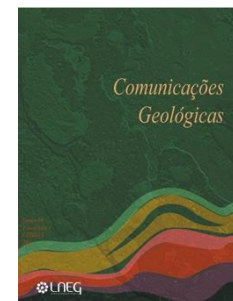


Occurrence of sulphate efflorescences in São Domingos mine

Ocorrência de eflorescências sulfatadas na mina de São Domingos

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Abstract: The intense exploration of sulphide ore deposit in São Domingos mine, produced considerable amount of sulphide material that when are exposed to weathering generates acid mine drainage (AMD). The main goal of this paper is to study a specific occurrence regarding composition and morphology of the salts that arise at the end of the dry season. Soluble salts appear at the banks of the drainage channels and over the waste materials, exhibiting different colours and aspects. The obtained results showed by X-Ray diffraction and scanning electronic microscopy, that the mineralogy of salt efflorescences is dominated by sulphates, displaying different occurrence modes. Melanterite and copiapite are the main iron sulphates while minerals from the series of pickeringite-halotrichite dominate the aluminium sulphates. In addition, dehydration and dissolution laboratory experiments were carried out in order to simulate the transformations suffered by soluble salts and evaluate the environmental effect in aquatic system.

Keywords: Acid mine drainage, Iberian Pyrite Belt, São Domingos mine, soluble salts, sulphate efflorescences.

Resumo: São Domingos é uma das minas portuguesas mais emblemáticas da Faixa Piritosa Ibérica (FPI). A intensa exploração de depósitos de sulfuretos produziu consideráveis quantidades de material sulfuretado que quando exposto aos agentes de meteorização gera drenagem ácida. O presente estudo foca-se numa ocorrência específica de eflorescências salinas precipitadas a partir das águas de drenagem ácida associadas a uma acumulação de minério lavado. O principal objetivo é estudar a composição e morfologia dos sais colhidos no fim da estação seca. Foi possível observar eflorescências salinas de diferentes cores e aspetos nas margens dos canais de drenagem e sobre os resíduos mineiros. Do ponto de vista metodológico, utilizou-se a difração de raios-X e a microscopia eletrónica de varrimento para a análise mineralógica. Os resultados obtidos revelaram que a mineralogia dos sais solúveis é dominada por sulfatos, exibindo diferentes modos de ocorrência. Melanterite e copiapite são os principais sulfatos de ferro, enquanto os minerais da série pickeringite-halotrichite dominam os sulfatos de alumínio, refletindo assim a composição dos resíduos mineiros (sulfuretos e gangas). Foram também realizados testes de desidratação e dissolução com o objetivo de simular as transformações sofridas por estes sais e os efeitos provocados no meio aquático.

Palavras-chave: Drenagem ácida, Faixa Piritosa Ibérica, Mina de São Domingos, sais solúveis, eflorescências salinas.

1. Introduction

The Iberian Pyrite Belt (IPB) constitutes a region known for its large massive sulphide ore deposits, located in the southwest of the Iberian Peninsula. There are several mines in IPB with more than thousands years of mining history (Grande *et al.*, 2013). Sulphide-rich materials when exposed to weathering processes generate a global environmental problem related with mining operations: acid mine drainage (AMD) (*e.g.*, Candeias *et al.*, 2015). This occurrence involves numerous process as a result of exposure to microorganisms, water and oxygen (Valente and Gomes, 2009; Pérez-Sirvent *et al.*, 2016). In the rainy season, waters interact with sulphide materials which are related to the release of acidity, sulphate and metallic dissolution, forming acid sulphate-rich drainage. So, mining wastes are responsible for strong effects on environment, often causing complete degradation of the ecosystems (Pérez-López *et al.*, 2008; Gomes 2011; Gomes *et al.*, 2015; Grande *et al.*, 2016).

In another perspective, AMD contributes to the development of secondary minerals, which are dependent of processes such evaporation, oxidation, hydrolysis, and neutralization (Valente and Gomes, 2009). These phases are mainly represented by efflorescent salts. Efflorescences, product of evaporative processes, are composed by salts of soluble metals, appearing monomineralic or as mineral assemblages (Valente *et al.*, 2013). The study of sulphate efflorescences allows understanding the environmental conditions of the affected systems as well as the evolution processes undergone by AMD (Valente *et al.*, 2016). Moreover, they have a significant environmental importance in monitoring pollutants in contaminated environments by their solubility and ability for retention, even if temporary, of many potentially toxic elements mobilized by AMD solutions. Although, efflorescent salts may provide significant information about paragenetic evolution and composition of water courses from which they formed (Valente and Gomes, 2009; Pérez-Sirvent *et al.*, 2016).

