Geochemistry and mineralogy of AMD in the Iberian Pyrite Belt (Spain).

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1 Introduction

A long mining history has left the Iberian Pyrite Belt (IPB) province (Huelva, SW Spain) with a legacy of abandoned waste rock piles, tailings ponds and pit lakes. These mine wastes are sources of environmental contamination, mostly in the form of acid mine drainage (AMD). These acid waters transfer dissolved metals (Fe, Al, Mn, Cu, Zn, Cd, As, Pb), sulphate and acidity to the Odiel river, reducing aquatic life to just a few species of algae and bacteria that are specially adapted to these environments.

There is evidence of this mine-related pollution at the Odiel river mouth (flow-rate 320 Hm^3/year), where pH values of 3.0±0.5, and average concentrations of 16 mg/L Fe, 12 mg/L Mn, 7 mg/L Cu, 20 mg/L Zn and 66 μg/L Cd, are typical (Confederación Hidrográfica del Guadiana, *unpubl. report*).

This paper summarises the preliminary results of a project focused on the geochemistry of AMD in the IPB, and its effects on the waters of the Odiel basin. The mineralogy and chemistry of mine drainage precipitates and soluble sulphates usually found in these mine environments is also discussed.

2 Geology

The Odiel fluvial system drains an area of 2,300 km^2 in the province of Huelva, from Sierra de Aracena in the North, to the Huelva estuary in the South, recieving most of the acid mine waters from the IPB mines (Fig. 1).

The IPB comprises more than 80 mines, including historical deposits like Río Tinto, Tharsis, La Zarza, Sotiel, Aznalcóllar, Aljustrel, Loussal and Neves-Corvo. It still hosts 1,700 Mt of sulphides, including 35 Mt Zn, 14.6 Mt Cu, and 13 Mt Pb (Leistel et al., 1998). This mining has resulted in a total volume of 158 Hm^3 of mine wastes (IGME, *unpubl. report*).

Ore mineralogy is dominated by fine-grained (framboidal, colloform), brecciated pyrite, in addition to sphalerite, chalcopyrite and galena, whereas gangue minerals include abundant silicates (quartz, chlorite, sericite), and minor carbonate and barite (Sánchez España, 2000). The practical absence of carbonates to neutralize the acidity released by pyrite oxidation favours the subsequent formation of AMD.

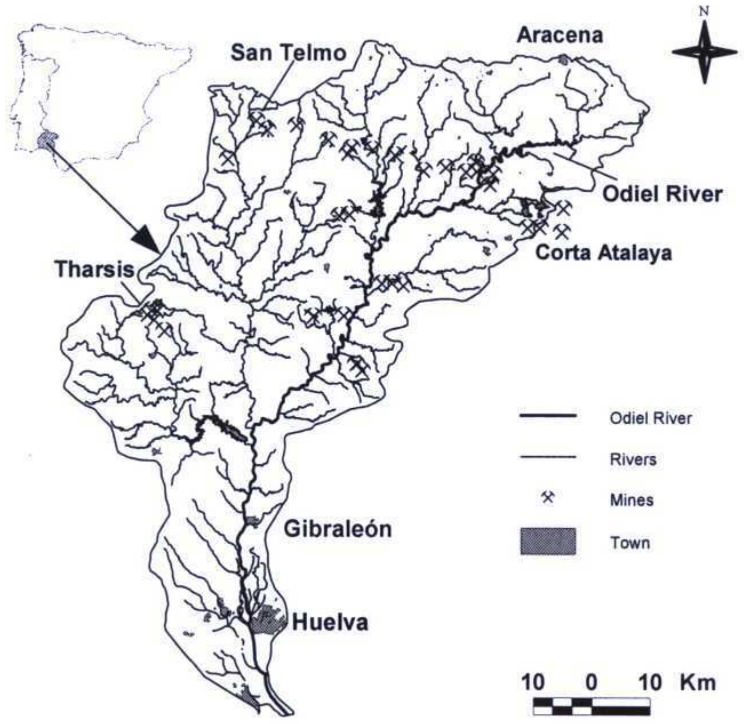

Fig. 1. Location of the Odiel river basin and the most important IPB mines.

