

Arsenopyrite Weathering Products in Barruecopardo Mine Tailings (Salamanca, Spain)

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INTRODUCTION.

Mining and ore processing, where tungsten is associated with arsenopyrite (FeAsS), produce As-rich mine wastes. Oxidation of arsenopyrite can result in the mobilization and migration of As from these wastes into the environment.

This study considers the arsenopyrite-rich mine wastes that have undergone more than two decades of oxidation in the Barruecopardo ore deposit (exploited during several decades). This deposit is one of the most important tungsten deposits in Spain. It is constituted by subvertical quartz veins disposed in parallel intragranitic bands. The main minerals present are: scheelite and wolframite, that constitute the ore, arsenopyrite, pyrite, chalcopyrite and ilmenite, as primary minerals, and tungstite, scorodite, melanterite and calcantite, as secondary minerals. These minerals appear in the veins and on the borders of granite (Pellitero, 1981).

The aim of this work is to identify the arsenopyrite oxidation products in order to evaluate if this toxic element is fixed by them or, on the contrary, is easily released from them, likely causing the contamination of surrounding ecosystem compartments.

MATERIALS AND METHODS.

Samples of arsenopyrite from the Barruecopardo wastes, showing different weathering stages, have been studied.

Polished thin sections have been employed to observe the different phases by polarization microscope in transmitted and reflected light. Electron microprobe (EMPA) and micro-Raman

analysis were used to characterise every microscopically distinguished phase.

The sample portions equivalent to polished thin sections have been separated into two subsamples according to their different colour (greenish and orange-brown-reddish tonalities) and pulverised to be characterised by X-ray diffraction.

To identify the weathering products a combination of cited techniques has been used.

RESULTS AND DISCUSSION.

The weathering products in hand sample show yellowish-greenish tonalities, graduating towards orange-reddish in the borders, where the sample displays numerous holes (fig.1).



fig 1. Hand sample of weathered arsenopyrite.

Microscopically, the arsenopyrite weathering occurs on the borders, along small cracks, and following the crystallographic planes, completely replacing some crystals, pseudomorphizing them (figs. 2 and 3). It is very usual to observe small amounts of weathered arsenopyrite inside scorodite.



fig 2. Backscattered electron image of arsenopyrite (white) weathered to scorodite (grey).



fig 3. Microscopic image in transmitted light (X4) arsenopyrite (1), scorodite (2), unidentified iron-arsenic products (3) and As-Fe oxyhydroxides (4).

Three types of weathering products have been distinguished optically: scorodite (2), colourless to pale brown, and unidentified reddish phases (3), and black phases (4) (fig.3)

Scorodite is the most abundant oxidation product. It shows different textures:

- Microcrystalline aggregates with some dispersed spherulites. This is the closest to arsenopyrite.

- Spherulitic aggregates (spherical or bubbly texture).
- Concentrically banded texture, colloform texture.
- Prismatic crystals (with size varying from μm to tens of μm) occurring into cavities. Electron-backscattered images derived from microprobe reveal zonation in concentrically banded textures as well as in crystals (figs. 4 and 5).

The X-ray diffraction patterns confirm the formation of scorodite, the presence of gangue minerals (Q, muscovite) and arsenopyrite, but the identification of other likely present phases arising from the arsenopyrite weathering is not possible with this technique due to their low crystalline or amorphous character.

The chemical analyses of scorodite aggregates reveal that this mineral displays low contents of P (P_2O_5 : 0.2-0.3 (%wt)) and S (SO_3 : 0.3-0.7 (%wt)) and traces of other elements (K, Al, Si, Mn, Cu, Zn, Ba, Pb).

In the zoned crystals an enrichment in P is observed from the borders to the core (P_2O_5 : from 1 to 9 (%wt)). The different P contents result in different grey intensities in BSE images (fig.4): more clear zones correspond to the lower P contents. In these crystals there are also traces of other elements. It seems to be intermediate terms between scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), named P-rich scorodite or phosphoscorodite.

In the concentric textures the content of P also varies importantly (P_2O_5 : from 0.7 to 6 (%wt)), narrower is the content range found for S (SO_3 : undetected-up to 1.5 (%wt)).

The chemical analyses with microprobe show the presence of unidentified iron-arsenic phases (with a molar Fe/As ratio comprised in the range 1.7-2.1) and hydrated Fe oxides (HFO) of amorphous or poorly crystalline nature, with an arsenic maximum adsorbed amount of 78 mg/g. This value is similar to those derived experimentally in As adsorption studies (García-Sánchez et al., 2002), and to those found in other mining areas where arsenopyrite is present (Moldovan & Hendry, 2005).

The micro-Raman spectra correspond to scorodite with the characteristic bands

about 180, 800 and 900 cm^{-1} . Unidentified iron-arsenic phases spectra show these two last bands with minor intensity and other at 385 cm^{-1} , present in lepidocrocite micro-Raman spectra.

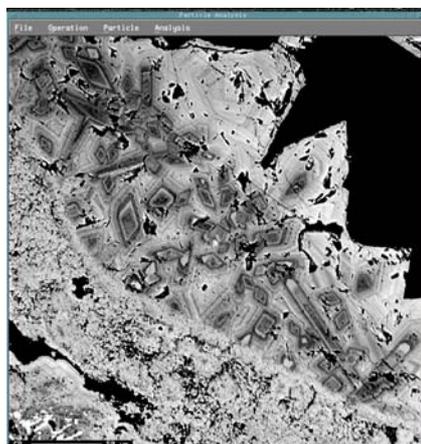


fig 4. Scorodite in spherulitic texture and zoned crystals of phosphoscorodite towards the cavity (black).

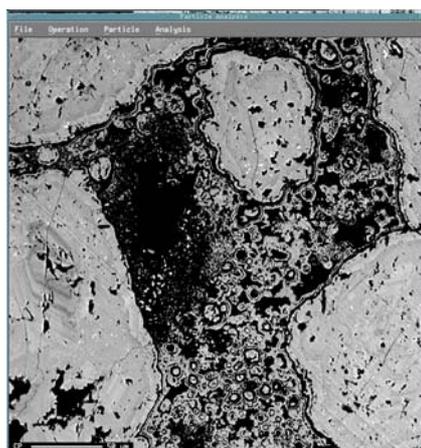


fig 5. Electron-backscattered image obtained in microprobe of colloform and spherulitic scorodite.

Arsenic-bearing sulphides such as arsenopyrite exposed to atmospheric weathering processes (oxidizing conditions) in Barruecopardo mine produce the neo-formation of arsenic-bearing mineral phases: firstly, arsenates such as scorodite (relatively rich in P), afterwards unidentified Fe-As phases and, finally, fine-grained HFO.

Scorodite is considered to be the most stable solid that immobilizes arsenic whereas the pH is < 3 (Moldovan & Hendry, 2005). When the pH attains values > 3 , the mechanism of As immobilization is its adsorption on the neo-formed Fe-oxihydroxides or its inclusion in other new formed phases.

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