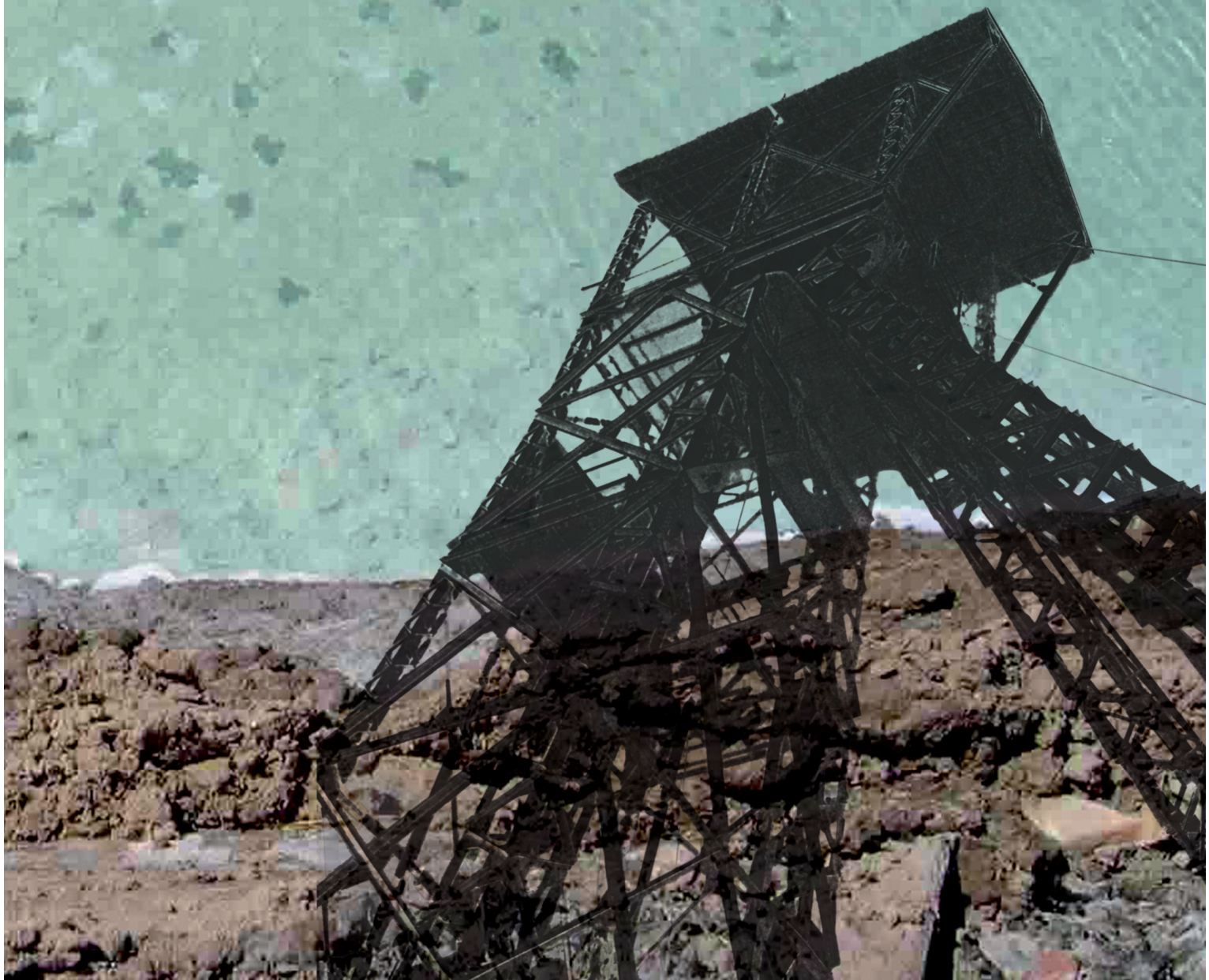
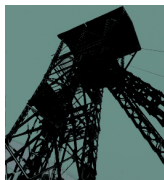


SESIÓN 3. MÉTODOS MATEMÁTICOS Y ANALÍTICOS





SALT EFFLORESCENCES IN THE IBERIAN PYRITE BELT: OCCURRENCE AND DISTRIBUTION

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ABSTRACT

The evolution of sulfide wastes promotes acid mine drainage and phenomena of supergenetic neoformation. These contribute to a secondary paragenesis, often dominated by salt efflorescences. These can be used as mineralogical indicators of reactivity conditions and of AMD potential. The present study shows the salt efflorescences that develop in the Spanish sector of the Iberian Pyrite Belt, as a result of the strong acid mine drainage observed in this region. The obtained results showed dominance of metallic sulfates. Depending on the proximity to the sulfide sources, there are different types of assemblages. Iron and copper minerals dominate inside the mining areas, whereas magnesium sulfates occur more abundantly in the receiving river network.