3 Methodology

Field work included detailed identification of the different AMD discharges, *in situ* measurement of pH, Eh, temperature (T), dissolved oxygen (DO), electrical conductivity (EC), and flow rate, as well as sampling of AMD and stream waters, sediments and precipitates. The parameters pH, Eh, DO and EC were measured with portable HANNA instruments calibrated against supplied calibration standards. Most AMD discharges have been sampled and analyzed several times through the period 2003-2004, in order to study seasonal variations in chemistry and flow rate.

Water samples for chemical analyses were filtered with 0.45 μm cellulose acetate membrane filters, stored in 125-polyethylene bottles, acidified with HNO_3, and cooled during transport.

Consistent solid samples (ferric crusts, sulphate salts) were directly stored in 125 ml-polyethylene bottles. Ochreous, water-saturated, colloidal precipitates were taken with 60 ml-shringe and/or by filtering large volumes of acid water with suction kits.

All chemical compounds have been analyzed in the laboratory, except acidity and Fe^{2+}/Fe^{3+} concentration, which were calculated *in situ* by colorimetric, titration-based tests using HACH Instruments.

Water samples have been analyzed by AAS (Na, K, Mg, Ca and Fe), and ICP-MS (major and trace metals, Si and Cl). Sulphate was gravimetrically measured as $BaSO_4$.

Solid samples were analyzed by XRF for the elements Si, Al, Fe, Ca, Ti, Mn, K, Mg and P, a LECO elemental analyzer was used for total S, and ICP-MS or AAS for other major and trace metals. Also, these minerals have been mineralogically characterized by powder XRD.

4 Characterization of AMD

By May-2004, 62 AMD discharges from 25 different mines of the IPB had been studied. Acid mine waters comprise leachates from waste rock piles (50%), tailings impoundments seepages (10%), and outflows from mine adits (30%), mine holes (7%), and pit lakes (3%). These mine sites include some of the largest mine districts in the IPB (Río Tinto, Tharsis, La Zarza, San Telmo, Sotiel-Almagrera) and many others which, together, represent virtually the entire volume of the AMD discharged to the Odiel river.

Both water volume and chemical composition of AMD are very variable, either seasonally or among different deposits, with the most important AMD discharges coming from the largest deposits.

Based on field evidence, three main hydrogeochemical facies of AMD can be recognized in the area, namely: (1) *ferrous* (pH=1.4-4.0, Eh=400-640 mV, DO~0-30% sat., Fe^{2+}/Fe_t~0.5-1, green-coloured), (2) *ferric* (pH=2.5-3.5, Eh=640-800 mV, DO=50-100% sat., Fe^{2+}/Fe_t~0.1-0.5, yellow to reddish-coloured), and (3) *aluminous* (pH=4.0-5.7, Eh≤500 mV, DO~100% sat., Fe^{3+}~0 mg/L, white-coloured).

This distinction is only valid at the source points (mine adits, waste pile seepage), as iron oxidation and hydrolysis at pH~2.5-3 is very fast and therefore provokes the transition from ferrous/anoxic to ferric/suboxic and, in some cases, aluminous/oxygen-saturated facies, within a few kilometres of the discharge point.

5 Chemistry

The mine water chemistry of these discharges includes cases with extreme concentrations of dissolved sulphate (up to 44 g/L) and metals (up to 7.7 g/L Fe, 2.6 g/L Al, 1.4 g/L Zn, 435 mg/L Cu and 440 mg/L Mn). Trace metals are also significantly enriched (maximum values of 17 mg/L As, 8 mg/L Cd, 48 mg/L Co, 17 mg/L Ni, 725 µg/L Pb). Other elements like U and Th (peak values of 1,100 and 400 µg/L, respectively) are also evident in unusually high concentrations.

