the iron-oxidising metabolism of acidophilic prokaryotes are critical factors for the formation of TIFs, whereas abiotic parameters such as water composition, flow rate and velocity, or stream channel geometry, also appear to be essential variables.

Aluminum (oxy)hydroxysulphates

If compared with the Fe(III) solids, the aluminum minerals formed at pH~4.5-5.0 in the IPB mine sites are not so well characterized. These solids are nearly amorphous to XRD, although two broad reflections (near 7 and 20 °2θ) are usually recognized by XRD (Figure 2).

This diffraction pattern, along with their chemical composition, suggest that these waite Al precipitates probably consist of poorly ordered hydroxysulpha-
tes with composition intermediate between hydrobasaluminite and basaluminate (Figure 3h; see Bigham and Nordstrom (2000) and Sánchez-España et al. (2006b), and references cited therein). Alunite and aluminite have been also suggested to precipitate from waters with high concentrations of Al and sulphate (0.1M and 0.4M, respectively), although both minerals are rarely found as direct precipitates).

Hydrobasaluminite is metastable with respect to basaluminate, which forms by dehydration of the former. Basaluminate is a common Al hydroxysulphate in mine drainage environments, although it also tends to be transformed to alunite during maturation or heating (Bigham and Nordstrom, 2000). The hydrolysis of Al$^{3+}$ to form hydrobasaluminite may be written as follows:

$$4\text{Al}^{3+} + \text{SO}_4^{2-} + 22\text{H}_2\text{O} \Leftrightarrow \text{Al}_4(\text{SO}_4)\text{(OH)}_{12} \cdot 12\text{H}_2\text{O} + 10\text{H}^+$$

(16)

The formation of this mineral during neutralization of AMD can also imply a significant removal (by sorption) of toxic trace elements (e.g., Cu, Cr, Zn, U, etc.) from the aqueous phase (Sánchez-España et al., 2006b).

**Natural attenuation of metal concentrations due to metal precipitation and sorption**

Downstream from the sources, the geochemical evolution of AMD is usually controlled by (1) oxidation of Fe(II) to Fe(III), (2) progressive pH increase and dilution of metal concentrations by mixing with pristine waters, (3) hydrolysis and precipitation of different metal cations (e.g., Fe$^{3+}$, Al$^{3+}$) as pH increases, and (4) sorption of different trace elements (As, Pb, Cr, Cu, Zn, Mn, Cd) onto the solid surfaces of precipitated metal hydroxides/hydroxysulphates. The pH-dependent sequences of precipitation and sorption are very similar and follow the order:

$$\text{Fe(II)} > \text{Pb} > \text{Al} > \text{Cu} > \text{Zn} > \text{Fe(II)} > \text{Cd}$$

(Dzombak and Morel, 1990; Nordstrom and Alpers, 1999a). The overall result of these processes represents a mechanism of natural attenuation, as has been shown in AMD-impacted rivers of the IPB (Sánchez-España et al., 2005b, 2006a, 2007a, 2008).

As an example of this self-mitigating capacity, the graphs provided in Figure 5 show the spatial evolution of metal loadings in an acidic effluent emerging from a waste-pile in Tharsis mine (Sánchez-España et al., 2005b). This effluent emerged with a pH of 2.2, and subsequently converged with a number of small creeks of unpolluted water, thus provoking a slight but progressive pH increase from around 2 to values close to 5. This pH increase allowed the precipitation of Fe(III) (mostly schwertmannite) during the first 11 km of the AMD course (pH<3), and of Fe(III) and Al compounds (Al as amorphous hydro-basaluminite) during the next 9 kms of the stream course (pH 3-5). The evolution shows that the precipitation of Fe(III) resulted in a strong decrease of the total iron loading to around a tenth of its initial content at only 10 km from the source. The precipitation of Al compounds in the last reach also accounted for an important loss of the Al loading. Interestingly, both the Fe and Al solids acted as efficient sorbents for a number of trace elements. Arsenic (present mainly as HAsO$_4^{2-}$ species, as suggested by geochemical modelling with PHREEQC) showed a strong tendency to be adsorbed by the ferric iron colloids at low pH (<3), having been totally removed from the water at less than 10 km from the discharge point. Other trace metals such as Cr(VI) (mainly present as HCrO$_4^{-}$), was significantly sorbed onto the Al compounds formed at pH~4.5-5, also implying a total scavenging of this toxic element at 20 km from the source. Finally, divalent metal cations like Cu$^{2+}$, Zn$^{2+}$ and Mn$^{2+}$ behaved conservatively until pH~5, and then, they were only slightly removed by sorption onto the Al minerals during the final reach.

Such metal scavenging may imply important water quality improvements at a basin scale. For example, it has been estimated that only 1% of the total Fe and As dissolved load and around 20-40% of the total Al, Mn, Cu, Zn, Cd, Pb and SO$_4$ dissolved load initially released from the mine sites, was transferred from the Odil river basin (including more than 25 studied mines) to the Huelva estuary in 2003 (although this still represented very high metal fluxes; Sánchez-España et al., 2005a). Most of the iron and arsenic load seems to remain in solid form near the pyrite sources within the mines, mainly in ochreous Fe(III) precipitates covering the stream channel, whereas the rest of metal cations (Al, Cu, Zn, Mn) migrate further downstream.

**CONCLUSIONS**

The microbially-catalyzed oxidation of pyrite and other sulphides present in piles, tailings, pits, shafts and galleries of the presently abandoned mines of the Iberian Pyrite Belt, generates an important volume of highly acidic and metal-polluted water which drains the mining areas and transport this acidity and metal content to streams, rivers and dumps, thus provoking and important environmental damage as regards to the water quality of the water resources. The singular chemical composition of the acidic mine waters, dominated by a low pH and high concentrations of sulphate and metals (especially Fe and Al), gives rise to a number of
characteristic mineral phases that precipitate downstream from the discharge points as the acidic waters are neutralized by mixing with pristine waters (e.g., schwertmannite at pH > 2.5, hydrobasaluminite at pH > 4.5) and/or by evaporation in the margins of streams or in pools (e.g., eflorescent sulphate salts like melanterite, rozenite, epsomite, hexahydrite, coquimbite, halotrichite, copiapite, etc.). The iron and aluminum precipitates usually sorb trace metals and are thus responsible for a certain degree of natural attenuation, although this self-mitigating mechanism can be reversible and the trace metals may be released to the solution phase as the mineral phases are mineralogically matured (e.g., transformed to more stable phases). The sulphate salts are also temporal sinks of acidity and metals (especially Fe, Al, Cu and Zn), but these elements are readily re-incorporated to the aqueous phase during rainstorm events. The problem of acid mine drainage in the IPB is of regional scale, and any attempt to mitigate or attenuate its environmental impact should be afforded by all the government authorities involved in decision making and environmental quality regulation.

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