Keywords: Acid mine drainage, AMD-precipitates, Sulfates, Iberian Pyrite Belt, Spain

1. INTRODUCTION

The overall process of acid mine drainage production is accompanied by the development of newly-formed solid phases that result from processes such as evaporation, oxidation, hydrolysis and neutralization (Hammarstrom et al., 2005; Jerz and Rimstidt, 2003). Thus, these phases are generically called AMD-precipitates. They are mainly represented by efflorescent salts and by ochre products composed of iron oxyhydroxides and iron oxyhydroxysulfates. The current study presents data about the AMD-precipitates that compose typical mineralogical assemblages of the Spanish sector of the Iberian Pyrite Belt (IPB).

The study comprises the entire fluvial network of this metallogenic province, including the main river basins that are receiving AMD discharges (Guadiana-Chanza, Tinto, Odiel and Guadiamar (Figure 1).

The Iberian Pyrite Belt assumes as a paradigmatic region for such type of study, taken in consideration features, such as antiquity (more than 5000 years of metals exploitation), and environmental contamination related to the mining legacy. The region is

known as one of the largest accumulations of pyritic wastes in the World (e.g., Davis et al., 2000; Sánchez-España et al., 2005) with an estimation of AMD-affected land of about 4,847 ha. Taking into account this figure and combining it with the annual average precipitation it gives about 31,504,000 m³/year of discharging water affected by the presence of sulfides (Grande et al., 2013). The Figure 2 illustrates the typical aspect of the contaminated rivers in the IPB, while table 1 presents average data of Tinto River, which is well-known by its AMD contamination. The region has a Mediterranean climate, which can be classified as semi-arid, due to low precipitation rates. Annual precipitation is about 630 mm/year, being mostly concentrated in the wet season from October to May. Monthly precipitation ranges from 3 to 121 mm, corresponding to June and December, respectively. Average annual temperature is 17.1°C, January being the coldest month with a mean of 9.8°C, while in the summer, July and August have the highest temperatures (mean 25.7 °C) (Instituto Nacional de Meteorología; unpublished data). It should be noted that sampling for this study was performed in July, with temperature and relative humidity readings consistent with the typical mean annual values (temperature up 25°C and relative humidity around 50%). Taken into account the mining, environmental and climate contexts described below, AMD-precipitates assume critical relevance as indicators of the reactivity of the AMD solutions and of the contamination magnitude in the IPB. Therefore, the main objectives of the present study are: i) to present an inventory of AMD-precipitates in the IPB; ii) to know local temperature and humidity conditions that control stability of secondary phases; iii) to present the main characteristics of the efflorescent minerals, such as chemical composition, morphology, typical assemblages, and iv) to evaluate their role controlling retention/mobilization cycles of acidity, sulfate and metal(oids) in the river network.

2. METHODOLOGY

The sampling campaign was performed under strong evaporation and low flow hydrological conditions (July 2015). The sampling network comprised two distinctive environments. One refers to waste-dumps, seepages and leachates inside the mining complexes, representing the main sources of AMD. The other environment corresponds to the watercourses, which represent the global receiving system. For this last, eight sampling areas were established, in order to represent the affected sub-basins defined in the IPB by Perez-Ostalé (2014). At each sampling