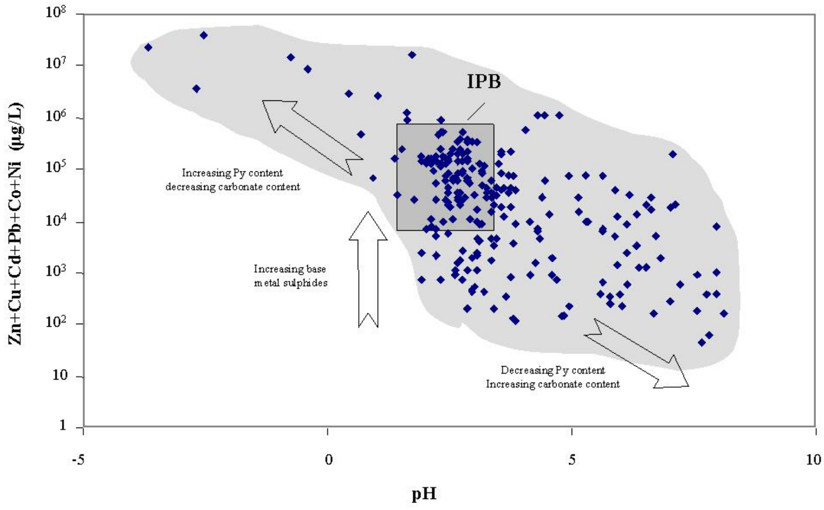

Fig. 2. Ficklin diagram for AMD compositions of the IPB province. Shaded area encloses world-wide AMD of diverse deposit types (from Plumlee et al., 1999).

These metal concentrations are among the highest of those reported for world-wide AMD of diverse deposit types (Fig. 2), and suggests significant pyrite oxidation and dissolution, as well as oxidative dissolution of other sulphides (chalcopirite, sphalerite, galena, arsenopyrite)Additionally, the maximum concentrations of Ca (529 mg/L), Na (206 mg/L), K (36 mg/L), Mg (2.9 g/L), and Cl (0.6 g/L) found in the AMD, suggest the dissolution of the abundant aluminosilicates (K-feldspar, albite, sericite, chlorite) present in the oxidising mine wastes.

Metal concentrations, however, decrease gradually downstream from the source points due to: (1) dilution by unaffected stream waters that also increase pH values, and (2) subsequent precipitation of Fe and Al-phases at pH values around 2.5-3.0 and 4.0-4.5, respectively.

5.1 Redox chemistry

Field Eh data are strongly correlated with the Fe^{2+}/Fe^{3+} ratio, and provide relevant information about the redox chemistry of AMD and the oxidation rate of ferrous to ferric iron. In fact, the variation of Eh with the Fe^{2+}/Fe^{3+} ratio is well adjusted to a sigmoidal, Nernst-type curve which allows a quantitative estimation of the ferrous to ferric iron ratio of the acid mine waters (Fig. 3).

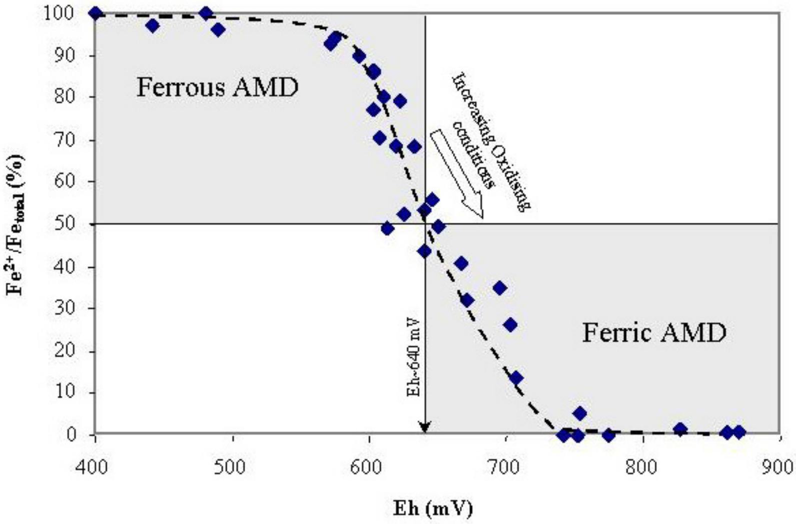

Fig. 3. Relation between Eh and oxidation state of iron (Fe^{2+}/Fe_t ratio), with distinction between the fields of *ferrous* and *ferric* types of AMD in the Odiel river basin, Spain.