São Domingos mining area have been previously investigated by a number of authors for the geochemistry, mineralogy and environmental issues. For example, the project MINEO (IST-1999-10337) (Quental, 2003) contributed significantly for the knowledge about the environmental state of the São Domingos mine, including with the identification of the minerals that contribute to acidity. Other authors have dedicated research efforts to the study of geochemistry and mineralogical issues with

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environmental relevance (*e.g.*, Abreu *et al.*, 2004; Bourguignon, 2002; Quental *et al.*, 2013; Abreu *et al.*, 2008; Álvarez-Valero *et al.*, 2008; Pérez-López *et al.*, 2008; Rosado *et al.*, 2008; Tavares *et al.*, 2008; Durães *et al.*, 2016; Mil-Homens *et al.*, 2016; Santos *et al.*, 2016). Durães *et al.* (2008) identified the sulfate efflorescences in several sites in the Iberian Pyrite Belt, including São Domingos mine.

Specifically, the main purpose of the present work is to study the composition and morphology of the mineralogical associations which are part of the salt efflorescences that represent a specific and located occurrence at the end of the dry season, in São Domingos mine. In particular, this study is focused on: 1) the identification and characterization of efflorescent salts, 2) the role of these soluble salts in controlling the ecotoxic metals in AMD, demonstrated by dissolution experiments, and 3) description of their behaviour and environmental relevance.

2. Site description

The studied site, São Domingos mine (Fig. 1), is located in the northern sector of the IPB in Portugal in the Sud-Portuguese Zone of the Variscan belt (Oliveira *et al.*, 2006; Pérez-López *et al.*, 2008). It is characterized by an open pit exploitation of massive sulphide ores that are located near the top of the Volcanic Sedimentary Complex, and underground exploitation, with numerous galleries and mining wells. It was an important mining centre dating back to pre-Roman times, remaining in activity until 1966 when it was definitely halted due to the exhaustion of the ore (Álvarez-Valero *et al.*, 2008). There were two types of exploitation phases: the mining activity started, primarily, with the exploitation of gold, silver and silver through intensely oxidized and weathered rock, the gossan. Afterwards, in modern times, mainly sulphur and copper were exploited both in the gossan and volcanogenic massive sulphides. The production was estimated in more than 25 Tg (Carvalho, 1979 in Quental *et al.*, 2013), and for several decades it was produced material from mineral extraction which was crushed, milled and stored in large waste dumps and tailings in open air. Nowadays there are enormous waste-dumps with sulphide materials that are exposed to the weathering conditions (Rosado *et al.*, 2008). Inserted in the semi-arid climate typical of this area (Pérez-López *et al.*, 2008) and without applied remediation measures, the waste-dump properties, such as geotechnical stability, mineralogical, chemical and physical conditions (Candeias *et al.*, 2015), create significant environmental imbalances. The waste dumps are of very different composition and origin, from previous and subsequent rejections from the mineralogical treatment, to waste materials proceeding from metallurgical activity and from artificial cementation. The type of process undergone by the accumulated materials exerts influence over the hydrochemistry of each effluent. In any case, there are more than 480 ha of affected area, responsible for acidic contributions to the fluvial network. These mine wastes represent a unique scenario in the IPB as they are scattered along approximately 5.5 km in the margin of the Chança river, that finally discharge their highly contaminated waters into a reservoir used for human supply (Chança Dam).

Regarding the open pit, the waters appear to have reached the dynamic interannual balance and place the water sheet at a height of 70 meters below the upper berm. The waste dumps are the main contaminant focus.

The present work focused specifically at the base of a milled and leached pyrite pile, which discharge the AMD leachates into the dam is represented in the figure 1. The AMD at this site presents highly acidic and sulphate-rich, as shown in figure 1.

3. Methods

The sampling campaign for efflorescent salts was carried out under strong evaporation and low flow hydrological conditions (end of summer 2016). The samples were collected close to the water dam, at the base of the waste piles, in a manner to represent the diversity of mineralogical conditions observed by macroscopic properties, such colour and texture.

During the sampling campaign, efflorescences were collected with plastic spatulas, stored in closed plastic bags and transported to the laboratory soon after the collection, in order to prevent mineralogical changes of the most soluble assemblages.