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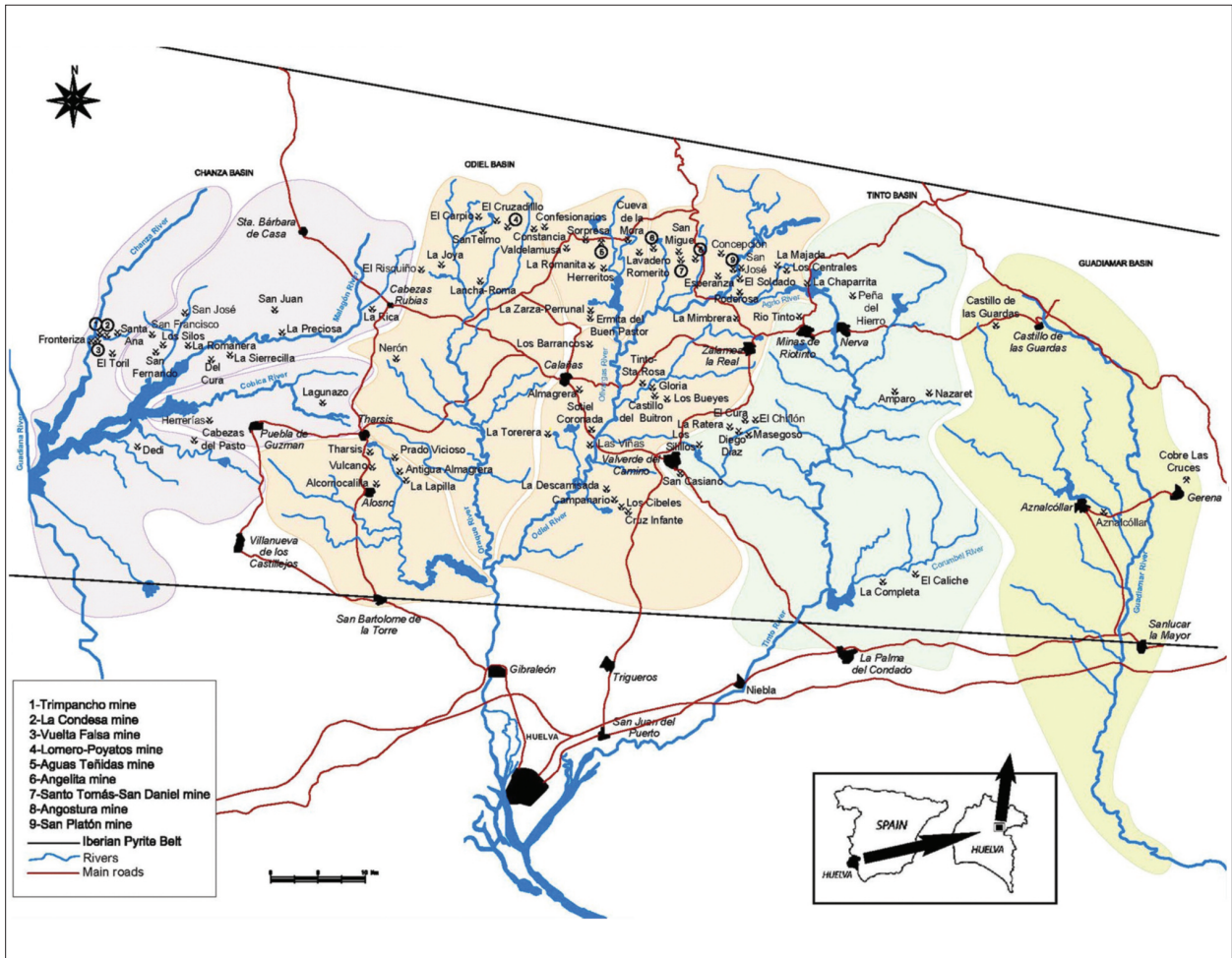


Figure 1 – Location map of the Iberian Pyrite Belt, including the main watersheds (Grande et al., 2013).



Figure 2 – Deposition of ochre products and filamentous algae that give typical aspects to the AMD-affected river network. Images from Tinto River (left) and Odiel River (right).

TABLE 1 – AVERAGE WATER PROPERTIES OF THE TINTO RIVER NEAR THE MINE (UPSTREAM-NAYA) AND DOWNSTREAM -NIEBLA). DATA FROM DE LA TORRE ET AL. (2011)

Sampling station	pH	CE (µS/cm)	SO ₄ (mg/l)	As (mg/l)	Cd(mg/l)	Cu(mg/l)	Fe (mg/l)	Zn (mg/l)	Mn (mg/l)
Naya	2.50	12,760	8,257	0.640	2.00	329.8	2,353	494.6	141.6
Niebla	2.53	2,239	371.0	0.042	0.094	23.84	316.4	20.26	10.36