5.2 Acidity

Acidity is very variable, with a range of 1,000-30,000 mg/L $CaCO_3$ eq. among the different mine effluents. It is strongly positively correlated with total iron and aluminium concentrations (r=0.95, $p<0.01$). In fact, titration curves are clearly marked by two sharp slope breaks at pH~2.7 and 4.0 (Fig. 4), which indicate hydrolysis of dissolved Fe^{3+} and Al^{3+} ionic species.

Additionally, Fe^{2+} hydrolysis causes slope breaks at pH~6.5-7.0 in the ferrous samples that were not oxidized with H_2O_2 before titration, although this process has rarely been observed in the field.

Thus, it is concluded that iron and aluminium act as chemical buffers, stabilizing the acid solutions at pH values around 2.7 and 4.5.

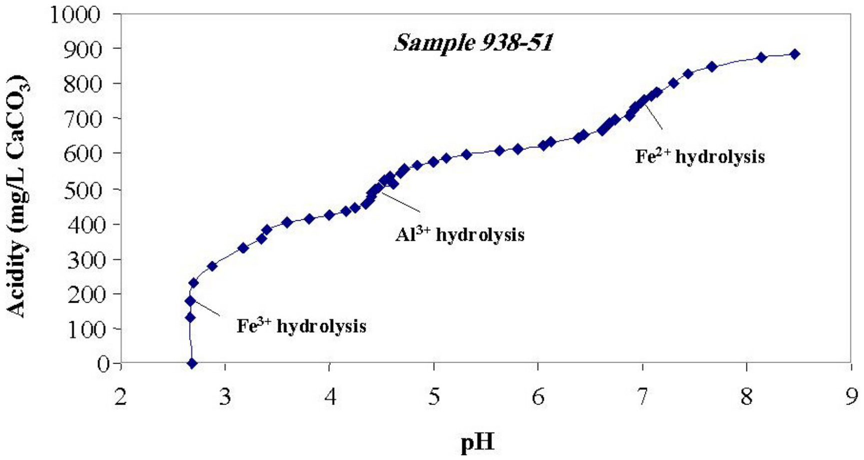

Fig. 4. Titration curve for AMD sample 938-51 (Cueva de la Mora mine).

6 Mineralogy

A number of mineral phases, including hydroxides, oxyhydroxides, oxy-hydroxysulphates and soluble hydrated sulphates, form as natural products of pyrite weathering and Fe oxidation/hydrolysis. The formation of these minerals is favoured by processes such as (1) pH increase when AMD solutions mix with stream waters, (2) oversaturation in the parent solutions due to extreme sulphate and metal concentrations, or (3) capillarity and evaporation of AMD in saturated soils during the summer season.

6.1 Hydroxides/oxyhydroxides/oxyhydroxysulphates

The minerals formed in mine sites and affected streams mainly consist of schwertmannite, with variable amounts of jarosite and/or goethite.

Although schwertmannite is poorly crystallized, it is possible to recognize characteristic reflections in the XRD patterns (Fig. 5). These diffractometric results, coupled with pe-pH data of parent acid solutions (Fig. 6), and chemical composition of these precipitates ($(Fe/S)_{molar}$=5.3), are conclusive evidence for schwertmannite identification.