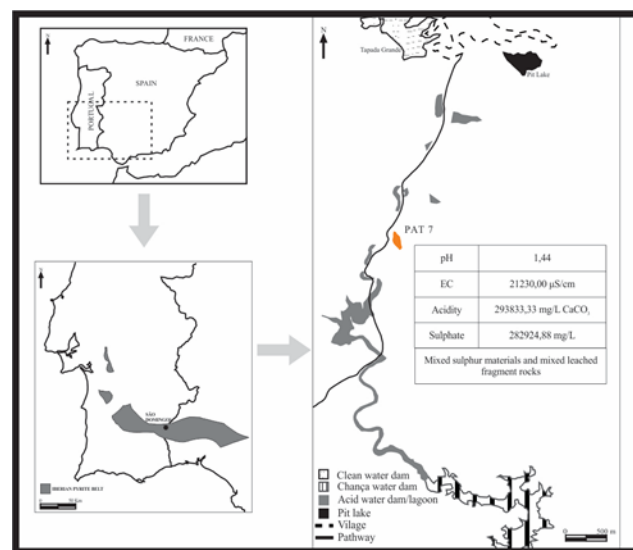


Figura 1. Map location of São Domingos and detailed sketch of acid mine drainage stream.

Figure 1. Mapa de localização da mina de São Domingos e esquema detalhado da linha de água afetada.

After that, in laboratory, efflorescent salts were examined for morphology, photographed and sorted by binocular microscopy. Subsequently, samples were lightly ground in preparation for mineralogical analysis by XRD.

The mineralogical composition was studied by X-ray diffraction (XRD) and the diffractograms were obtained with a Philips PW1710 (APD-version 3.6 j) diffractometer operating with CuK α radiation at 40 kV and 30 mA. The diffractometer was equipped with an automatic divergence slit and graphite monochromator. The XRD data were processed with the X'pert Pro-MPD software, which help to identify the most probable phases. The samples were reanalysed to evaluate aging effects.

This type of sample poses particular problems, which imply the use of an iterative procedure to accomplish mineralogical identification (Jerz and Rimstidt, 2003; Hammarstrom *et al.*, 2005). Therefore, binocular microscope was firstly used to obtain subsamples consisting of a lower number of phases. SEM allowed verification of the XRD analyses and, in some cases, it aided in the identification of complex assemblages.

Morphological and compositional aspects were analysed by scanning electron microscopy (SEM on platinum coated samples) with a LEICA S360 microscope, combined with an energy dispersive system (SEM-EDS), using X-rays and standard ZAF corrections that allow information on the elemental composition of the samples.

To study and simulate the behaviour of some efflorescences, namely transformations promoted by dehydration, samples were

submitted to the following treatments: air-dried, heating at 40 °C and heating at 60 °C, successively.

Dissolution experiments were conducted on selected samples, considered representative of the most common types of efflorescent salts in the sampling site. For these experiments 2.5 g of solid material was suspended in 25 mL of ultra-pure water (from Millipore system) in glass beakers at room temperature, and agitated for around 50 minutes with a magnetic stirrer. The pH and electric conductivity were measured each minute, until the end of the experiment, using multiparameter portable meter CRISON, MM40+.

4. Results and discussion

4.1 Occurrences modes

At the end of the dry season, the waste dumps, piles as well as the banks of the small drainage channels appear with a variety of colours promoted by the presence of blooms of salt efflorescences. They are mainly white-yellowish, blue and green salts which develop dense and thick masses over the waste materials. Often, these masses form crusts and appear with spongy or alveolar aspects. Moreover, very fine powdered efflorescences are also observed.

Figure 2a records the appearance of one of these occurrences, observed at the banks of the main drainage channel. The different colours suggest the occurrence of a mineralogical assemblage composed by different neoformed minerals with a specific paragenesis sequence. Generally, the green iron sulphates (here with vitreous luster) are covered by yellowish iron sulfates and white aluminium sulphates. Other iron sulphates, such as copiapite, typically form green botryoidal encrustations mixed with the sulphide wastes.

Efflorescence mineralogy is formed when AMD becomes more concentrated by evaporation in the dry season. Due to the processes that involve oxidation and dehydration, sulphates form typically hard crusts. When well-developed, such encrustation products act like cement for primary and secondary minerals.

Highly soluble efflorescences (*e.g.* melanterite) are present as ephemeral grains in the presence of remnant effluent (Fig. 2b). This fact may be attributed to dry and rainfall events that allows the complete dissolution and removal of highly soluble mineral and on the other hand, reprecipitation of new crystals (Carbone *et al.*, 2013). Melanterite occurs preferably near the most acidic permeation, indicating the proximity to its paragenetic precursors (the sulphides) (Fig. 2c). This figure shows the perfect green,

vitreous, prismatic crystals of melanterite. Moreover, other mineral phases (*e.g.* alunogen) occur in association with melanterite, which enhances the formation of surface encrustations. Due to their high solubility, efflorescent salts play an important role in cycling metals and acidity through solids and solutions in surface environments (Carbone *et al.*, 2013).