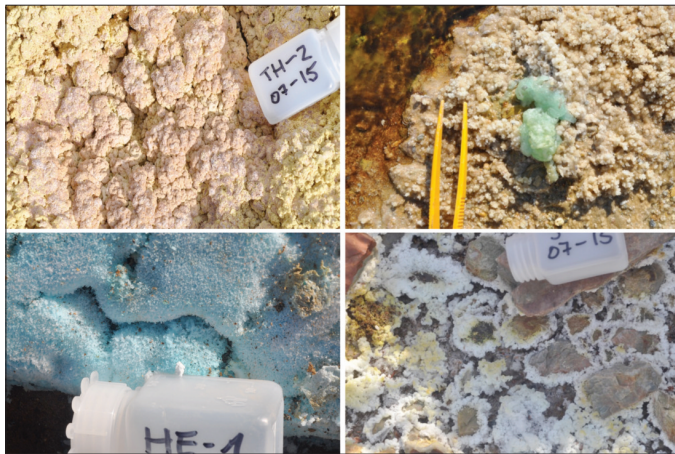


Figure 3 - Field images of typical sulfate efflorescences. a) yellow-reddish crustified efflorescences of copiapite and coquimbite from Tharsis mine; b) globular green efflorescences of melanterite from Riotinto mine; c) Blue powder efflorescences of chalcantite from Herrerías mine; d) white globular cotton-like bunches of epsomite from San Telmo mine.

area, the AMD-precipitates were collected in order to represent the field variability, given rise to approximately 200 complex samples, mainly composed by efflorescent salts. Inside each sampling area there were a variable number of samples, which were meant to cover the diversity observed in the field on the basis of macroscopic properties. Occurrence modes, color, and texture were used to define this diversity.

Efflorescent salts and crusts were examined for morphology, photographed and sorted by binocular microscopy. Then, samples were lightly ground and analyzed by X-ray powder diffraction (XRD) with a Philips X'pert Pro-MPD diffractometer, using Cu K α radiation. Morphological and compositional features were analyzed by scanning electron microscopy (on gold or platinum-coated samples) with a LEICA S360 microscope, combined with an energy dispersive system (SEM-EDS, 15 keV).

3. RESULTS AND DISCUSSION

In the present work, the inventory of AMD-precipitates is mainly focused on the minerals that occur as efflorescences, resulting from evaporative processes in the semi-arid condition of the territory under study.

Figure 3 are field images, showing occurrence modes of salt efflorescences from different mines in the IPB.

Most of the identified minerals are sulfates or oxyhydroxysulfates. Sulfates usually occur as efflorescences of varied colors (white or grayish, yellowish, green, orange, and blue) and habit (rosaceous, botryoidal, or very fine powders).

The inventory of AMD-precipitates put in evidence the distribution of the identified phases, allowing differentiating the sampling conditions:

- One relates to the mineralogical phases occurring in the river network, corresponding to samples taken in each of the eight basins. Here, in the river network, some of the most abun-

dant minerals are: Epsomite, gypsum, hexahydrate, alpersite, pickeringite, alunogen, tamarugite and jarosite.

- A second one comprises the AMD-precipitates occurring in representative abandoned mining complexes of the Iberian Pyrite Belt. Among the dominant minerals are: melanterite, chalcantite, rozenite, gypsum, epsomite, hexahydrate, copiapite, magnesiocopiapite, aluminocopiapite, ferricopiapite, pickeringite, halotrichite, apjohnite (?), rhomboclase, szomolnokite, coquimbite, paracoquimbite, starkeyite, butlerite, fibroferrite, jarosite, and schwertmannite.

To exemplify the properties of the salt efflorescences, Figure 4 shows the morphologies of one of the most typical assemblages found in the river systems, which is dominated by magnesium and aluminum sulfates as demonstrated by the respective XRD. Although XRD allowed identifying only epsomite and tamarugite, the SEM analysis showed the growth of acicular aggregates of pickeringite over the magnesium sulfate.

The other scenario, correspondent to the efflorescences that occur near the sulfide sources, is exemplified by the SEM results of two minerals occurring in the the Riotinto Mines: butlerite and fibroferrite (Figure 5).

