

# Arsenic distribution and mobility in mine wastes at different weathering stages

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## INTRODUCTION

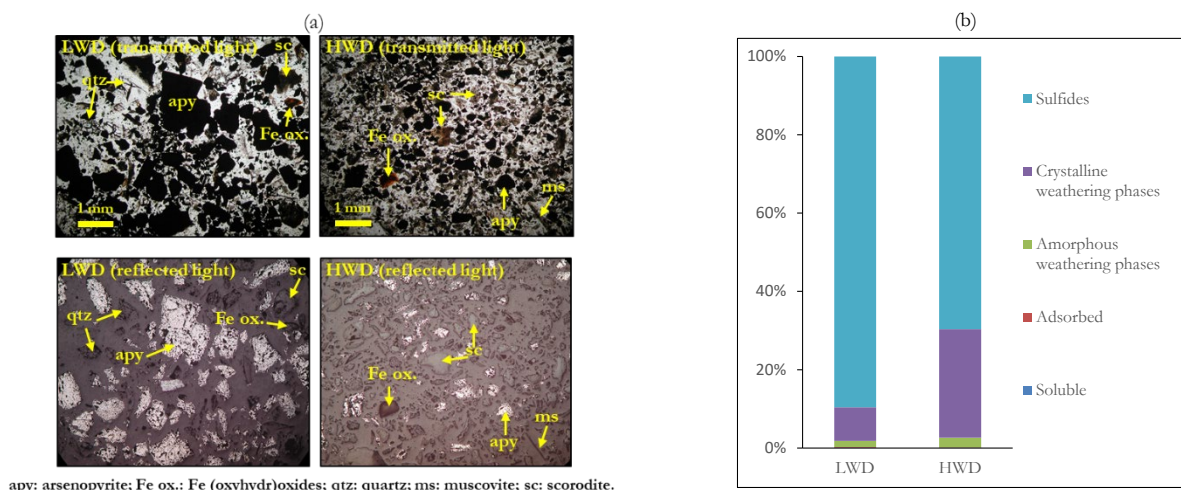
Arsenopyrite (FeAsS), the most common of the As minerals, appears associated with diverse ore minerals containing valuable elements (e.g., Au, Ag, Co, Cu, Pb, Ni, Zn, Sb, Sn, and W) (Alloway, 1995). The exploitation of such deposits has generated important amounts of arsenopyrite-bearing mine wastes. Usually, these wastes have been poorly managed, being dumped and exposed to the atmosphere. Under such conditions the oxidative dissolution of arsenopyrite takes place, with the risk of As release to the surrounding area and the consequent negative impacts on affected ecosystems. The main objective of this study was to assess the As distribution and mobility in mine wastes resulting from the exploitation of arsenopyrite-bearing ores and to establish the current and eventual risks of further As spreading to the neighboring environment.

## MATERIALS AND METHODS

The Barruecopardo mine in Salamanca (Spain), the most important tungsten mine in Spain, were considered in this study. The mineral association of the exploited deposit is mainly composed of scheelite (CaWO<sub>4</sub>), wolframite ((Fe,Mn)WO<sub>4</sub>), arsenopyrite, and pyrite (FeS<sub>2</sub>). Mine wastes were collected from dumps of the former exploitation of this deposit. Two types of samples were subject of study: mine wastes with low weathering degree (LWD) and with high weathering degree (HWD). The mineralogical composition of mine wastes was determined by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer and by polarized light microscopy studying polished thin sections of mine waste samples embedded in resin in transmitted and reflected light by means of a Nikon Eclipse E400 POL optical microscope. The pH of mine wastes was measured by the water-saturated paste method. Their NNP was estimated as the difference between their neutralization potential (NP) and their acid potential (AP). The NP was assessed according to the method of Sobek et al. (1978) and the AP was calculated considering the sulfur content of mine wastes. The leachable As content of mine wastes was evaluated according to the European leaching test EN 12457-4 (2002) and their toxicity was established following the TCLP procedure. The chemical fractionation of As was determined according to the sequential extraction procedure developed by Drahotá et al. (2014), established specifically to determine the As distribution between different As minerals/phases. It comprises five stages, which target the following As fractions: (1) readily soluble As; (2) adsorbed As; (3) As associated with amorphous/poorly-crystalline Fe arsenates (AFA), oxides, and hydroxy sulfates; (4) As associated with well-crystalline Fe arsenates (scorodite), oxides, and hydroxy sulfates; and (5) As present as sulfides.

## RESULTS AND DISCUSSION

According to the XRD analyses, the mineralogical composition of LWD samples mainly included quartz and arsenopyrite, also some feldspars (albite and microcline) and muscovite were present together with small amounts of scorodite. In HWD samples the occurring minerals were muscovite (very abundant), scorodite, arsenopyrite, feldspars, and quartz. Polarized light microscopy analyses confirmed the presence of the minerals detected by XRD and the occurrence of accessory phases (Fig. 1a); these phases were orange-red in color and could correspond to Fe-oxyhydroxides. In LWD mine wastes, arsenopyrite occurred as unaltered anhedral and subhedral crystals or slightly altered to scorodite along borders and cracks. Also, some scorodite crystals were observed. In HWD mine wastes scorodite crystals were abundant containing sometimes relicts of arsenopyrite.



apy: arsenopyrite; Fe ox.: Fe (oxyhydr)oxides; qtz: quartz; ms: muscovite; sc: scorodite.

**Fig 1.** (a) Microscopy images of LWD and HWD mine wastes. (b) As distribution in mine wastes between different As minerals/phases.

Both LWD and HWD mine wastes exhibited an acidic character ( $\text{pH} = 3.5$ ) and presented important negative NNP values ( $-1969$  and  $-815$  kg  $\text{CaCO}_3/\text{t}$ , respectively), characteristic of acid-producing materials ( $< -30$  kg  $\text{CaCO}_3/\text{t}$ ). The leachable As content of LWD and HWD mine wastes showed values of 608 and 161 mg/kg, respectively, greatly surpassing the limit value (25 mg/kg) for acceptance at hazardous waste landfills (Council Decision 2003/33/EC). Likewise, the As concentration released from mine wastes following the TCLP procedure attained values of 13.8 and 10.8 mg/L. These concentrations also exceed the limit set for wastes to be classified as toxic (5 mg/L). Therefore, measures should be undertaken to lessen the As leaching from both LWD and HWD mine wastes and reduce their toxicity. The As distribution in LWD mine wastes showed the following sequence (Fig. 1b): soluble (0.10%) < adsorbed (0.17%) < amorphous weathering phases (1.59%) < crystalline weathering phases (8.54%) < sulfides (89.60%). The same sequence was observed in HWD mine wastes, showing increased As partitioning values in amorphous weathering phases (2.54%) and crystalline weathering phases (27.71%), whereas those in soluble (0.03%), adsorbed (0.08%), and sulfide (69.63%) fractions decreased (Fig. 1b). Such distributions and the mineralogical composition of mine wastes reflect the arsenopyrite transformation mainly to scorodite and to some Fe-oxyhydroxides as weathering progresses. Although the precipitation of weathering phases attenuates the most labile As pools (soluble and adsorbed), representing very low fractions of total As, both LWD and HWD mine wastes entail a great risk of As spreading to surrounding environment.

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