4.2 Mineralogy and chemistry of soluble salts

Mineralogy of soluble salts is dominated by sulphates, displaying different occurrence modes. The XRD data provide identification of several iron, magnesium, aluminium, calcium, and copper sulphates. Table I summarize the minerals identified by integrating XRD data with SEM information. Copiapite and melanterite are the main iron sulphates while minerals from the series of pickeringite-halotrichite dominate the aluminium sulphates. It is common for melanterite to appear with traces of Al-sulphates, which sometimes are difficult to isolate in unique phases, but discriminated by SEM (Fig. 3).

The efflorescences may be composed by pure minerals, but more often they form complex assemblages. Figure 3a allowed the discrimination of pure melanterite (monoclinic prismatic crystal in SEM image). The SEM-EDS information allowed to present the chemical composition of melanterite, dominated by iron sulphate, but with traces of copper. The complete spectrum is shown in figure 4b. The respective XRD pattern is shown in figure 4c. The presence of this mineral was detected by the planes 002 and 224 corresponding to 4.88-4.85 Å and 2.01 Å, respectively.

Table 1. Inventory of identified efflorescent salts.
Tabela 1. Inventário das eflorescências salinas identificadas.

Mineral	Ideal formula
Pickeringite	$MgAl_2(SO_4)_4 \cdot 22H_2O$
Halotrichite	$FeAl_2(SO_4)_4 \cdot 22H_2O$
Alunogen	$Al_2(SO_4)_3 \cdot 17H_2O$
Alpersite	$(Mg,Cu)SO_4 \cdot 7H_2O$
Tamarugite	$NaAl(SO_4)_2 \cdot 6H_2O$
Melanterite	$Fe^{+2}SO_4 \cdot 7H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Copiapite	$(Fe,Mg)Fe_4(SO_4)_6(OH)_2 \cdot 20H_2O$

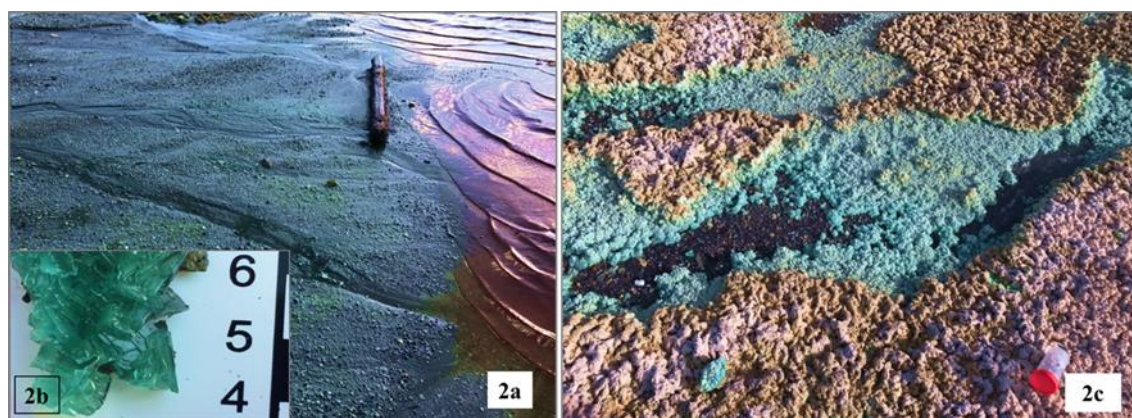


Figure 2. a) field image showing crystals of salt efflorescences of melanterite appearing nearby of remnant effluent; b) melanterite located at the banks of the drainage channels with vitreous luster and green colour; c) spongy typical occurrence mode of salt efflorescences.

Figura 2. a) imagem de campo evidenciando os cristais de melanterite que ocorre como eflorescências salinas perto do efluente; b) melanterite localizada nas margens dos canais de drenagem, de cor verde e com brilho vítreo; c) eflorescências salinas com modo de ocorrência típica esponjosa.

