

Preliminary Study of a Former Waste Dump in the Barruecopardo Mining Area (Salamanca, Spain)

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INTRODUCTION

The Barruecopardo mining area corresponds to the most important tungsten deposit in Spain. This is constituted by subvertical quartz veins disposed in parallel intragranitic bands. The mineral association is composed of scheelite (CaWO_4) and wolframite ($(\text{Fe,Mn})\text{WO}_4$), which constitute the ore, arsenopyrite (FeAsS), pyrite (FeS_2), marcasite (FeS_2) and other sulfides in much minor amount, together with quartz, feldspar, mica and apatite.

Mining activity started in the early thirties, reached its highest production between 1942 and 1945 and ceased in 1982. Nowadays, vestiges of the past mining activities remain in the area, including the ancient processing plant, a flooded open pit and dumps containing about several millions of tons of wastes.

This study is focused on the most ancient waste dump arisen from the artisanal mining performed in the early exploitation period in which the ore minerals were separated from the gangue minerals (including sulfides) by a manual process. This waste dump is composed of host rocks and/or hydrothermal veins fragments of very different size (from mm to tens of cm), containing mainly gangue minerals, different weathering products of sulfides and rarely ore minerals. A hardpan (a cemented, indurated layer in sulfide-bearing mine tailings) is present in the basal part of this waste dump.

The purpose of this study is to characterize the As-bearing secondary products directly generated from the weathering of arsenopyrite and pyrite/marcasite and those which constitute the binding phase in the hardpan in this waste dump.

MATERIALS AND METHODS

Surface samples of the former waste dump containing sulfides with different weathering degree were selected for this study. Some of these samples are surrounded by small particles of the waste dump bound by a cementing phase. Hardpan samples were also studied. A total of thirty representative samples were chosen.

These samples were characterized by X-ray powder diffraction (XRD), polarizing microscopy, electron microprobe analysis (EMPA) and microRaman spectroscopy.

RESULTS AND DISCUSSION

X-Ray Diffraction

The identified primary minerals are scheelite, wolframite, quartz, micas (muscovite and phlogopite), feldspar, kaolinite (in minor amount) and sulfides (arsenopyrite, pyrite and marcasite). The identified secondary minerals are mainly scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), goethite ($\alpha\text{-FeO}(\text{OH})$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), hydroniumjarosite ($(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$) and native sulfur.

Polarizing microscopy

Polarizing microscopy in transmitted and reflected light shows that arsenopyrite, pyrite and marcasite are the opaque minerals more abundant, appearing as unweathered euhedral crystals, as totally weathered crystals that keep their original shape and in relicts with corroded borders. Arsenopyrite seems more altered compared with other sulfides.

The hardpan sample is constituted by arsenopyrite partial or completely altered, pyrite/marcasite and grains of

scheelite, quartz and mica, being all of them bound by a yellowish phase with cracked texture.

The observed secondary products are:

- scorodite with different textures (microcrystalline mainly, colloform and spherulitic) and yellowish phases in concentric bands with mud-cracks. Both occur on the arsenopyrite crystal borders, along small cracks and inside of arsenopyrite. The yellowish phases also appear rimming and cementing grains of sulfides, silicate minerals and apatite (scarce).
- goethite, hematite and cracked reddish phases pseudomorphically replacing pyrite/marcasite. The reddish phases appear sometimes surrounding the cracked yellowish phases.
- jarosite-group minerals bordering pyrite/marcasite crystals.

Electron microprobe analysis

About 380 analyses were carried out on sulfides and different secondary products, most of them on these latter. The As content in pyrite/marcasite is negligible ($< 0.1 \text{ wt.}\%$ As_2O_5), indicating that arsenopyrite is the only primary mineral source of As in this waste dump. Scorodite analyses show variable contents of As_2O_5 (42.2-49.7 wt.%) and Fe_2O_3 (31.1-37.2 wt.%), minor contents of SO_3 (up to 1.1 wt.%) and P_2O_5 ($< 0.05 \text{ wt.}\%$) and traces of Al_2O_3 and SiO_2 . P_2O_5 contents are much lower than those of other scorodites studied in this mining area (Murciego et al., 2011). The Fe/As molar ratio in this mineral varies in the range 1.0-1.1, differing slightly from the theoretical value of scorodite.

Chemical analyses of yellowish phases (Fig. 1) reveal that As_2O_5 and Fe_2O_3 contents are comprised in the ranges

29.4-48.3 wt.% and 33.8-50.5 wt.%, respectively. Noteworthy are the relatively high SO_3 contents (1.9-22.1 wt.%), so these phases can be considered as hydrous ferric (sulfo)arsenates. Their P_2O_5 contents (up to 2.8 wt.%) are higher than those in scorodite. The Fe/As molar ratio in these phases varies in the range 1.1-1.9.

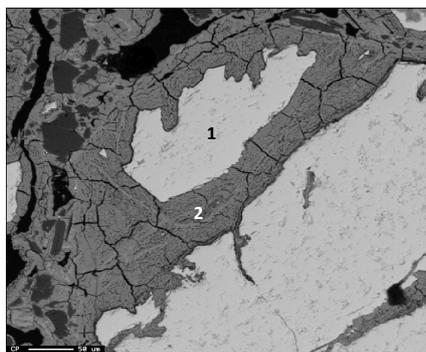


fig 1. Electron backscatter image of arsenopyrite (1) altered to hydrous ferric (sulfo)arsenates (2).