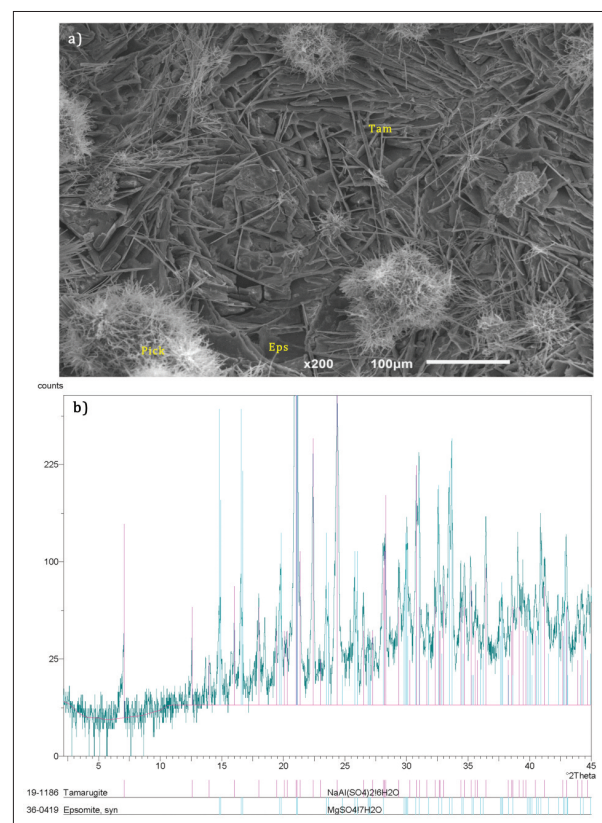


Figure 4 – SEM-ES image of a sample collected in the Meca River (a) and respective XRD (b). The mineralogical assemblage is dominated by epsomite (Eps; MgSO $_4$ 7H $_2$ O; mass aggregates), accompanied by tamarugite (Tam; NaAl(SO $_4$) $_2$ 6H $_2$ O; plate habit) and pickeringite (Pick; MgAl $_2$ (SO $_4$) $_4$ 22H $_2$ O) acicular aggregates).

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The above results show that in distal conditions (in the receiving watersheds), the mineralogical assemblages are dominated by magnesium and aluminum sulfates. Usually jarosite (and or goethite) are the only iron minerals. Meanwhile, near the sulfide sources, in the mining complexes, there is higher mineralogical diversity. In such proximal conditions, in addition to magnesium sulfates, iron and copper sulfates assemblages are very common. Often, the iron sulfates put in evidence specific paragenetic relationships, namely controlled by hydration/dehydration cycles. For example, the sequence melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) – rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) – szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) was observed in distinctive environments, with melanterite always near the water, then, for the most humid conditions, while rozenite and szomolnokite appear usually in more dry conditions, forming association with other iron minerals.

4. CONCLUSIONS

The present paper presents the salt efflorescences that occur in the entire Spanish sector of the Iberian Pyrite Belt. The obtained inventory stressed the distribution of sulfate efflorescences. In proximal conditions, iron and copper sulfates are very common. In more distal conditions, the depletion of iron is accompanied by the dominance of magnesium and aluminum sulfates. Here, iron occurs mainly in the oxyhydroxysulfates and/or oxyhydroxides. However the aluminum sulfate pickeringite is ubiquitous, occurring generally as a late phase. Paragenetic relationships are controlled by hydration/dehydration and oxidation cycles. Differences in ore paragenesis appear reflected in the secondary sulfate assemblages. Hence, paradigmatic mines, such as riotinto mines, shows great abundance of iron sulfates, with the three valence states of iron: such as melanterite (Fe(II)) and copiapite (Fe(II,III)) and coquimbite (Fe(III)). Moreover, copper sulfates, mainly alpersite and chalcantite are highly present in the mining environments, like in San Telmo and Herrerías mines. Copiapite is ubiquitous near the sulfide wastes, being detected in all the studied mining sites.

5. ACKNOWLEDGEMENT

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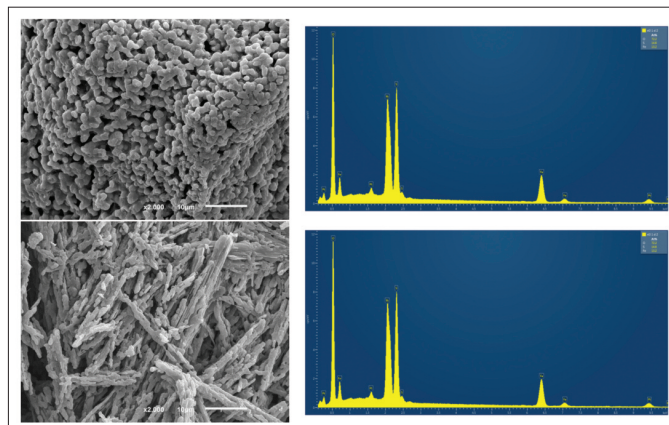


Figure 5 – Typical morphology and chemical composition of fibroferrite (above) and butlerite (below) (SEM-EDS results).

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