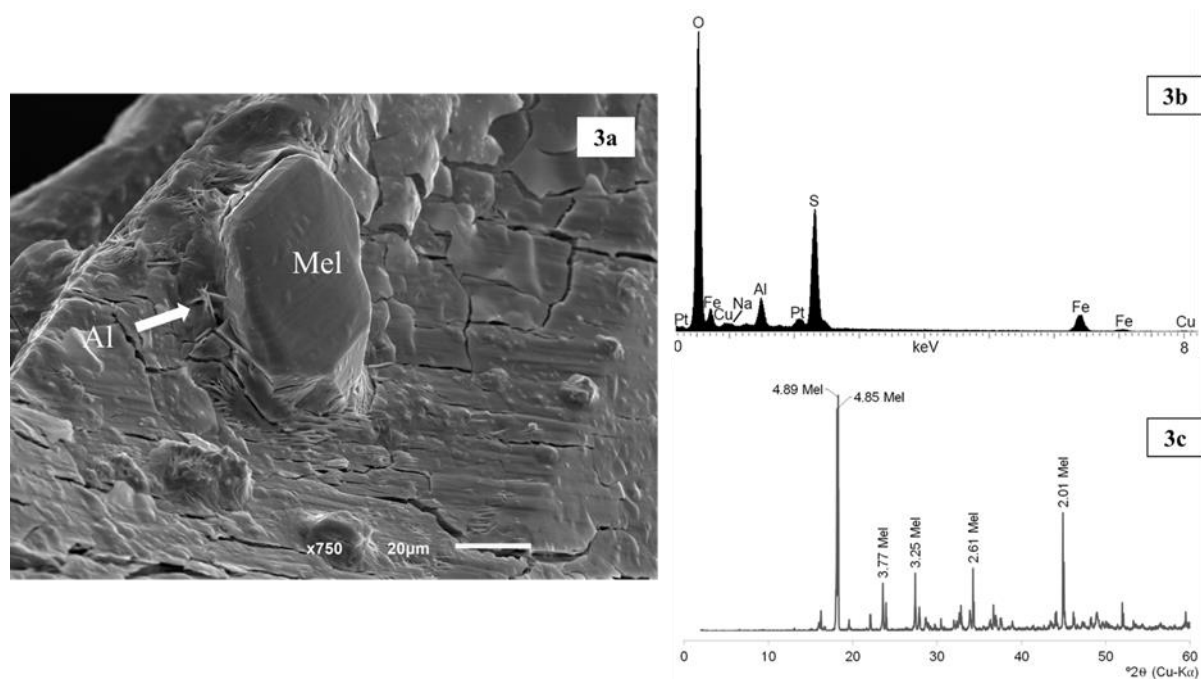


Figure 3. a, b) SEM-EDS (image and spectrum) of melanterite and Al- sulphate (Al: aluminium sulphate, Mel: melanterite); c) XRD pattern of a typical sample composed by melanterite.

Figura 3. a, b) MEV-SDE (imagem e espectro) de melanterite e Al-sulfato (Al: sulfato de alumínio, Mel: melanterite); c) Padrão de DRX de uma amostra composta por melanterite.