The analyses carried out on goethite/hematite/cracked reddish phases show Fe_2O_3 and As_2O_5 contents comprised in the ranges 50.8-88.6 wt.% and 0.8-23.3 wt.%, respectively. These As_2O_5 values agree well with the As adsorption capacities reported in the literature for these phases (García-Sánchez et al., 2002). The lower Fe_2O_3 contents and the higher As_2O_5 contents correspond to the cracked reddish phases (Fig. 2).

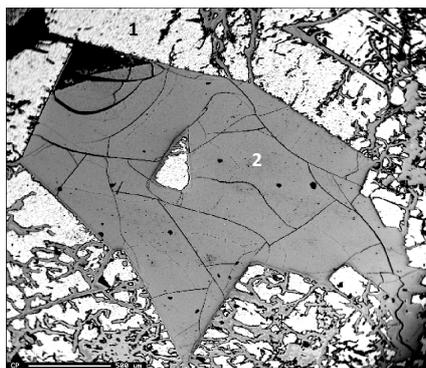


fig 2. Electron backscatter image of pyrite/marcasite (1) altered to Fe (oxyhydr)oxides (2).

This chemical composition suggests that these phases could correspond to hydrous Fe oxides or mixtures of these and goethite. SiO_2 , Al_2O_3 and SO_3 contents are high in these phases (up to 11.7, 6.8 and 5.7 wt.%, respectively). Lower contents are found for P_2O_5 (up to 1.9 wt.%). The Fe/As molar ratio in these Fe (oxyhydr)oxides varies within a wide range (7.3-156).

The distribution of Fe_2O_3 and As_2O_5 contents as well as the Fe/As molar

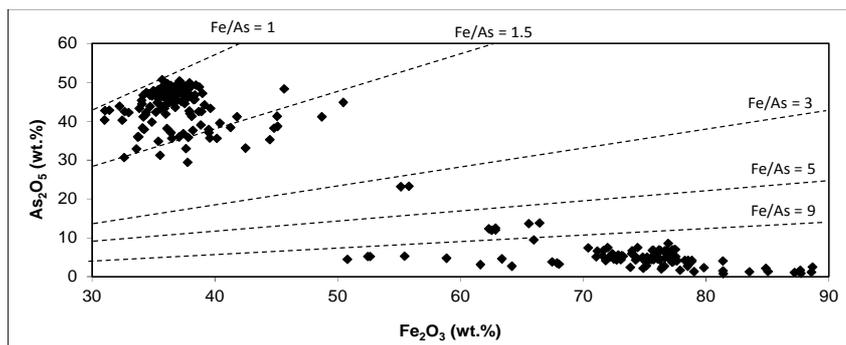


fig 3. Scatter plot of Fe_2O_3 vs. As_2O_5 determined by EMPA analysis on ferric arsenates and Fe (oxyhydr)oxides. Dashed lines represent the Fe/As molar ratios.

ratios of ferric arsenates and Fe (oxyhydr)oxides are shown in Fig. 3. The As_2O_5 content in hydroniumjarosite attains values up to 0.88 wt.%. Its K_2O and Na_2O contents are < 1 wt.%.

The following weathering sequence has been observed in the hardpan (Fig. 4): (1) hydrous ferric (sulfo)arsenates → (2) hydrous Fe oxides/goethite (< Fe_2O_3 and > As_2O_5) → (3) goethite (> Fe_2O_3 and < As_2O_5).

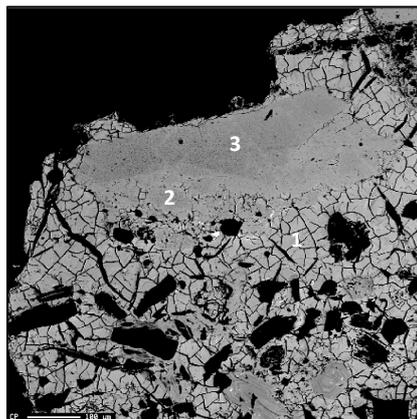


fig 4. Electron backscatter image of a hardpan sample showing the hydrous ferric (sulfo)arsenates (1) cementing tailing particles and Fe (oxyhydr)oxides with different As contents (2 and 3).

MicroRaman spectroscopy

About 80 microRaman spectra were carried out on the different phases considered in this study. The microRaman analyses were obtained from the same positions as those performed by EMPA. These spectra confirm the occurrence of the phases identified by XRD (scorodite, goethite, hematite, hydroniumjarosite) and the presence of hydrous ferric (sulfo)arsenates. In those of Fe (oxyhydr)oxides the band position at about 835 cm^{-1} represents As-O stretching and vibration of the arsenate adsorbed on these phases (Jia et al., 2006). The intensity of this band increases with the arsenate content (Fig. 5).

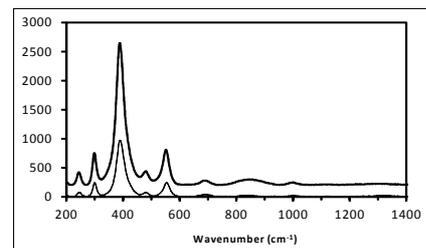


fig 5. Raman spectra of the Fe (oxyhydr)oxides.

CONCLUSIONS

The As-bearing secondary products generated from the weathering of arsenopyrite, pyrite and marcasite in a former waste dump from the Barruecopardo mine include mostly hydrous ferric (sulfo)arsenates, scorodite, goethite, hematite, hydrous Fe oxides and hydroniumjarosite. All these phases contribute importantly to mitigate the migration of As to the surrounding environment.

ACKNOWLEDGEMENTS

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