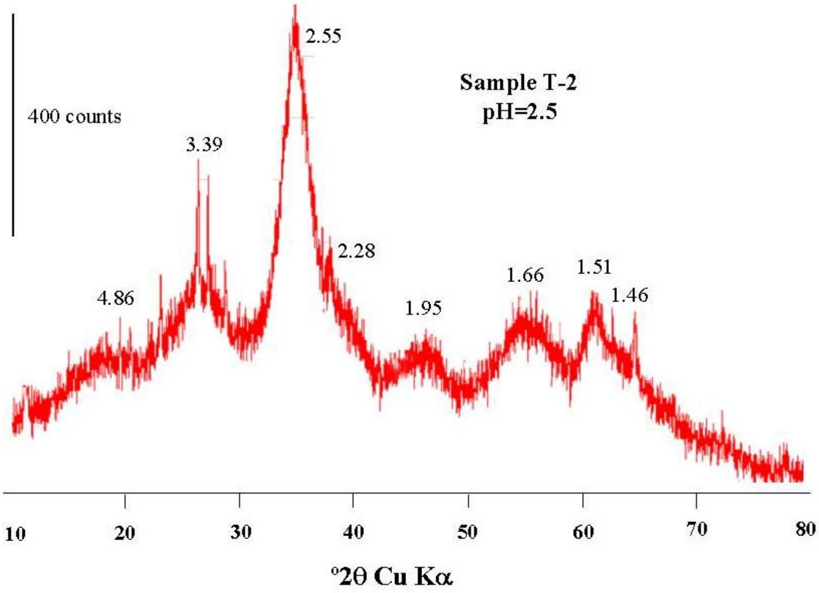

Fig. 5. XRD pattern of a schwertmannite sample from Corta Atalaya (Río Tinto). The d-spacing of characteristic peaks (in Å) is also indicated.

Additionally, 2 line-ferrihydrite and an Al-bearing amorphous phase, have been identified in samples collected in the Odiel river (pH~7; $(Fe/S)_{molar}$=12.1). Two artificially obtained samples after titration of AMD are composed of a mixture of schwertmannite and an XRD-amorphous, white-coloured, Al-phase probably consisting of basaluminite.

Average compositions of the analyzed ferric precipitates include significant trace metal contents (24-13,000 ppm As, 80-4,800 ppm Cu, 5-6,230 ppm Zn, 4-1,100 ppm Pb, 4-274 ppm Co, 4-452 ppm Ni, 1-31 ppm Cd), indicating co-precipitation and/or adsorption of these metals onto the schwertmannite, ferrihydrite and jarosite mineral surfaces.

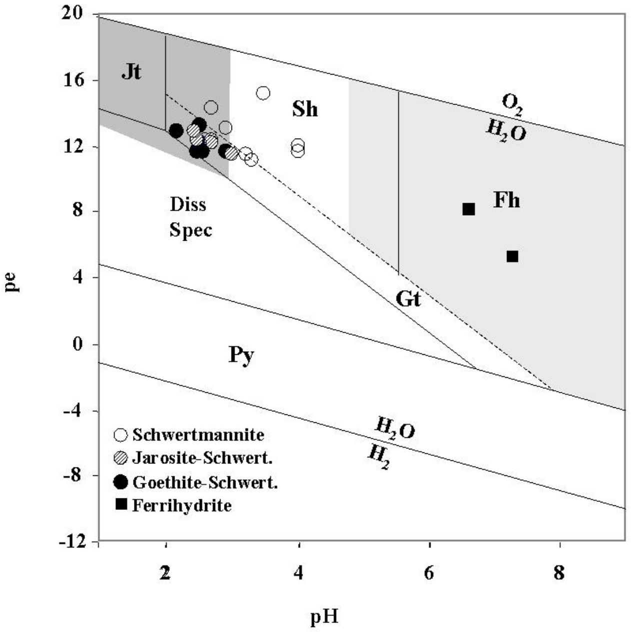

Fig. 6. pe-pH plot for AMD-related phases in the IPB (stability fields for mineral phases adapted from Bigham et al., 1996).

6.1.1 Solubility of Fe- and Al-phases

The reported chemical and mineralogical results agree with performed solubility calculations of mineral phases. These calculations have been made with the PHREEQC 2.0 geochemical code (Parkhurst and Appelo, 1999). At the geochemical conditions normally found in the ferric-type AMD systems, schwertmannite, jarosite, goethite and hematite are always supersaturated (SI>0) in the acid solutions.

On the other hand, ferrihydrite and some amorphous to poorly crystalline Al-phases (basaluminite, jurbanite, alunite, gibbsite) are always undersaturated (SI<0), usually being dissolved under these conditions.

This is well illustrated in Fig. 7, where the solubility evolution of these minerals is plotted along a km-scale profile of an AMD-system.

These solubility calculations, as well as kinetic considerations, suggest that schwertmannite controls Fe^{3+} solubility in the AMD solutions under pH~2-3.5, whereas Al^{3+} solubility would be mainly controlled by amorphous Al-phases like basaluminite at the pH range of 4-5.