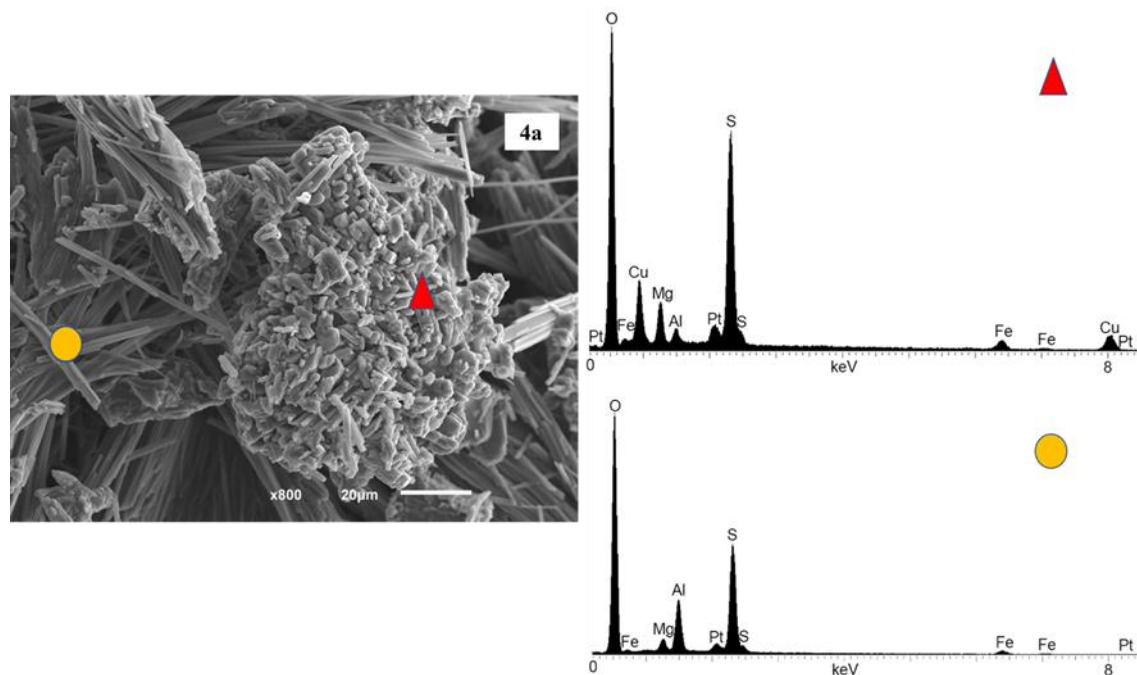


Figure 4. a) SEM-EDS (image and spectrum) of alpersite (spectrum above) and acicular pickeringite (spectrum below).

Figura 4. a) Imagem MEV-SDE (imagem e espectros) de alpersite (em cima) e pickeringite acicular (em baixo).

Alpersite, although relatively rare, occurs at this sampling site reflecting the abundance of copper in the system. Figure 4a shows an aggregate of alpersite crystals with acicular pickeringite. The respective EDS spectra, revealing the composition of both phases are presented in figure 4b-c.

A progressive transition from melanterite-, to rozenite-, to szomolnokite was observed (Fig. 5a). This evolution was simulated in laboratory, induced by dehydration of melanterite to

form rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) and szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$). The XRD data shows the mineralogical evolution of melanterite salt by controlled heating in the laboratory (Fig. 5a). Furthermore, it was possible to identify pyrrhotite in the air-dried diffractogram related to melanterite. Figure 5b shows an image of rozenite covering the most hydrated salt (melanterite). These results are in accordance with the literature and paragenetic knowledge. As previously mentioned, it is known that

melanterite occurs preferably near the most acidic seepages, indicating the proximity to pyrrhotite (Valente and Gomes, 2009).

Associated to the seasonal variations, the efflorescent salts are mainly controlled by wet/dry cycles (Candeias *et al.*, 2015; Durães *et al.*, 2008). The water chemical composition also results from the interaction with the host rock and tailings, since the waste-dumps absorb water from rainfall episodes and release these waters carrying the chemical potential for salt precipitation.

The mineralogical study performed by SEM has led to the chemistry of these secondary minerals and to the morphological characterization of some typical associations (Fig. 6). The study has revealed that pickeringite is one of the most abundant minerals that occur as late soluble salt. Nevertheless, there are other aluminum phases, such as alunogen and halotrichite. The minerals from the halotrichite-pickeringite series form radiated aggregates with acicular habit. Alunogen occur as white or yellow aggregates with plate morphology. Iron is mainly retained by copiapite and melanterite, while copper occurs in the form of alpersite.

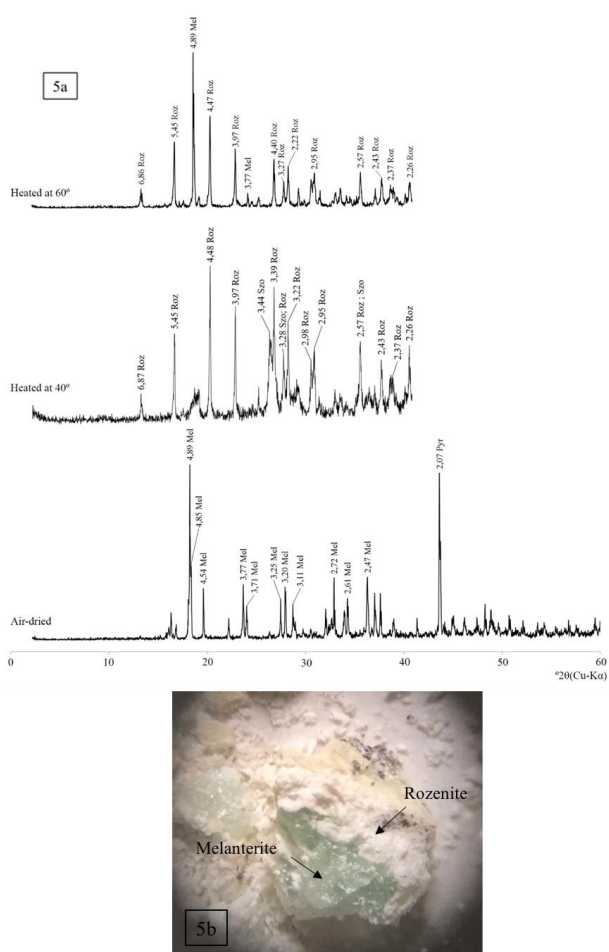


Figure 5. a) XRD pattern showing the mineralogical evolution of melanterite salt by – a) XRD patterns showing the mineralogical evolution of melanterite by controlled heating in order to identify the sequence melanterite - rozenite - szomolnokite formed by dehydration. Mel: melanterite, Roz: rozenite, Szo: szomolnokite, Pyr: pyrrhotite; b) Microscope image of efflorescent salts after heating 40°C (10.5x).

Figura 5. a) Padrão de DRX evidenciando a evolução mineralógica da melanterite por aquecimento controlado, mostrando a sequência resultante da desidratação (melanterite, rozenite e szomolnokite). Mel: melanterite, Roz: rozenite, Szo: szomolnokite, Pyr: pirrotite; b) Imagem em lupa binocular das eflorescências salinas após o aquecimento de 40°C (10,5x).

Melanterite is a common mineral in the IPB and it has been proposed as the first mineral phase forming as a result of iron sulphides oxidation (Durães *et al.*, 2008). On the other hand, copiapite is a subsequent phase, formed by the progressive oxidation of iron. The process that contributed to neutralization, oxidation and precipitation-re-dissolution cycles play a significant role in AMD sites.

4.3 Dissolution experiments

The dissolution experiments carried out on samples of pure melanterite were performed by controlling the pH and EC. According to some authors (Frau, 2000), a common property associated with the dissolution of efflorescent sulphate minerals related to acid mine drainage is observed: decrease in pH and an increase in EC (Fig. 7). This event occurs very suddenly, indicating the almost complete dissolution of the solid material in the first moments. Moreover, dissolution introduces new elements that are released into the receiving aquatic system, making this event especially concerned after prolonged dry periods, in the episode of rainfall. Then, a strong and prolonged rainy event may assure dilution and therefore minimize the environmental risk, while small rains produce a major concern (Valente and Gomes, 2009).

5. Conclusions

This study shows that iron, aluminium and magnesium sulphates occur associated with piles of fine leached pyrite in São Domingos mine. They arise as efflorescences composed more often by copiapite, directly over pyrite wastes, and by melanterite at the base of the piles, near the leachates.

Dissolution experiments simulate the adverse influence that soluble efflorescences have in the quality of aquatic system, potentiating acidic, metal and sulphate rich solutions.

The secondary efflorescent minerals represent great relevance in environmental mineralogy, with regard to their role in controlling pollutants in contaminated environments. However, at the beginning of the rainfall period, the highly soluble salts will dissolve. In this way, it is expected that the metal concentrations in water and sediments increase, contributing to ecosystem deterioration.

In summary, the study of these AMD-precipitates contributes to outline the high degree of environmental degradation, expressing their value as mineralogical indicators of AMD contamination. In accordance, the identified phases are typical from other study sites in the Iberian Pyrite Belt, namely in Lousal, Aljustrel and Tharsis mines in the Spanish sector of the Iberian Pyrite Belt (Durães *et al.*, 2008; Valente *et al.*, 2013).