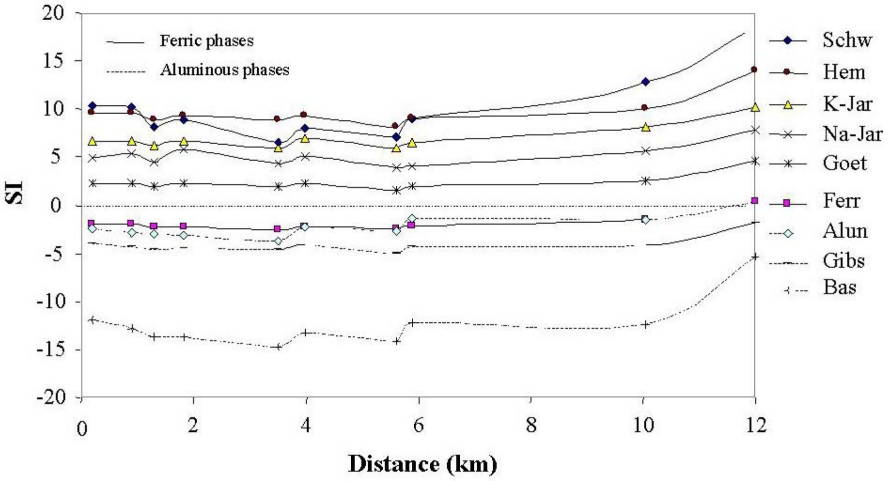

Fig. 7. Evolution of the saturation index (SI) of ferric and aluminous minerals along the course of an AMD-polluted, acid fluvial system in Corta Atalaya.

6.2. Soluble Sulphates

Efflorescent sulphate salts are ubiquitous around waste piles and ore dumps during the dry season. These minerals commonly consist of mixtures of Mg-Fe-Al hydrated sulphates such as epsomite, hexahydrite, pickeringite, szomolnokite, rozenite, halotrichite, copiapite, and alunogen. Gypsum is also frequent in mine adits and waste piles.

Base metal concentrations of the analyzed sulphates (average values of 2,800 ppm Cu and 9,000 ppm Zn) are significantly higher than those of schwertmannite (810 ppm Cu and 750 ppm Zn on average). On the other hand, As contents of sulphates are very low in comparison with those of schwertmannite (195 ppm and 1,700 ppm, respectively), whereas Co, Ni and Cd show average values of 240, 155 and 30 ppm, respectively.

7 Conclusions

The study of acid mine drainage in the Iberian Pyrite Belt provide an exceptional example of the environmental impact that uncontrolled extensive mining can inflict on a fluvial system.

Chemistry of AMD is highly dependent on the mineralogy of mine wastes, revealing a high dissolution rate of pyrite and the accompanying sulphides and aluminosilicates in the waste piles and ore dumps.

Redox chemistry of AMD is governed by the iron oxidation rate, being highly correlated with the Fe^{2+}/Fe^{3+} ratio.

The acidity potential of AMD is controled by the concentration of Fe^{3+} and Al^{3+}, which act as buffers of the acid waters at pH 2.7 and 4.5, respectively.

Finally, a good correlation between pH and mineralogy of the AMD has been found, with ferrihydrite precipitating at pH>6, basaluminite at pH>4, and schwertmannite-jarosite-goethite at pH~2-3.5.

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References

Bigham JM, Schwertmann U, Traina SJ, Winland RL, Wolf M (1996) Schwertmannite and the chemical modelling of iron in acid sulphate waters. *Geochim. et Cosmochim. Acta*, 60-12, 2111-2121

Leistel JM, Marcoux E, Thiéblemont D, Quesada C, Sánchez A, Almodóvar GR, Pascual E, Sáez R (1998) The volcanic-hosted massive sulphide deposits of the Iberian Pyrite Belt. Review and preface to the Thematic issue. *Miner. Deposita*, 33, 2-30

Parkhurst DL, Appelo CAJ (1999) User´s guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS Report 99-4259, Denver, 312 pp

Plumlee GS, Smith KS, Montour MR, Ficklin WH, Mosier EL (1999) Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. *Reviews in Econ. Geology*, 6B, 373-432

Sánchez-España FJ (2000) Mineralogy and geochemistry of massive sulphide deposits in the Northern Iberian Pyrite Belt (San Telmo-San Miguel-Peña del Hierro), Huelva, Spain. *PhD Thesis*, Universidad del País Vasco, 307 pp