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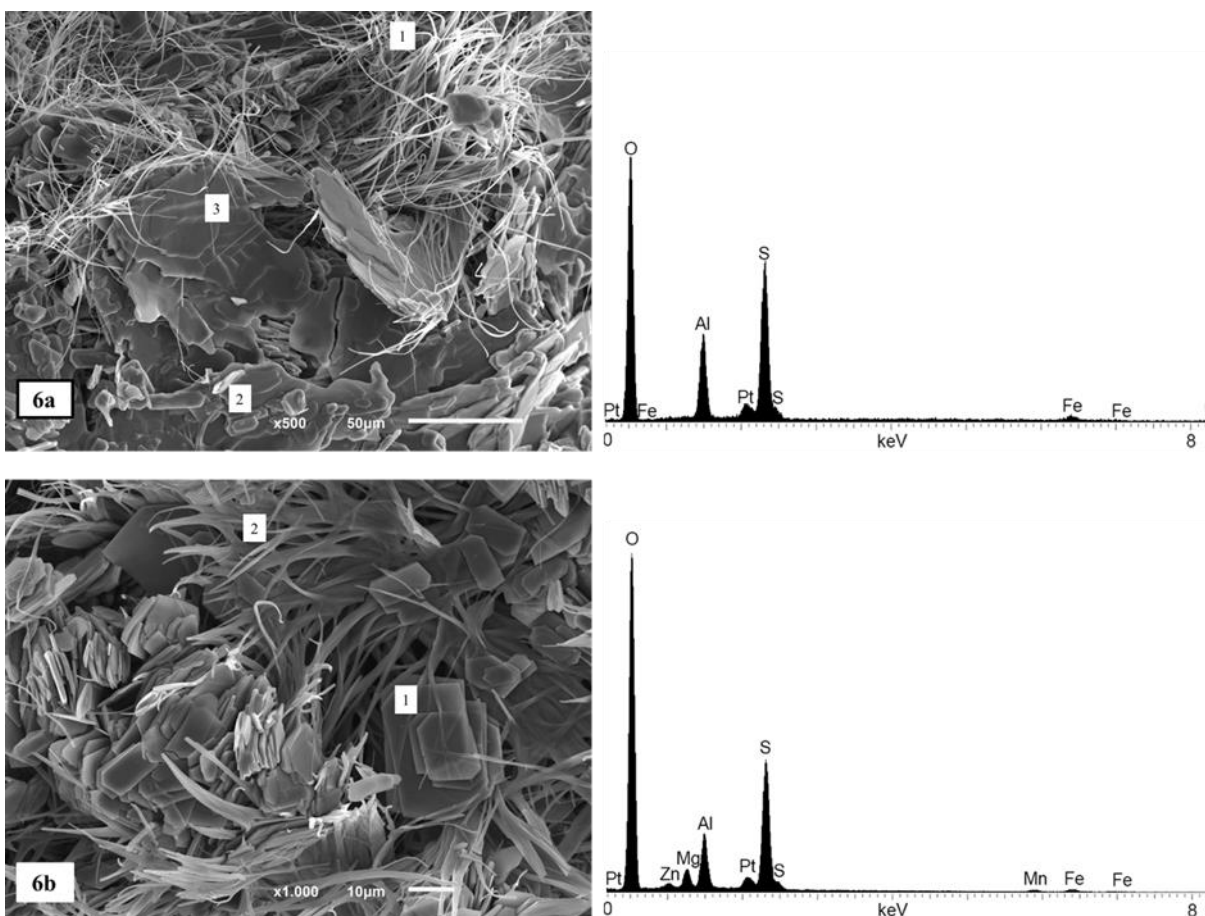


Figure 6. SEM images showing morphology of typical mineralogical assemblages: 6a) 1 - pickeringite, 2 - copiapite, 3 - alunogen; 6b) 1 - pickeringite (acicular habit), 2 - copiapite (plate crystals).

Figura 6. Imagens MEV que mostram a morfologia de associações mineralógicas típicas: 6a) 1 - pickeringite, 2 - copiapite, 3 - alunogénio; 6b) 1 - pickeringite (hábito acicular), 2 - copiapite (cristais em placa).

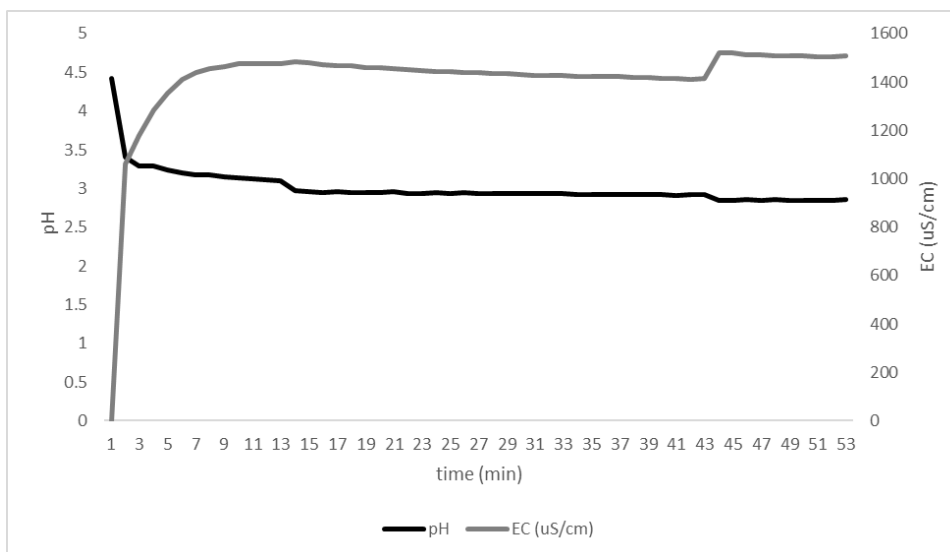


Figure 7 Results of experimental dissolution of melanterite: pH and electrical conductivity (EC) behaviour.

Figura 7. Resultado experimental da dissolução de melanterite: comportamento do pH e da condutividade eléctrica (EC).

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